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REPORT

DEVELOPMENT OF LUBRICATING OILS SUITABLE
FOR USE WITH LIQUID OXIDIZERS

FINAL SUMMARY REPORT
4 March 1968 - 4 March 1969

Contract NAS8-21269
Control DCN 1-8-54-10111 (1F)

MRI Project No. 3165-C

For

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

Attn: PR-SC

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DEVELOPMENT OF LUBRICATING OILS SUITABLE
FOR USE WITH LIQUID OXIDIZERS

by

L. W. Breed
J. C. Wiley, Jr.
R. L. Elliott

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PREFACE

This report was prepared by Midwest Research Institute, 425
Volker Boulevard, Kansas City, Missouri 64110, under Contract NAS8-21269,
"Development of Lubricating Oils Suitable for Use with Liquid Oxidizers."
The work was administered under the direction of the Propulsion and Vehicle
Engineering Laboratory, George C. Marshall Space Flight Center, with
Mr. C. F. Key acting as the Contracting Officer's technical representative.

This report covers work conducted from 4 March 1968 - 4 March 1969.

The work at Midwest Research Institute was designated Project
3165-C and was carried out by Mr. J. C. Wiley, Jr., Mr. R. L. Elliott,
Miss Mary Whitehead, and Mr. L. W. Breed, who acted as principal investi-
gator, under the supervision of Dr. C. C. Chappelow, Jr., Head, Organic
and Polymeric Materials Section. The following people also contributed to
the program: Mr. C. Bricker, Mr. K. Robertson, Mr. D. House, Mr. D. Inmon,
and Mrs. I. King.

Approved for:

MIDWEST RESEARCH INSTITUTE

R. L. Hughes, Director
Physical Sciences Division

26 March 1969

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ABSTRACT

A series of polyfluoroalcohol derivatives, including esters, ethers, phosphates, phosphonates, cyanurates, and phosphonitrilates, was prepared and each of the materials was screened for its stability against impact in the presence of liquid oxygen. Fluid range data, including atmospheric pressure boiling points and pour points, were determined. Details of the experimental work is summarized in which attempts were made to modify the originally prepared structures and improve the liquid range without decreasing the liquid oxygen stability. In addition to determining the fluid properties of some of the esters, including viscosity, volatility, corrosiveness, and hydrolytic stability, a fluorocarbon telomer-thickened polyfluoroalkyl ester grease was prepared and consistency, oil separation, dropping point, and aluminum shear sensitivity were determined. Samples of this grease were prepared for detailed evaluation at Marshall Space Flight Center.

I.   INTRODUCTION

The objective of this program has been the development of lubricants that retain useful lubricating properties and related characteristics at the temperature of liquid oxygen and are compatible with liquid oxygen and nitrogen tetroxide. Target properties for such a fluid include the following. The fluid must be stable under conditions of impact with liquid oxygen; it must have a wide liquid range--the target pour point is -150°C and evaporation rate is less than 1 percent after 24 hr. at 149°C and less than 5 percent after 24 hr. at 204°C; it must be hydrolytically stable; and it must be nonreactive under high shear stress with aluminum. 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 gellation, and lubricity--must also be satisfied.

From a literature survey it was concluded that the target properties could be approached by variations in the structures of fluorinated fluids. All completely fluorinated and/or chlorinated fluids that have been tested have proved satisfactory from the standpoint of impact sensitivity. These materials include the perfluoroalkylamines, the perfluoroalkyl ethers, and the chlorotrifluoroethylene polymers. The latter type of polymer, however, is shear sensitive in the presence of aluminum. The fluorosilicone fluids, which do not contain a large portion of fluorine, are much less sensitive in the LOX compatibility test than the silicones. They will not, however, consistently pass the test. Other partly fluorinated compounds, trimethyltrifluorobenzene and the fluoroalkyl camphorates, are reported to have a low sensitivity. Most test data available are for materials with commercial or generic designations so that virtually no reliable correlations with structure can be made.

Some conclusion about liquid range can be made by analogy with known structures of low molecular weight materials, but these conclusions must be regarded as extrapolations, since the structures or molecular weights of known compounds differ from materials that might satisfy the requirements. Moreover, the structural requirements for meeting the LOX impact specification impose an inherent limitation on the fluid range properties. Liquid range can be profoundly affected by degree of halogenation or fluorination of organic molecules. Fluorination usually increases melting points of low molecular weight materials and lowers their vapor pressure, although other factors may outweigh this generalization. Substitution of chlorine for hydrogen in a fluorine-containing compound also increases its melting point. The profound difference that the degree of fluorination can have on volatility is illustrated by the following boiling points for related compounds having about the same number of chain atoms in the pendant groups:

$C_3N_3(OCH_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-OCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-OCF_2CF_2CF_3)_3$ boils at 118-125°C at 0.2 mm., while $C_3N_3(OCH_2(CF_2)_8H)_3$ boils at 205-215°C at 0.04 mm.

In higher molecular weight materials, the viscometric properties become most important in limiting the low temperature range. Perfluoro-paraffins not only have a greater viscosity, but also a greater change in viscosity with temperature than corresponding hydrocarbons. The greater dependence of viscosity on temperature can also be related to lack of hydrogen bonding in the fluorocarbons. Less thermal energy is required for the breaking of intermolecular attractions so that a larger portion of the thermal energy is available for moving planes of molecules with respect to each other. Viscosity indices of even partially fluorinated materials may be very low. This limitation is inherent in the structure of fluorinated materials.

In summary, increased fluorination in a molecule will narrow its liquid range and increase its viscosity change with temperature. On the other hand, increased fluorination will decrease the LOX impact sensitivity. Chlorination will probably also decrease the liquid range and introduce the problem of shear sensitivity with aluminum. It thus appears necessary to decrease the degree of fluorination in order to meet target requirements, but no estimation can be made on the basis of existing literature of the extent to which fluorination can be decreased without impairing the stability of the fluid in the LOX impact test. An important part of the work then is to establish that the LOX-compatibility requirements can be met in substances containing sufficient hydrogen to provide the needed liquid range properties.

II. DISCUSSION OF THE EXPERIMENTAL WORK

A. Fluid Synthesis

The first step in the research was to examine the relationship between chemical structure and the LOX compatibility threshold of fluids and to verify some of the conclusions on the effect of structure on liquid range. Since the LOX compatibility of a fluid will be primarily determined by the ratio of hydrogen to fluorine in a molecule, but also influenced by the presence of functional groups and the manner in which fluorine is introduced in the structure, a series of known fluids with various fluorine to hydrogen ratios were selected for synthesis and evaluation. Fluorine was introduced into the fluids through the use of α,α,ω-trihydropolyfluoro-alkanols (telomer alcohols) as a component of the fluid structure. Functional groups present in the series included ester, ether, phosphate, phosphonate, phosphonitrilate, and cyanurate.

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Even though some of these pilot fluids had a substantial proportion of hydrogen in their structures, all performed too well under the conditions of the LOX compatibility test to allow establishing a clear limitation on the allowable amount of hydrogen. Also some of these fluids had better-than-expected low temperature properties. The data for these fluids are summarized in Table I.

In general, the properties of these substances confirmed the conclusions concerning liquid range that were made on the basis of the literature survey. The effect of decreased liquid range with increased extent of fluorination is particularly apparent and the effect of increasing the pour point through the presence of longer perfluoroalkylene segments can also be observed. The improvement in the low temperature properties through the use of many shorter chain segments rather than fewer longer chain segments is evident in the -55°F pour point of bis(ψ'-amyl)phosphonitrilate trimer* compared with -15°F pour point of bis(ψ'-amyl)(ψ'-nonyl) $\underline{s}$-triazine. The shorter segments in the phosphonitrilate derivative also imply greater branching.

Tricarballylic acid, being trifunctional, was used in preparing esters with shorter chain fluoroalkoxy groups without impairing the volatility. It also provides a branched structure. Although both of these factors should contribute to lowering the pour point, tris(ψ'-amyl) tricarballylate had a pour point of -45°F compared with a pour point of -75°F for bis(ψ'-heptyl) 3-methylglutarate.

In the selection of the initially prepared fluids for screening, it was recognized that they would satisfy neither the pour point requirement nor the volatility limitation set for the target fluid. However, the excellent performance of a number of these substances prompted the synthesis of some variations of these structures to effect improvement in the high and low temperature properties.

Several fluorinated alcohol derivatives of various methylglutaric acids were prepared and their properties are included in Table II. For comparison, the properties of some of the earlier prepared esters are also included in the table. The ψ'-heptyl alcohol esters, including the derivatives of 2-methylglutaric acid, 3-methylglutaric acid, 2,2'-dimethylglutaric acid, and 3,3-dimethylglutaric acid, all had pour points between -75°F and -80°F, indicating that the minor amount of branching introduced in in this way did not significantly improve the low temperature properties.

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* ψ'-alcohol, $H(CF_2)_{n-1}CH_2OH$.

TABLE I

PROPERTIES OF FLUIDS SYNTHESIZED

	Formula Weight	Pour Point (°F)	Boiling Point (°C-Atm. Pressure)	Boiling Range (°C)	LOX Compatibility Test[b]
$P_3N_3[OCH_2(CF_2)_4H]_6$ Bis(ι'-amyl) phosphonitrilate trimer	1527	-55°	369° (696°F)	170-175° (0.03 mm.)	1/20
$P_3N_3[OCH_2(CF_2)_4H]_3[OCH_2(CF_2)_4H]_3$ (ι'-amyl)(ι'-propyl) phosphonitrilate trimer	1221	-55°	365° (689°F)	157-172° (0.03 mm.)	0/20
$C_3N_3[OCH_2(CF_2)_4H]_2[OCH_2(CF_2)_8H]$ 2,4-Bis(ι'-pentyloxy)-6-(ι'-nonyloxy)-s-triazine	1019	-15°	367° (693°F)	175-180° (0.20 mm.)	0/40
$OP[OCH_2(CF_2)_4H]_3$ Tris(ι'-amyl) phosphate	740	< -90°	305° (577°F)	115-116° (0.05 mm.)	0/40
$OP[OCH_2(CF_2)_6H]_3$ Tris(ι'-heptyl) phosphate	1050	-30°	343° (649°F)	147° (0.07 mm.)	0/40
$OP[OCH_2(CF_2)_4H]_2[C_6H_5]$ Bis(ι'-amyl) benzenephosphonate	586	-70°	319° (606°F)	126-127° (0.06 mm.)	0/20
$H(CF_2)_8CH_2O(CH_2)_4OCH_2(CF_2)_8H$ 1,4-Bis(ι'-nonyloxy)butane	918	20°	339° (642°F)	137-138° (0.06 mm.)	1/40
$H(CF_2)_6CH_2O(CH_2)_6OCH_2(CF_2)_6H$ 1,6-Bis(ι'-heptyloxy)hexane	746	< -98°	323° (613°F)	132° (0.07 mm.)	1/40
$H(CF_2)_4CH_2OCCH_2CH-CH_2COCH_2(CF_2)_4H$ (O, CH₃, O) Bis(ι'-amyl) 3-methylglutarate	574	< -90°	302° (576°F)	130-132° (0.03 mm.)	0/40
$H(CF_2)_6CH_2OCCH_2CH-CH_2COCH_2(CF_2)_6H$ (O, CH₃, O) Bis(ι'-heptyl) 3-methylglutarate	774	-75°	324° (615°F)	145-167° (0.03 mm.)	0/40
$H(CF_2)_6CH_2OCCH_2-CH_2CHCOCH_2(CF_2)_6H$ (O, H₃C, O) Bis(ι'-heptyl) 2-methylglutarate	774	-80°	331° (628°F)	140-142° (0.09 mm.)	0/20
$H(CF_2)_6CH_2OC-C_{18}H_{14}-COCH_2(CF_2)_6H$ (O, O) Bis(ι'-heptyl)-d-camphorate	828	-30°	357° (675°F)	140-145° (0.02 mm.)	1/40
$H(CF_2)_4CH_2OCCH[CH_2COCH_2(CF_2)_4H]_2$ (O, O) Tris(ι'-amyl) tricarballylate	818	-45°	353° (667°F)	155-157° (0.04 mm.)	0/20

a/ Impact energy 10 kg-m.

TABLE II

PROPERTIES OF POLYFLUORESTERS

Ester	Pour Point (°F)	Boiling Range (°C)	Boiling Point (°C Atm. Pressure)
Bis(ψ'-amyl) 3-methylglutarate	< -90°	130-132° (0.03 mm.)	302° (576°F)
Bis(ψ'-heptyl) 3-methylglutarate	-75°	145-167° (0.03 mm.)	324° (615°F)
Bis(ψ'-heptyl) 2-methylglutarate	-80°	140-142° (0.09 mm.)	331° (628°F)
Bis(ψ'-heptyl) 2,2'-dimethylglutarate	-80°	130-131° (0.05 mm.)	327° (621°F)
Bis(ψ'-heptyl) 3,3-dimethylglutarate	-80°	126-131° (0.02 mm.)	--
Ester from 3-methylglutaric acid, ψ'-propyl alcohol, and 2,2,3,3,4,4-hexafluoropentanediol	-25°	--	--
Bis(ψ'-amyl) tricarballylate	-45°	155-157° (0.04 mm.)	353° (667°F)
(ψ'-amyl)(ψ'-propyl) Tricarballylate	-35°	150-155° (0.10 mm.)	--
Bis(ψ'-amyl) Citrate	-25°	--	--
Bis(ψ'-heptyl) d-Camphorate	-30°	140-145° (0.02 mm.)	357° (675°F)
Tetrakis(ψ'-amyl) Pyromellitate	m.p. 37-39°C	244-246° (0.20 mm.)	--

A higher molecular weight 3-methylglutaric acid derivative was prepared from a mixture of ¥'-propanol and 2,2,3,3,4,4-hexafluoropentane-diol. This modification increased the boiling point to the extent that the fluid was not distillable at 191°C under a pressure of 0.15 mm., but the pour point also increased to -25°F. A mixed tricarballate ester prepared from ¥'-propyl and ¥'-amyl alcohols was also no improvement. It had a pour point of -35°F. Attempts were also made to prepare esters from the trifunctional citric acid, but the esters were thermally unstable. It appears that the use of trifunctional acids to introduce branching into the fluid molecules is not effective in reducing the pour points.

Another variation was to prepare diphosphates with branched structures.

$$O=\overset{\overset{R_F}{|}}{\underset{\underset{R_F}{|}}{P}}-OCH_2(CF_2)_3CH_2O-\overset{\overset{R_F}{|}}{\underset{\underset{R_F}{|}}{P}}=O \qquad R_F = -OCH_2(CF_2)_2H$$

$$-OCH_2(CF_2)_4H$$
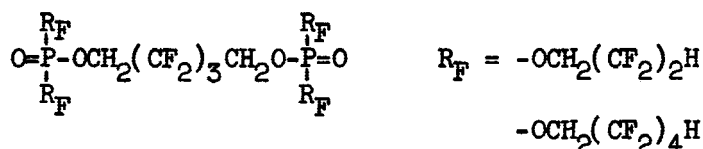
Initially, this approach appeared promising because the phosphate based on ¥'-amyl alcohol had a much higher boiling point than the monophosphate and a pour point of -65°F. However, in their synthesis, these compounds could be obtained in only very low conversion. When samples that had been previously distilled and isolated in a narrow boiling range were redistilled, significant quantities of low boiling components were separated. This result would suggest either that the product had disproportionated with heat to a simple triply-substituted phosphate, or that hydrolysis had occurred during the purification procedures. In any case, the composition was not satisfactory for consideration as a fluid.

B. Approaches to The Development of Structural Modifications for Fluids

In the experimental work, additional approaches were taken to the modification of the original fluids, but none of these approaches proved successful. Each of the pilot fluids had been prepared by the nucleophilic displacement of a good leaving group by a fluorine-containing anion. Structural modifications, then, were sought through the use of other anions that contained branching and heteroatoms as well as a sufficient proportion of hydrogen to insure good low temperature properties.

Initially, it had been planned that alcohols prepared by the reduction of the oligomerization products of hexafluoropropylene oxide could be used in these displacement reactions. This approach was abandoned when hexafluoropropylene oxide was withdrawn from the market shortly after the program was initiated.

A second approach was to use hemiketals of fluorine-containing alcohols and ketones in the displacement reactions. It was known that these hemiketals were hydrolytically stable and that they could be methylated and acetylated in displacement reactions. It was possible that phosphates, cyanurates, phosphonitrilates, and esters could be prepared with hemiketal ligands.

As a first step, n-propyl hexafluoroacetone hemiketal was prepared according to an established procedure.[1] The experimental method was then extended to the preparation of t'-amyl hexafluoroacetone hemiketal.

$$H(CF_2)_4CH_2OH + (CF_3)_2CO \longrightarrow H(CF_2)_4CF_2OC(CF_3)_2OH$$
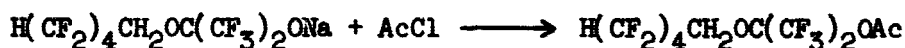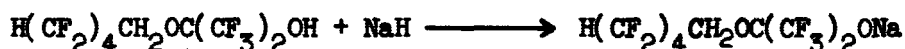
The structures of the two compounds were confirmed by their n.m.r. spectra. The data in Table III show that the n.m.r. chemical shift of the CH_2O group in the hemiketals was downfield from the corresponding shift for the corresponding protons in the parent alcohols. Both the infrared band and the proton chemical shifts in the spectra of the hemiketal derivatives were useful in verifying structures of their derivatives.

TABLE III

PROTON CHEMICAL SHIFTS OF HEXAFLUOROACETONE HEMIKETALS
AND THEIR PARENT ALCOHOLS

	τ CH_3	τ HCF_2	τ CH_3CH_2	τ CH_2O
$CH_3CH_2CH_2OH$ ($CDCl_3$)	9.08		8.43	6.42
$CH_3CH_2CH_2O-C(CF_3)_2-OH$ (cyclohexane)	9.06		8.42	6.21
$H(CF_2)_2CH_2OH$ (benzene)		4.51		6.43
$H(CF_2CH_2OC(CF_3)_2OH$ (carbon tetrachloride)		3.98		5.65

These hemiketals could be converted to their sodium salts with sodium hydride, and subsequently treated with acetyl chloride to obtain the hemiketal acetates.

$$H(CF_2)_4CH_2OC(CF_3)_2OH + NaH \longrightarrow H(CF_2)_4CH_2OC(CF_3)_2ONa$$

$$H(CF_2)_4CH_2OC(CF_3)_2ONa + AcCl \longrightarrow H(CF_2)_4CH_2OC(CF_3)_2OAc$$

The structures of the acetates that were obtained were also confirmed by their infrared and n.m.r. spectra. An attempt to acetylate the hemiketals with acetic anhydride and pyridine, however, led to the formation of only the parent alcohol acetate.

The formation of the alcohol acetates in attempts to acetylate hexafluoroacetone hemiketals with acetic anhydride and pyridine is consistent with the report that hemiketal acetates of hexafluoroacetone undergo decomposition to the ketone and ester.[2] However, no decomposition was observed when the hemiketal acetates were prepared from the hemiketal sodium salts and acetyl chloride, even though their distillation required a mantle temperature of about 250° for an hour. The acetates were obtained in good yields under these conditions. The acetates were stored as long as 22 days without any sign of decomposition; however, when _t_'-amyl hexafluoroacetone hemiketal acetate was heated at its normal boiling point, 171°, it rapidly decomposed to _t_'-amyl acetate.

$$H(CF_2)_4CH_2O-C(CF_3)_2OAc \xrightarrow{\text{heat}} H(CF_2)_4CH_2OAc + (CF_3)_2CO$$
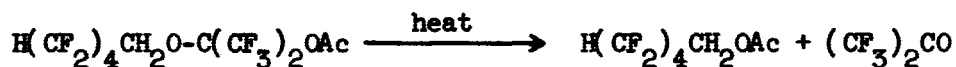
This observation, unfortunately, precludes the consideration of the hexafluoroacetone hemiketal derivatives of 3-methylglutarate as candidate fluids. It did not preclude consideration of phosphate or cyanurate derivatives. A first attempt to prepare a fluid derivative from the anion of _t_'-amyl hexafluoroacetone hemiketal was made in a condensation reaction with cyanuric chloride.

$$H(CF_2)_4CH_2OC(CF_3)_2ONa + C_3N_3Cl_3 \longrightarrow C_3N_3[OC(CF_3)_2OCH_2(CF_2)_4H]_3$$
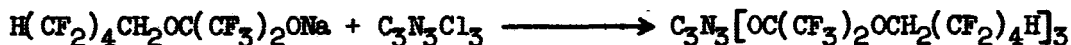
The conversion in the reaction was low (24 percent) and the product surprisingly boiled at a lower temperature than tris(_t_'-amyloxy)-_s_-triazine. Although the 1240 cm.$^{-1}$ (CF$_3$) band was evident in the infrared spectrum and the chemical shift for the CH$_2$O group was τ 5.03 in the n.m.r. spectrum, the elemental analyses results for the product did not agree with any of the possible structures. The low value for fluorine suggested incomplete substitution on the _s_-triazine ring.

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Similar results were obtained in an attempt to prepare the corresponding s-triazine derivative of n-propyl hexafluoroacetone hemiketal. Spectral evidence clearly supported the presence of the n-propyl, the bis-trifluoromethylene, and the s-triazine groups, but the conversion was low.

In another experiment, the anion from t'-amyl hexafluoroacetone hemiketal was condensed with phosphorus oxychloride.

$$H(CF_2)_4CH_2OC(CF_3)_2ONA + POCl_3 \longrightarrow PO[OC(CF_3)_2OCH_2(CF_2)_4H]_3$$
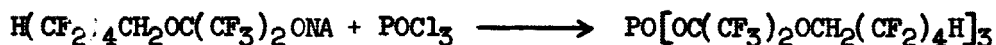
Again, the infrared and n.m.r. data were consistent with the required structure, but the conversion was only 21 percent. The product had about the same boiling point as t'-amyl phosphate and no lower a pour point.

The results of elemental analyses confirmed that the hemiketal derivative had not been obtained and that the product was chiefly tris-(t'-amyl) phosphate containing perhaps a minor portion of the hemiketal structure.

Another approach to the use of different anions in the preparation of fluids was through the synthesis of fluorinated secondary alcohols. Difficulties in the preparation of the necessary fluorinated ketone intermediates prevented a complete investigation of this approach.

A final approach was the use of fluorinated alcohols containing an ether linkage that could be prepared by replacing one alcohol group in 2,2,3,3,4,4-hexafluoropentanediol or its bis(hemiketal) with a polyfluoroalkoxy group. Most of the work on this approach centered in attempts to find methods for establishing the -CF_2CH_2OCH_2CF_2- group or the -CF_2CH_2OC(CF_3)_2OCH_2CF_2- group, which were unsuccessful.

In the initial study of ether formation, an attempt to prepare methyl propyl hexafluoroacetone ketal by an established procedure failed.[3] The method subsequently proved successful for preparing t'-amyl methyl hexafluoroacetone hemiketal in a 19 percent yield. The conversion was increased to 28 percent when the sodium salt of t'-amyl hexafluoroacetone hemiketal was treated with dimethylsulfate.

It was first assumed that the properties of dimethylsulfate and the fluoroalcohol tosylates would be similar in their condensation with hemiketal anions. But when t'-amyl hexafluoroacetone hemiketal sodium salt was treated with t'-pentanol p-toluenesulfonate under similar conditions that were used in the dimethylsulfate reaction, 92 percent of the tosylate was recovered. This result was consistent with the report of the resistance of the carbon-oxygen bond in fluoroalcohol tosylates to cleavage.[4]

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In an earlier attempt to prepare 1,5-bis(ψ'-heptyloxy)-2,2,3,3,4,4-hexafluoropentane by treating 2,2,3,3,4,4-hexafluoropentanediol bis($\underline{p}$-toluene-sulfonate) with ψ'-heptyl alcohol in the presence of potassium hydroxide, the half tosylate, 1-hydroxy-5-(ψ'-heptyloxy)-2,2,3,3,4,4-hexafluoropentane $\underline{p}$-toluenesulfonate was obtained. It would be assumed therefore that ether formation could occur between fluoroalcohols and fluoroalcohol tosylates despite the statement in the literature that such reactions do not occur.[4]

In view of the finding that an ether bond could be established via a tosylate, the simpler reaction of a fluoroalcohol anion with a fluoro-alcohol tosylate was attempted under more forcing conditions. The reactants were heated in dimethylformamide at 100° for 2 hr., but again 65 percent of the tosylate could be recovered. The use of the more reactive fluoroalcohol sulfate[4] in a nonpolar aprotic solvent was also unsatisfactory.

Other experimental approaches failed to provide ether structures. An unsuccessful attempt was made to condense pentaerythritol tetra-$\underline{p}$-toluenesulfonate with ψ'-amyl alcohol. Only a small proportion of a par-tially substituted pentaerythritcl derivative was obtained. A similar ex-periment with trimethylolethane tri-$\underline{p}$-toluenesulfonate also failed, which was surprising in view of the easy condensation of difunctional tosylates reported earlier.

C. Fluid and Grease Evaluation

Various properties of selected fluids were examined in order to determine the extent to which they met the target properties. Because the ester fluids appeared to approach these properties closer than any of the other series, more complete screening tests were carried out for the esters, and particularly for bis(ψ'-heptyl) 3-methylglutarate. Details of the vis-cosity, dropping point, hydrolytic stability, evaporation, corrosion, pour point, oil separation, and aluminum shear tests are described in the experi-mental section of this report. A comparison of some of the properties for a bis(ψ'-heptyl) 3-methylglutarate-based grease and some commercially avail-able greases is provided in Table IV or for the corresponding base fluids in Table V.

Two of the tests merit some discussion. Hydrolytic stabilities were examined for the phosphates by a procedure that has been described in the literature.[5] Under the conditions of the procedure, which involved titration with sodium hydroxide, mixtures containing the telomer alcohol phosphates hydrolyzed too rapidly to give stable end points. Gunderson has said that while phosphates are less stable hydrolytically than organic esters, they are more stable than silicate or borate esters.[6] The results obtained here would put the telomer alcohol esters of phosphorous oxychloride in the class with silicate and borate esters and make them unsuitable for lubricant applications.

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TABLE IV

PROPERTIES OF VARIOUS SYNTHETIC LUBRICATING GREASES

Base Fluid Type	Thickener	Penetration at 77°F Unworked	Penetration at 77°F Worked[a]	Dropping Point (°F)	Wt. % Oil Separation After 30 Hr. 212°F	300°F	400°F	Evaporation Time (hr.)	Temp. (°F)	Wt. Loss (%)	LOX Compatibility
Dibasic fluoroester	Tetrafluoroethylene polymer	276	312	365	4.7	8.2	--	--	--	--	--
Chlorotrifluoroethylene polymers	--	--	225-255	400	6.3	9.8	--	22	210	0.84	Satisfactory[b]
Fluorosilicones	Silica	180-220	300	> 500	--	--	--	24	390	2.0	Significant Insensitivity[c]
Fluorosilicones	High-melt solid	--	310	> 450	--	--	> 12	22	400	< 7.0	Passes test[c]
Perfluoroalkyl ethers	Tetrafluoroethylene polymer	266	275	--	--	--	--	22	400	1.6	Passes test[c]
Mixed perfluorotrialkylamines	Tetrafluoroethylene polymer	265	310	--	--	--	--	22	210	40-50	Passes test[c]

a/ Sixty reciprocal strokes.
b/ NASA TMX-53052.
c/ Impact compatibility, ARMA tester, 70 to 72 ft/lb impact.

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TABLE V

PROPERTIES OF VARIOUS SYNTHETIC LUBRICATING FLUIDS

Fluid Type	Pour Point (°F)	Viscosity (cs.)			Evaporation			LOX Compatibility
		77°F	100°F	210°F	Time (hr.)	Temp. (°F)	% Wt. Loss	
Dibasic fluoroester	-75	30[a]	26.11	3.57	1	400	78	Passed[b]
Chlorotrifluoro-ethylene polymers	< -90	--	3.1	1.0	--	--	--	Satisfactory[c]
	-40	--	25.0	3.0	--	--	--	Satisfactory[c]
	+10	--	25.0	10.0	--	--	--	Satisfactory[c]
	+70	--	--	40.0	--	--	--	Satisfactory[c]
Fluorosilicones	-55[d]	300	--	30.0	48	392	10	--
	-40[d]	1,000	--	74.0	48	392	3.0	--
	-25[d]	10,000	--	690.0	48	392	1.5	--
Perfluoroalkyl ethers	-45	--	95.0	11.0	6.5	400	15.0	--
	-20	--	300.0	28.0	6.5	400	Negl.	--

a/ Value interpolated.
b/ Evaluated as outlined in MSFC-SPEC-1068.
c/ NASA TMX-53052.
d/ Freezing point.

It has been recently reported that phosphate esters with good low temperature properties and hydrolytic stability could be prepared from telomer alcohols and dichlorophenylphosphine oxide.[7] Such a phosphate was prepared from t'-amyl alcohol, which also passed the LOX-compatibility test, and did exhibit a level of hydrolytic stability, equal to the telomer alcohol carboxylic and esters.

As a method of screening fluids that might successfully meet the volatility requirements, the criterion advanced by Murphy[8] that a boiling point of more than 204°C (400°F) at 0.5 mm. would be required if fluorinated ester fluids were to have less than 5 percent evaporation at 204°C for 24 hr. Data reported by McTurk[9] seem to confirm this generalization. On the basis of the reported work, it was estimated that a normal boiling point of 432°C would provide a fluid with less than 5 percent evaporation after 24 hr.

Evaporation in an open dish can provide data that approximate ASTM evaporation results. An example of such a correlation can be found in a patent by Sommers and Sturgis.[10] When evaporations were determined on the polyfluoroesters at 400°F in this way, much higher evaporation rates than would be predicted from the boiling points were found. Whereas it was predicted that bis(t'-heptyl) 3-methylglutarate would be only 9 percent evaporated after 1 hr., a 79 percent evaporation was observed. The apparent reason for the disagreement is that the distillation data do not represent the vapor pressures at the indicated temperatures to a sufficient degree of accuracy.

It was found that log of the weight percent evaporation for 1 hr. gave a straight line when it was plotted against $1/t + 230$ (t in °C). Since the vapor pressure of a pure compound would be directly proportional to the rate of evaporation, such a plot would be validated by the Clausius-Clapeyron equation. Interpolation of these curves allows an estimation of the temperature at which the fluid would have 1 or 5 percent evaporation after 24 hr. since the evaporation of a pure compound would be directly proportional to time at one temperature. These interpolations for four fluids are reported in Table VI.

TABLE VI

ESTIMATED TEMPERATURE AT WHICH 1 AND 5% OF THE
FLUOROESTER EVAPORATES AFTER 24 HR.

| | Estimated Temperature (°F) at Which | |
Fluoroester	1% Evaporates After 24 Hr.	5% Evaporates After 24 Hr.
Bis(t'-amyl) 3-Methylglutarate	145	177
Bis(t'-heptyl) 3-Methylglutarate	167	205
Bis(t'-heptyl) 2-Methylglutarate	183	217
Tris(t'-amyl) Tricarballylate	205	241

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When the temperatures at which 5 percent evaporation occurs after 24 hr. are plotted against the normal boiling points of the fluids, a straight line is obtained. If this curve is extrapolated to an evaporation of 5 percent at 400°F, the requirement of a normal boiling point of 880°F or 472°C is obtained, somewhat higher than the earlier predicted value.

Wear tests on a bis(ψ'-heptyl) 3-methylglutarate grease, which was thickened with 16% of a fluorocarbon telomer thickener, were made at Marshall Space Flight Center, and the grease did not show effective extreme pressure characteristics in comparison with a commercial extreme pressure lubricant. The following wear scar diameters were found under the specified loads: 0.49 mm. at 10 kg., 0.70 mm. at 30 kg., and 1.72 mm. at 50 kg. An earlier comparison of data from the literature of a bis(ψ'-heptyl) 3-methylglutarate oil with other synthetic oils had shown that the bis(ψ'-heptyl) 3-methyl-glutarate compared favorably with those oils. The latter data were obtained with a Shell four-ball wear machine run at 70° for 2 hr. at a speed of 600 rpm with balls made of Type 52-100 steel. The following wear diameters at specified loads were obtained: bis(ψ'-heptyl) 3-methylglutarate, 0.42 mm. at 10 kg. and 0.52 mm. at 20 kg.; bis(ψ'-propyl) siloxane ester, 0.45 mm. at 10 kg. and 0.62 when at 20 kg.; and di-2-ethylhexyl sebacate, 0.53 mm. at 10 kg. and 0.72 mm.at 20 kg.[11]/

III. EXPERIMENTAL PART

Elemental analyses were by Sprang Microanalytical Laboratory, Ann Arbor, Michigan. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer.

A. Polyfluroalkyl Ester Fluids

The following is a typical experiment for the preparation of fluids in this series. To 56.5 g. (0.39 mole) of 2-methylglutaric acid in 300 ml. of toluene was added 289.0 g. (0.87 mole) of ψ'-heptyl alcohol. The mixture was warmed to 50°, treated with 2 g. of sulfuric acid, and refluxed 7 hr. At the end of the period 15.7 ml. of water (calcd., 14.1 g.) had been collected in a Dean-Stark trap. The cooled mixture was poured into 800 ml. of diethyl ether, washed once with 200 ml. of 5% potassium carbonate, twice with 200 ml. portion of water, dried over calcium sulfate, and the ether removed by evaporation. Vacuum distillation gave 179.0 g. of crude bis(ψ'-heptyl) 2-methylglutarate, b.p. 153-158° (0.07 mm.). This material, a yellow liquid, was decolorized by passing it through a charcoal bed in a steam-jacketed Buechner funnel. A second vacuum distillation of this compound afforded 166.0 g. (55%) of bis(ψ'-heptyl) 2-methylglutarate, b.p. 140-142° (0.09 mm.). The data for the preparation of each of the esters in the series are

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summarized in Table VII and the properties of the esters are reported in Table VIII.

The citrate ester was not distilled because it appeared to decompose thermally, probably through transesterification involving the free hydroxyl group. The following attempt was made to methylate the hydroxy group and obtain the more stable methoxy derivative, tris(t'-amyl) 3-methoxy-tricarballylate.

To a mixture of 40.0 g. (0.05 mole) of tris(t'-amyl) citrate in 100 ml. of petroleum ether, b.p. 60-90°, was added dropwise 35.4 g. (0.28 mole) of dimethylsulfate. After addition of the dimethyl sulfate was completed, 34.5 g. (0.25 mole) of anhydrous potassium sulfate and 100 ml. of petroleum ether were added. The mixture was refluxed for 14 hr., cooled, filtered, and the filtrate washed with 200 ml. of water. The organic layer was dissolved in 100 ml. of diethyl ether, dried over anhydrous calcium sulfate, and the ether evaporated. Vacuum distillation afforded 3.8 g. (10%) of a fraction tentatively identified as tris(t'-amyl) 3-methoxytricarballylate, boiling range 154-163° (0.10 mm.), n_D^{20} 1.3734, infrared spectrum, Figure 12.

B. Phosphate and Phosphonate Fluids

1. General procedure: A typical experiment for the preparation of these fluids follows. A mixture of 50.0 g. (0.33 mole) of phosphorus oxychloride and 249 g. (1.03 moles) of t'-amyl alcohol was heated to reflux, treated with 1 ml. of pyridine, and purged with nitrogen (50 ml/min) during a 5-hr. reaction period. The cooled product, dissolved in 500 ml. of ether, was washed with 250 ml. of 2% potassium carbonate, 300 ml. of water, and dried over anhydrous sodium sulfate. After the ether was evaporated, fractional distillation afforded 195 g. of an oil, b.p. 122-125° (0.03 mm.), n_D^{20} 1.3340. The oil in 200 ml. of acetone was percolated through a column of 50% Florisil and neutral alumina. Evaporation of the acetone and a second distillation gave 171 g. (70%) of tris(t'-amyl) phosphate, b.p. 115-116° (0.05 mm.).

Details for the preparation of the phosphate and phosphonate fluids are reported in Table IX and their properties are summarized in Table X. In the preparation of bis(t'-amyl) benzenephosphonate and bis-(di-t'-propylphosphonyloxy)-2,2,3,3,4,4-hexafluoropentane, a stoichiometric quantity of pyridine was used in place of a catalytic quantity, and the resulting pyridine hydrochloride was filtered off. Both the bis(di-t'-propyl-phosphonyloxy)-2,2,3,3,4,4-hexafluoropentane and the bis(di-t'-amylphosphonyl-oxy)-2,2,3,3,4,4-hexafluoropentane disproportionated at higher temperatures, and substantial losses of material were incurred in successive distillations.

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TABLE VII

SYNTHESIS OF POLYFLUOROALKYL ESTERS

Acid	Alcohol	Ester	Calculated			Found		
			C	H	F	C	H	F
3-Methylglutaric acid 0.39 mole 0.39	t'-Amyl alcohol 0.88 mole 0.88 mole	Bis(t'-amyl) 3-methylglutarate 63% 91% (crude)						
3-Methylglutaric acid 1.55 mole 0.39 mole	t'-Heptyl alcohol 3.58 mole 0.87 mole	Bis(t'-heptyl) 3-methylglutarate 62% 70%	31.02	1.82	58.98	31.21	1.92	59.00
2-Methylglutaric acid 0.39 mole 0.68 mole	t'-Heptyl alcohol 0.87 mole 1.50 mole	Bis(t'-heptyl) 2-methylglutarate 55% 61%	31.02	1.82	58.89	30.90	1.86	58.75
Camphoric acid 0.36 mole	t'-Heptyl alcohol 0.82 mole	Bis(t'-heptyl) camphorate 59%	34.79	2.43	55.05	35.23	2.52	55.70
2,2'-Dimethylglutaric acid 0.39 mole	t'-Heptyl alcohol 0.88 mole	Bis(t'-heptyl) 2,2'-dimethyl-glutarate 81%	31.99	2.05	57.84	32.08	2.17	57.80
3,3-Dimethylglutaric acid 0.39 mole	t'-Heptyl alcohol 0.88 mole	Bis(t'-heptyl) 3,3-dimethyl-glutarate 66%	31.99	2.05	57.84	31.95	2.10	57.60
Tricarballylic acid 0.33 mole 0.33 mole	t'-Amyl alcohol 1.10 moles 1.10 moles	Tris(t'-amyl) tricarballylate 63% 60%	30.82	1.73	55.72	30.79	1.69	55.85
Tricarballylic acid 0.65 mole	t'-Propyl alcohol 0.65 mole and t'-Amyl alcohol 0.65 mole	Mixed (t'-propyl) (t'-amyl) tricarballylate 40%						
Pyromellitic dianhydride 0.20 mole	t'-Amyl alcohol 1.00 mole	1,2,4,5-Tetrakis (t'-amyl)-pyromellitate 62%						
3-Methylglutaric acid 0.56 mole	2,2,3,3,4,4-Hexa-fluoropentane-1,5-diol 0.29 mole and t'-Propyl alcohol 0.70 mole	Mixed ester 48%	39.66	3.76	38.19	39.84	3.84	35.60
Citric acid 0.33 mole	t'-Amyl alcohol 1.10 mole	Tris(t'-amyl) citrate 25%						

TABLE VIII

PROPERTIES OF POLYFLUOROALKYL ESTERS

Ester	B.P. (°C)(mm.)		n_D^{20}	d (t-°C)	Pour Point (°F)	Infrared Spectrum
Bis(i'-amyl) 3-methyl-glutarate[a]	130-132	(0.03)	1.3606	1.571 (24)	< -90	Figure 1*
	109	(0.10)	1.3610		< -90	
Bis(i'-heptyl) 3-methyl-glutarate[b]	145-148	(0.02)	1.3518	1.648 (20)	-75	Figure 2
	145-167	(0.03)	1.3515		-75	
Bis(i'-heptyl) 2-methyl-glutarate	140-142	(0.09)	1.3509	1.649 (26)	-80	Figure 3
	153-155	(0.02)	1.3511			
Bis(i'-heptyl) camphorate[c]	140-145	(0.02)	1.3725	1.59 (26)	-30	Figure 4
Bis(i'-heptyl) 2,2'-dimethyl glutarate	130-131	(0.05)	1.3525	1.627 (26)	-80	Figure 5
Bis(i'-heptyl) 3,3-dimethyl-glutarate[d]	130-132	(0.02)	1.3551	1.636 (27)	-80	Figure 6
Tris(i'-amyl) tricarballyl-ate[e]	155-157	(0.04)	1.3608	1.667 (26)	-45	Figure 7
	152-155	(0.02)	1.3623			
Mixed(i'-propyl)(i'-amyl) tricarballylate	150-155	(0.10)	1.3814	1.609 (24)	-35	Figure 8
1,2,4,5-Tetrakis(i'-amyl) pyromellitate	244-246	(0.20)	--	--	m.p. 37-39	Figure 9
Mixed ester from 3-methyl-glutaric acid, 2,2,3,3,4,4-hexafluoropentane-1,5-diol, and i'-propyl alcohol	not distilled		1.4062	1.451 (26)	-25	Figure 10
Tris(i'-amyl) citrate	not distilled		1.3638	1.732	-25	Figure 11

a/ Reported b.p. 129° (0.5 mm.); n_D^{20} 1.3595; d_4^{20} 1.5570; pour point, -75°F.[12]

b/ Reported b.p. 147° (0.5 mm.); d_4^{20} 1.6484; n_D^{20} 1.3505; pour point, -30°F.[12]

c/ Reported b.p. 174-177° (0.8 mm.).[10]

d/ Reported, no data.[13]

e/ Reported b.p. 172° (0.5 mm.); n_D^{20} 1.3588; d_4^{20} 1.6800; pour point, -30°F.[10]

* Figures 1 through 39 are found in Appendix A.

TABLE IX

SYNTHESIS OF POLYFLUOROALKOXY PHOSPHATES AND PHOSPHONATES

Phosphorus Chloride	Alcohol	Phosphate or Phosphonate	Calcd.				Found			
			C	H	F	P	C	H	F	P
Phosphorus oxychloride 0.33 mole	t'-Amyl alcohol 1.03 moles	Tris(t'-amyl) phosphate 70%	24.34	1.23	61.60	--	24.44	1.30	61.50	--
Phosphorus oxychloride 0.25 mole	t'-Heptyl alcohol 0.78 mole	Tris(t'-heptyl) phosphate 45%	24.01	0.86	66.08	--	24.00	0.85	66.00	--
Phosphorus oxychloride 0.52 mole	t'-Propyl alcohol 1.10 moles and 2,2,3,3,4,4-hexafluoropentane-1,5-diol 0.52 mole	Bis(di-t'-propylphosphonyloxy)-2,2,3,3,4,4-hexafluoropentane 9%	24.65	1.95	50.47	7.48	24.75	2.01	50.25	7.52
Phosphorus oxychloride 0.40 mole	t'-Amyl alcohol 0.50 mole and 2,2,3,3,4,4-hexafluoropentane-1,5-diol 0.10 mole	Bis(di-t'-amylphosphonyloxy)-2,2,3,3,4,4-hexafluoropentane 9%	24.44	1.31	58.78	5.04	24.34	1.36	59.00	4.95
Dichlorophenylphosphine oxide 0.66 mole	t'-Amyl alcohol 1.44 moles	Bis(t'-amyl) benzenephosphonate 46%	32.78	1.89	51.86	5.28	32.95	1.86	52.02	5.12

TABLE X

PROPERTIES OF POLYFLUOROALKYL PHOSPHATES AND PHOSPHONATES

Phosphate or Phosphonate	B. P. °C (mm.)	n_D^{20}	d (t-°C)	Pour Point (°F)	Infrared Spectrum
Tris(ψ'-amyl) phosphate[a]	115-116 (0.05)	1.3340	1.847 (28)	-90	Figure 13
Tris(ψ'-heptyl) phosphate	147 (0.07)	1.3300	1.829 (28)	-30	Figure 14
Bis(di-ψ'-propylphosphonyl-oxy)-2,2,3,3,4,4-hexafluoro-pentane	177-178 (0.06)	1.3603	1.696 (26)	-30	Figure 15
Bis(di-ψ'-amylphosphonyl-oxy)-2,2,3,3,4,4-hexafluoro-pentane	205-206 (0.05)	1.3472	1.773 (25)	-50	Figure 16
Bis(ψ'-amyl) benzenephosphonate[b]	126-127 (0.06)	1.3922	1.624 (26)	-70	Figure 17

a/ Reported, b.p. 142° (0.5; n_D^{20} 1.3333; pour point, < -65°.[14]

b/ Reported, b.p. 119-121° (0.12-0.18), d 77°F, 1.61.[7]

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2. Tris[2,2-bis(trifluoromethyl)-5,5,6,6,7,7,8,8-octafluoro-

1,3-dioxa-n-octyl] phosphate (attempted): A solution of 5.1 g. (0.03 mole) of phosphorus oxychloride in 25 ml. of anhydrous ether was added dropwise to a mixture of 42.0 g. (0.10 mole) ψ'-amyl hexafluoroacetone hemiketal sodium salt (see paragraph III.G.4) in 75 ml. of ether. After the addition of phosphorus oxychloride was complete, the mixture was refluxed for 1.5 hr., cooled, and filtered to remove sodium chloride. Concentration of the filtrate on the rotary evaporator afforded 29.5 g. of a milky white liquid which was washed with petroleum ether to remove residual mineral oil remaining from the sodium hydride suspension used in preparing the sodium salt. Distillation gave 15.2 g. (21%) of a fraction tentatively identified as tris[2,2-bis(trifluoromethyl)-5,5,6,6,7,7,8,8-octafluoro-1,3-dioxa-n-octyl] phosphate, b.p. 122-142° (0.1 mm.), n_D^{20} 1.3310, infrared spectrum, Figure 18, n.m.r. peaks (neat, dimethylsulfoxide as an external standard), τ 5.31 (triplet, $J = 12$, $CF_2\underline{CH_2}O$) and τ 3.94 (triplet, $J = 5$, $\underline{H}CF_2$).

In a repetition of the procedure, 160 g. (0.38 mole) of the sodium salt of ψ'-amyl hexafluoroacetone hemiketal and 18.5 g. (0.12 mole) of phosphorus oxychloride were refluxed for 4 hr. in toluene. This treatment afforded 52.5 g. (35%) of the same compound, b.p. 109-115° (0.06 mm.), n_D^{20} 1.3350, pour point -90°F. In this sample, the intensity of the 1240 cm^{-1} band (CF_3) in the infrared was weaker in relation to other infrared bands than the same band in the spectrum of the first preparation. An unsatisfactory elemental analysis was obtᴀ.ᴇd for the compound.

Anal. Calcd. for $C_{24}H_9O_7F_{42}P$: C, 23.28; H, 0.73; F, 64.44; P, 2.50. Found: C, 24.96; H, 1.26; F, 65.64; P, 3.82. (Calcd. for tris-(ψ'-amyl) phosphate $C_{15}H_9F_{24}O_4P$: C, 24.34; H, 1.23; F, 61.60; P, 4.19.)

C. Ether Fluids

1. General procedure: The following procedure is typical of the method followed for the preparations described in Table XI. The properties of the ethers are reported in Table XII.

To a stirred solution of 32.8 g. (0.82 mole) of sodium hydroxide in 300 ml. of water was added 354 g. (0.82 mole) of ψ'-nonyl alcohol. Subsequently, over a 20-min. period, 143 g. (0.36 mole) of 1,4-butanediol bis(p-toluenesulfonate) was added, and the mixture was heated to reflux. Addition of about 200 ml. of water was required in order to maintain a fluid mixture. After 16 hr. of heating, the mixture was cooled and the lower layer was separatᴇd and filtered to recover 132 g. of unchanged ψ'-nonyl alcohol. A first fractional distillation through a 30-cm.

TABLE XI

SYNTHESIS OF POLYFLUOROALKYL ETHERS

Tosylate	Alcohol	Ether	Calcd.			Found		
			C	H	F	C	H	F
1,4-Butanediol bis-(p-toluenesulfonate) 0.36 mole	ψ'-Nonyl alcohol 0.82 mole	1,4-Bis(ψ'-nonyloxy)butane 23%	28.77	1.54	66.21	28.91	1.54	66.25
1,6-Hexanediol bis-(p-toluenesulfonate) 0.48 mole	ψ'-Heptyl alcohol 1.00 mole	1,6-Bis(ψ'-hexyloxy)heptane 40%						
2,2,3,3,4,4-Hexafluoro-1,5-pentanediol bis-(p-toluenesulfonate) 0.24 mole	ψ'-Heptyl alcohol 0.50 mole	Probably 1-hydroxy-5-(ψ'-heptyloxy)-2,2,3,3,4,4-hexafluoro-pentane p-toluenesulfonate[a]	35.06	2.10	53.10	33.54	2.07	50.27
Pentaerythritol tetra-(p-toluenesulfonate) 0.32 mole	ψ'-Amyl alcohol 1.30 moles	79% of the p-toluenesulfonate was recovered						
1,1,1-Tris(hydroxy-methyl)ethane 0.32 mole	ψ'-Amyl alcohol 1.00 mole	100% of the p-toluenesulfonate was recovered						

a/ Assignment based in part on an infrared band at 1600 cm^{-1} (C_6H_5).

TABLE XII

PROPERTIES OF POLYFLUOROALKYL ETHERS

Ether	B.P. (°C)(mm.)	n_D^{20}	d (t-°C)	Pour Point (°F)	Infrared Spectrum
1,4-Bis(ψ'-nonyloxy)butane	137-138 (0.05)	1.3361	1.713 (28)	20	Figure 19
1,6-Bis(ψ'-heptyloxy)hexane[a]	126-127 (0.07)	1.3480	1.572 (26)	<-95	Figure 20
1-Hydroxy-5-(ψ'-heptyloxy)-2,2,3,3,4,4-hexafluoropentane p-toluenesulfonate	120-126 (0.11)	1.4114	1.599 (26)	65	Figure 21

[a] Reported, b.p. 144° (0.5 mm.), d_4^{20} 1.5776, n_D^{20} 1.3467, pour point, -70°F. [12]

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vacuum-jacketed column gave an additional 28 g. of ψ'-nonyl alcohol, b.p. about 70° (0.04 mm.), 107 g. of crude 1,4-bis(ψ'-nonyloxy)butane, b.p. 140-150° (0.04 mm.), and 11.0 g. of a fraction, presumably 1,14-bis(ψ'-nonyloxy)-5,10-dioxatetradecane, b.p. 192-194° (0.06 mm.). Redistillation afforded 75.1 g. of 1,4-bis(ψ'-nonyloxy)butane, b.p. 137-138° (0.05 mm.).

2. Tetra(ψ'-amyl)neopentyl ether (attempted preparation in dimethyl formamide): To a stirred solution of 34.0 g. (0.85 mole) of sodium hydroxide in 200 ml. of water and 600 ml. of dimethylformamide was added 198.0 g. (0.85 mole) of ψ'-amyl alcohol. Subsequently, over a period of 30 min., 150.0 g. (0.20 mole) of pentaerythritol tetra-p-toluenesulfonate was added. After the temperature was slowly increased to 60°, the mixture was cooled to room temperature and stirred overnight. The mixture was then refluxed (120°) for 7 hr., cooled, and filtered to remove 92.1 g. (61%) of unchanged pentaerythritol tetra-p-tosylate. The filtrate was diluted with 800 ml. of ether and the ether phase was separated, dried over anhydrous calcium sulfate, and evaporated. Vacuum distillation afforded 197.3 g. of a mixture of unchanged ψ'-amyl alcohol and dimethylformamide, boiling range 41-46° (0.5 mm.), n_D^{20} 1.3500. The residue from the distillation, 56.8 g., was a highly viscous brown liquid from which precipitated additional pentaerythritol tetra-p-toluenesulfonate.

3. Bis(ψ'-amyl) ether (attempted preparations in dimethyl formamide and dimethylacetamide): After 23.2 g. (0.10 mole) of ψ'-amyl alcohol in 50 ml. of anhydrous dimethylformamide was added dropwise to a suspension of 2.4 g. (0.1 mole) of sodium hydride in 100 ml. of anhydrous dimethylformamide, the mixture was stirred at room temperature for 1 hr., treated with 38.6 g. (0.10 mole) of ψ'-pentanol p-toluenesulfonate in 50 ml. of anhydrous dimethylformamide, slowly heated to 99° and held there 2 hr. After the cooled mixture was poured into 500 ml. of water, the organic layer was dissolved in 100 ml. of diethyl ether, washed twice with 500 ml. portions of water, dried over calcium sulfate, and the ether was removed. Fractional distillation of the resulting oil gave 4.0 g. (19%) of recovered ψ'-amyl alcohol, b.p. 70-79° (36 mm.) and 25.2 g. (65%) of recovered ψ'-pentanol p-toluenesulfonate, b.p. 109-111° (0.03 mm.), n_D^{20} 1.4289, which were identified by their infrared spectra.

In a second experiment, the sodium salt of ψ'-amyl alcohol was prepared by the addition of 4.7 g. (0.02 mole) of the alcohol to 2.9 g. (0.02 mole) of sodium hydride suspended in anhydrous diethyl ether. The mixture was refluxed for 1 hr. and the ether was allowed to distill until the mixture became viscous. After 75 ml. of N,N-dimethylacetamide was added, 10.5 g. (0.02 mole) of bis(ψ'-amyl) sulfate was introduced over a period of 30 min. When addition of the bis(ψ'-amyl) sulfate was complete, the mixture was refluxed for 5 hr., cooled, and washed with 100 ml. of

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water. The organic layer was dissolved in 300 ml. of ether, dried over anhydrous calcium sulfate, and the ether was evaporated. Vacuum distillation provided the following fractions: a, 10.3 g., boiling range 32-74° (0.10 mm.), n_D^{20} 1.3693, i.r. bands at 3280 cm^{-1} (OH), 2950 cm^{-1} (CH_2), 1750 cm^{-1} (acid or ester C=O), 1640 cm^{-1} (N,N-dimethylacetamide C=O); and b, 3.5 g., boiling range 80-88° (0.08 mm.), n_D^{20} 1.3395, i.r. absorption 2960 cm^{-1} (CH_2), 1750 cm^{-1} (acid or ester C=O), 1610 cm^{-1} (N,N-dimethylacetamide C=O).

4. 1,1,1-Tris(ψ'-amyloxymethyl)ethane (attempted preparation in dioxane): 1,1,1-Tris(hydroxymethyl)ethane tri-p-toluenesulfonate, 15.0 g. (0.03 mole), was added to a stirred solution of 29.5 g. (0.12 mole) of sodium ψ'-amylate (prepared from 26.9 g. (0.12 mole) of ψ'-amyl alcohol and 2.8 g. (0.12 mole) of sodium hydride in 100 ml. of anhydrous dioxane. After the mixture was heated at 80-90° for 7 hr. and cooled, 12.4 g. (83%) of the unchanged tosylate, m.p. 280°, precipitated.

In a second experiment with the same quantities of reactants, the mixture was heated at 100° for 5 hr., cooled, filtered to remove the insoluble material, and the dioxane was evaporated. When the residue was dissolved in 100 ml. of ether and washed with water, 6.1 g. (40%) of unchanged tosylate precipitated. Fractional distillation of the soluble portion gave 7.6 g. of ψ'-amyl alcohol and 2.6 g. of an unidentified fraction, b.p. 75-78° (1.5 mm.), infrared bands at 3350 (OH, strong).

D. Polyfluoroalkyl Phosphonitrilate and Cyanurate Fluids

1. Bis(ψ'-amyl)phosphonitrilate trimer: Sodium hydride, 17.6 g. (0.72 mole), washed with two 100-ml. portions of ether and covered with 50 ml. of ether was treated with 278 g. (1.2 mole) of ψ'-amyl alcohol in 300 ml. of ether at a rate that allowed the ether to reflux gently. After the sodium salt was prepared, 200 ml. of toluene was added and the ether was distilled out. A solution of 41.8 g. (0.12 mole) of phosphonitrilic chloride trimer in 100 ml. of toluene was added over a period of 30 min., and the mixture was refluxed 9 hr., cooled, and filtered to remove the sodium chloride. The filtrate, washed with 400 ml. of 2% sodium chloride and dried over anhydrous sodium sulfate, was concentrated on a rotary evaporator and fractionally distilled to obtain 152 g. of bis(ψ'-amyl)-phosphonitrilate trimer, b.p. 170-175° (0.03 mm.), which was further purified by extraction with petroleum ether, b.p. 35-60° and percolation through a charcoal bed in a steam-jacketed Buechner funnel. There was obtained 138 g. (75%) of purified bis(ψ'-amyl)phosphonitrilate trimer, n_D^{20} 1.3519, d_{26}^{26} 1.807, infrared spectrum, Figure 22, pour point, -55°F (reported to b.p. 208-212° (0.45 mm.), n_D^{20} 1.3507, d_4^{20} 1.85, pour point, -50°F).[15]

2. (ψ'-Propyl)(ψ'-amyl)phosphonitrilate trimer: By the procedure described for the synthesis of bis(ψ'-amyl)phosphonitrilate trimer, 58.5 g. (0.45 mole) of ψ'-propyl alcohol, 116.0 g. (0.50 mole) of ψ'-amyl alcohol, 21.6 g. (0.90 mole) of sodium hydride, and 52.2 g. (0.15 mole) of phosphonitrilic chloride trimer gave 88.7 g. (29%) of (ψ'-propyl)(ψ'-amyl)phosphonitrilate trimer, b.p. 157-172° (0.03 mm.), n_D^{20} 1.3600, d_{25}^{25} 1.776, infrared spectrum Figure 23, pour point, -55°F (reported b.p. 180-200° (0.60 mm.), n_D^{20} 1.3627, d_4^{20} 1.69, pour point, -35°F).[15]

3. 2,4-Bis(ψ'-amyloxy)-6-(ψ'-nonyloxy)-s-triazine: A solution of 68.3 g. (0.37 mole) of cyanuric chloride in 750 ml. of toluene was treated sequentially with 172 g. (0.74 mole) of ψ'-amyl alcohol and 98.3 g. (0.74 mole) of s-collidine while the solvent temperature was maintained at 35° with an ice bath. The mixture was refluxed 1 hr., cooled, filtered to remove the collidine hydrochloride, and the solvent was partly evaporated. After the residue was treated sequentially with 173 g. (0.40 mole) of ψ'-nonyl alcohol and 49.6 g. (0.41 mole) of s-collidine, the mixture was refluxed for 15 hr., cooled, filtered, and concentrated on a rotary evaporator. Fractional distillation afforded 229 g. of a dark yellow oil, b.p. 167-176° (0.20 mm.), which was dissolved in 250 ml. toluene and 350 ml. of isopropyl alcohol and treated with 0.1 N sodium hydroxide until the mixture was permanently basic to phenophthalein. After the solvents were evaporated, the residue was washed several times with water. Fractional distillation gave a slightly yellow oil, b.p. 145-167° (0.03 mm.). The remaining color was removed with a charcoal bed laid in a steam-jacketed Buechner funnel. A total of 177 g. (49 percent) of 2,4-bis(ψ'-pentyloxy)-6-(ψ'-nonyloxy)-s-triazine, b.p. 144-167° (0.03 mm.), n_D^{20} 1.3619, d_{28}^{28} 1.796, infrared spectrum Figure 24, pour point -15°F (reported b.p. 175-180° (0.2 mm.), n_D^{20} 1.3587)[16] was obtained as a clear colorless oil.

4. 2,4,6-Tris[2,2-bis(trifluoromethyl)-5,5,6,6,7,7,8,8-octafluoro-1,3-dioxa-n-octyl]-s-triazine (attempted): A solution of 6.1 g. (0.03 mole) of cyanuric chloride in 125 ml. of toluene was added dropwise to to a stirred mixture of ψ'-amylhexafluoroacetone hemiketal sodium salt (see paragraph III.G.4) in 100 ml. of anhydrous ether. During the addition of the cyanuric chloride, the temperature was maintained at 55° with a heating mantle. After the addition was complete, the mixture was refluxed (75°) for 2.5 hr., then cooled and filtered to remove the sodium chloride. Concentration of the filtrate on the rotary evaporator afforded 35.5 g. of a viscous milky white liquid, which was washed with petroleum ether. Distillation gave 10.2 g. (24%) of a material that was tentatively identified as 2,4,6-tris[2,2-bis(trifluoromethyl)-5,5,6,6,7,7,8,8-octofluoro-1,3-dioxa-n-octyl]-s-triazine, b.p. 120-134° (0.35 mm.), n_D^{20} 1.3796, infrared spectrum Figure 25, n.m.r. peaks (CCl$_4$) at τ 5.03 (triplet, J = 13, CF$_2$CH$_2$O) and τ 3.93 (triplet, J = 6, HCF$_2$).

Anal. Calcd. for $C_{27}H_9F_{42}O_6H_3$: C, 25.55; H, 0.72; F, 62.88. Found: C, 26.97; H, 1.24; F, 55.50. (Calcd. for 2,4,6-tris(ψ'-amyl)-s-triazine $C_{18}H_9F_{24}N_3O_3$: C, 28.03; H, 1.18; F, 59.12.)

5. 2,4,6-Tris[2,2-bis(trifluoromethyl)-1,3-dioxa-n-hexyl]-s-triazine (attempted): By the procedure described for the synthesis of 2,4,6-tris[2,2-bis(trifluoromethyl)-5,5,6,6,7,7,8,8-octafluoro-1,3-dioxa-n-octyl]-s-triazine, 24.8 g. (0.10 mole) of n-propylhexafluoroacetone hemiketal sodium salt was treated with 6.1 g. (0.030 mole) of cyanuric chloride. Fractional distillation of the product afforded: a, 5.0 g., b.p. 60-65° (0.1 mm.), n.m.r. peaks (CCl_4) at τ 6.03 (triplet, J = 6, CH_2O), τ 8.26 (multiplet, J = 6, CH_3CH_2), τ 8.71 (singlet, unidentified), and τ 8.99 (triplet, J = 7, CH_3), and b, 3.1 g., b.p. 66-70° (0.1 mm.), n.m.r. peaks (CCl_4) at τ 6.06 (triplet, J = 6, CH_2O), τ 8.24 (multiplet, J = 7, CH_3CH_2), τ 8.75 (singlet, unidentified) and τ 9.03 (triplet, J = 7, CH_3). The infrared spectrum of Fraction b is reported in Figure 26.

E. Purification of Telomer Alcohols

1. Purity of the unpurified alcohols: A gas-liquid chromatogram of ψ'-amyl alcohol and ψ'-heptyl alcohol according to Felton's procedure[17] showed that ψ'-amyl alcohol was 92.8% pure (10 components). The ψ'-heptyl alcohol (6 components) was 87.7% pure.

2. Purification of ψ'-amyl alcohol and ψ'-heptyl alcohol: ψ'-Amyl alcohol (500 g.) was stirred with 50 g. potassium hydroxide in 150 ml. water at 90° $\pm$ 2° for 22 hr. The organic layer was separated, washed with water until neutral, dissolved in ether, and dried over sodium sulfate. The ether was removed and the residue distilled to obtain 219.0 g. (44% recovery) of ψ'-amyl alcohol, b.p. 138-140°. The purity indicated by gas-liquid chromatography was 99.4%.

ψ'-Heptyl alcohol (500 g.) was stirred with 50 g. potassium hydroxide in 150 ml. water at 90° $\pm$ 2° for 20 hr. The organic layer was separated, washed twice with water, taken up in ether, and washed with water until neutral. After the ether layer was dried over sodium sulfate, and the ether removed fractional distillation afforded 314.2 g. (63% recovery) of ψ'-heptyl alcohol, b.p. 114-118° (98 mm.). The purity indicated by gas-liquid chromatography was 98.5%.

The procedure, which followed the methods described by Ver Nooy[18] was repeated a number of times on a larger scale.

F. Alkyl and Polyfluoroalkyl p-Toluenesulfonate and Sulfate Intermediates

1. Alkyl and polyfluoroalkyl p-toluenesulfonates: The follow-
ing are typical examples of the three general procedures follcwed to pre-
pare these intermediates. Individual preparations are summarized in
Table XIII.

Procedure A: To a solution of 33.2 g. (0.10 mole) of ⱡ'-heptanol
in 50 ml. of pyridine was added a solution of 19.1 g. (0.10 mole) of p-
toluenesulfonyl chlo⁻ide in 30 ml. of pyridine while the temperature was
maintained at 55-60°. After the addition was complete, heating was con-
tinued at 55-60° for an additional hour and the mixture was cooled and
hydrolyzed in 1 liter of ice water. The organic phase was separated, di-.
luted with 100 ml. of toluene, washed with two 50-ml. portions of 15% am-
monium hydroxide and two 50-ml. portions of water, and dried over sodium
sulfate. When the toluene was evaporated aⱡd the unchanged alcohol was
removed by heating the residue to about 80° under reduced pressure, 23.6 g.
(49%) of ⱡ'-heptanol p-toluenesulfonate, m.p. 31-32° was obtained.

Procedure B: A solution of 10.0 g. (0.25 mole) of sodium hy-
droxide in 32 ml. of water was added dropwise to a solution of 26.4 g.
(0.20 mole) of ⱡ'-propanol and 43.8 g. (0.23 mole) of p-toluenesulfonyl
chloride in 70 ml. of water while the mixture was maintained at 55-60°.
After the addition was complete, the temperature was maintained at 60° for
an additional 1.3 hr. The oily phase was separated, diluted with 150 ml.
of toluene, washed with two 50-ml. portions of 15% ammonium hydroxide,
two 50-ml. portions of water, and dried over sodium sulfate. Fractional
distillation afforded 44.1 g. (77%) of ⱡ'-propanol p-toluenesulfonate,
b.p. 97-99° (0.3 mm.).

Procedure C: After 2.5 g. (0.015 mole) of sodium hydride in
75 ml. of ether was treated sequentially with 33.2 g. (0.10 mole) of
ⱡ'-heptanol and 21.0 g. (0.11 mole) of p-toluenesulfonyl chloride in 100
ml. of ether while the reaction mixture was maintained at 25-30°, the mixture
was refluxed for 1.75 hr. and filtered. The filtrate was washed with three
75-ml. portions of water, dried over sodium sulfate, and concentrated in
a rotary evaporator. Distillation gave 40.4 g. (83%) of ⱡ'-heptanol-p-
toluenesulfonate, b.p. 106-108° (0.06 mm.), m.p. 23-25° (d.t.a.).

2. Bis(ⱡ'-amyl) sulfate: Sodium wire, 23.0 g. (1.0 g-atom),
was dissolved in 580 g. (2.5 moles) of ⱡ'-amyl alcohol at 80-90°. Sulfuryl
chloride, 67.5 g. (0.5 mole), was mixed with 85 ml. of ⱡ'-amyl alcohol and
was slowly added to the sodium alcoholate at 70-80°. After addition of the
sulfuryl chloride was completed, the mixture was heated to 100° over a
period of 1 hr., cooled, and washed with two 400-ml. portions of water. The
organic phase dried over anhydrous calcium sulfate and vacuum distillate

TABLE XIII

SYNTHESIS AND PROPERTIES OF ALKYL AND POLYFLUOROALKYL p-TOLUENESULFONATE INTERMEDIATES

Procedure	Alcohol	p-Toluenesulfonate	M.P.	B.P.	n_D^{20}	Infrared Spectra
	i'-Propyl Alcohol	i'-Propyl p-toluenesulfonate				
B	0.25 mole	77%	13-15°[a]	97-99° (0.3 mm.)	1.4693	Figure 27
	i'-Amyl Alcohol	i'-Amyl p-toluenesulfonate				
A	0.30 mole	60%		104-106° (0.1 mm.)		Figure 28
A	0.20 mole	40%		105-109° (0.1 mm.)	1.4321	
C	0.10 mole	68%	5-12°[b]	103-104° (0.3 mm.)	1.4308	
C	0.10 mole	27%	12-14°	94° (0.1 mm.)	1.4355	
	i'-Heptyl Alcohol	i'-Heptyl p-toluenesulfonate				
A	0.10 mole	49%	31-32°[c]			Figure 29
A	0.20 mole	37%	31-32°			
B	0.20 mole	36% (crude)	25-26°	110-112° (0.06 mm.)	1.4152	
B	0.20 mole	47% (crude)				
C	0.10 mole	83%	23-25°	106-108° (0.06 mm.)	1.4142	
	1,4-Butanediol	1,4-Butanediol bis-p-toluenesulfonate				
A	0.50 mole	72%	81-82° (from ethanol)[d]			
	1,6-Hexanediol	1,6-Hexanediol bis-p-toluenesulfonate				
A	0.59 mole	61%	71-72° (from ethanol)[e]			
	2,2,3,3,4,4-Hexafluoro-pentane-1,5-diol	2,2,3,3,4,4-Hexafluoro-pentane-1,5-diol bis-p-toluenesulfonate				
A	0.39 mole	82%	94-96° (from ethanol)[f]			
	1,1,1-Tris(hydroxymethyl)-ethane	1,1,1-Tris(hydroxymethyl)-ethane tris-p-toluenesulfonate				
A	0.40 mole	80%	107-108°[g] (from methanol-acetone)			
	Pentaerythritol	Pentaerythritol tetra-p-toluenesulfonate				
A	0.33 mole	98%	150-154°[h]			Figure 30

[a] Reported m.p. 14-15°, b.p. 124-126° (2 mm.).[1]
[b] Reported m.p. 8-12°, b.p. 157 (5 mm.).[1]
[c] Reported m.p. ca. 33°, b.p. 126° (0.5 mm.).[19]
[d] Reported m.p. 81-82°.[20]
[e] Reported m.p. 71-72°.[12]
[f] Reported m.p. 96.5-97.5°.[21]
[g] Reported m.p. 108-108.5°.[22]
[h] Reported m.p. 154.5-155.5°.[23]

afforded 58.9 g. (22%) of crude milky white bis($\Downarrow$'-amyl) sulfate. This material was washed with two 75-ml. portions of petroleum ether, b.p. 35-60°, filtered, and the petroleum ether was evaporated. A second distillation of this material afforded 49.9 g. (19%) of bis($\Downarrow$'-amyl) sulfate, b.p. 75-80° (0.10 mm.), n_D^{20} 1.3379, infrared spectrum, Figure 31 (reported b.p. 105° (2.1 mm.), n_D^{20} 1.3379.[4]/

G. Preparation and Properties of Hexafluoroacetone Hemiketals and Their Intermediates

1. **n-Propyl hexafluoroacetone hemiketal:** n-Propyl alcohol, 50.0 g. (0.83 mole) was treated with 160 g. (0.96 mole) of hexafluoroacetone, which was added as a gas bubbled beneath the surface of the alcohol. Since the reaction was exothermic, an ice bath was used occasionally to maintain the temperature at 50°. After the addition of hexafluoroacetone was complete, the mixture was held at 50° for 1 hr. and then cooled, giving 185.7 g. (99%) of n-propyl hexafluoroacetone hemiketal, infrared spectrum, Figure 32, n.m.r. peaks (cyclohexane) at τ 6.21 (triplet, J = 6, CH$_2$O), τ 6.68 (singlet, OH), τ 8.42 (sextuplet, J = 3, CH$_3$CH$_2$), τ 9.06 (triplet, J = 6, CH$_3$CH$_2$).

In one repetition of the experiment, 186 g. (98%) of n-propyl hexafluoroacetone hemiketal was obtained from 50 g. (0.83 mole) of n-propyl alcohol and 160 g. (0.96 mole) of hexafluoroacetone. Another experiment in which 6.0 g. (0.10 mole) of n-propyl alcohol in 25 ml. of ether was treated with 16.6 g. (0.10 mole) of hexafluoroacetone afforded 20.1 g. (91%) of the hemiketal.

2. **$\Downarrow$'-Amyl hexafluoroacetone hemiketal:** $\Downarrow$'-Amyl alcohol, 195 g. (0.83 mole), was treated with 160 g. (0.96 mole) of hexafluoroacetone, which was added as a gas bubbled beneath the surface of the alcohol. Since the reaction was exothermic, an ice bath was used periodically to maintain the temperature at 40°. After the addition of hexafluoroacetone was complete, the reaction mixture was held at 40° for 1 hr. and then cooled, giving 328.5 g. (99%) of $\Downarrow$'-amyl hexafluoroacetone hemiketal, infrared spectrum, Figure 33, n.m.r. peaks (CCl$_4$) at τ 8.71 (singlet, unidentified), τ 8.39 (singlet, unidentified), τ 8.23 (singlet, unidentified), τ 6.52 (singlet, OH), τ 5.65 (triplet, J = 13, CF$_2$CH$_2$O), and τ 3.98 (triplet, J = 5, HCF$_2$-).

A repetition of this procedure with 195 g. (0.83 mole) of $\Downarrow$'-amyl alcohol and 160 g. (0.96 mole) of hexafluoroacetone gave 330 g. (98%) of $\Downarrow$'-amyl hexafluoroacetone hemiketal.

3. n-Propyl hexafluoroacetone hemiketal acetate: After 22.6 g. (0.10 mole) of n-propyl hexafluoroacetone hemiketal was added dropwise to a stirred mixture of 2.4 g. (0.10 mole) of sodium hydride in 50 ml. of ether, the mixture was diluted with 25 ml. of ether, treated with 7.9 g. (0.10 mole) of acetyl chloride, and stirred 1 hr. After the salts were filtered off and the filtrate was concentrated on a rotary evaporator, fractional distillation gave 16.6 g. (65%) of n-propyl hexafluoroacetone hemiketal acetate, b.p. 142-144°, n_D^{20} 1.3430, infrared spectrum, Figure 34, n.m.r. peaks (CCl_4) at τ 9.03 (triplet, J = 7, CH_3-CH_2), τ 8.37, (multiplet, $CH_3CH_2CH_2$), τ 7.82 (singlet, CH_3CO), and τ 6.22 (triplet, J = 6, CH_2CH_2O).

Anal. Calcd. for $C_8H_{10}F_6O_3$: C, 35.83; H, 3.76; F, 42.51. Found: C, 36.49; H, 3.87; F, 43.25.

In a previous experiment the procedure described by Husted had been followed.[3/] A solution of 20.0 g. (0.19 mole) acetic anhydride in 10 ml. of pyridine was added to 20.3 g. (0.09 mole) n-propyl hexafluoroacetone hemiketal. The reaction mixture was refluxed for 17 hr., cooled, washed with water and 10% sodium bicarbonate, dried over anhydrous calcium sulfate, and distilled to obtain 4.2 g. of n-propyl acetate, b.p. 97-98°. No n-propyl hexafluoroacetone hemiketal acetate was isolated.

4. ψ'-Amyl hexafluoroacetone hemiketal acetate: ψ'-Amyl hexafluoroacetone hemiketal sodium salt, prepared from 39.8 g. (0.10 mole) of ψ'-amyl hexafluoroacetone hemiketal and 2.4 g. (0.14 mole) of sodium hydride, in 100 ml. of ether was treated with 7.9 g. (0.10 mole) of acetyl chloride. After the salts were filtered off, the solvent removed, and the residue fractionally distilled, 22.2 g. (51%) of ψ'-amyl hexafluoroacetone hemiketal acetate was obtained, b.p. 111-112° (60 mm.), n_D^{20} 1.3233, infrared spectrum, Figure 35, n.m.r. peaks (CCl_4) at τ 7.79 (singlet, CH_3CO), τ 5.66 (triplet, J = 13, CF_2CH_2O), and τ 3.98 (triplet, J = 6, HCF_2).

Anal. Calcd. for $C_{10}H_6F_{14}O_3$: C, 27.29; H, 1.37; F, 60.45. Found: C, 25.55; H, 1.50; H, 58.37.

In another experiment a few drops of sulfuric acid was added to a solution of 11.2 g. (0.11 mole) of acetic anhydride and 39.8 g. (0.10 mole) of ψ'-amyl hexafluoroacetone hemiketal, and the mixture was heated at 50° for 7 hr. The cooled mixture was washed with water and 10% sodium bicarbonate, dried over anhydrous calcium sulfate, and fractionally distilled. No ψ'-amyl hexafluoroacetone hemiketal acetate was isolated, but 19.0 g. of ψ'-amyl acetate, b.p. 154-162° (reported 155-157°)[24/] was obtained and identified by its infrared spectrum.

5. Thermal decomposition of ψ'-amyl hexafluoroacetone hemiketal acetate: When 5 ml. of ψ'-amyl hexafluoroacetone hemiketal acetate was heated under nitrogen in a Wood's metal bath at its boiling point, 174°, the reflux temperature dropped to 158° over a period of 0.5 hr. The remaining material was identified as ψ'-amyl acetate by its boiling point (reported, 155-157°)[6] and its infrared spectrum. The hemiketal had been stable at room temperature and remained unchanged after 22 days storage. An infrared spectrum of ψ'-amyl acetate is reported in Figure 36, and the spectrum of a mixture of ψ'-amyl acetate and ψ'-amyl hexafluoroacetone hemiketal is reported in Figure 37. The latter spectrum demonstrates that the carbonyl absorption can be readily differentiated in the two compounds. After ψ'-amyl hemiketal acetate was boiled for 16 hr., the conversion to ψ'-amyl acetate was quantitative.

6. Methyl propyl hexafluoroacetone ketal (attempted): The method described by Simmons and Wiley was followed.[25] To 22.6 g. (0.10 mole) of n-propylhexafluoroacetone hemiketal was added sequentially 12.6 g. (0.10 mole) of dimethyl sulfate and 13.8 g. (0.10 mole) of potassium carbonate at 35-40°, and the mixture was stirred for 4 hr., at the same temperature. During the stirring, the mixture became viscous and 20 ml. of petroleum ether and 50 ml. of toluene were added. When the mixture was poured into water and the organic later was separated, dried over sodium sulfate, and heated at a mantle temperature of 90° under reduced pressure (53 mm.) to remove the solvent, less than 1 g. of residue was obtained.

7. Methyl ψ'-amyl hexafluoroacetone ketal: Dimethyl sulfate 12.8 g. (0.10 mole) was added to 39.8 g. (0.10 mole) of ψ'-amyl hexafluoroacetone hemiketal, and the mixture was subsequently treated with 13.8 g. (0.10 mole) of potassium carbonate, diluted with 55 ml. of toluene, and stored overnight. When the product was poured into water and the organic layer was separated, dried over sodium sulfate, and fractionally distilled, 7.9 g. (19%) of methyl ψ'-amyl hexafluoroacetone ketal, b.p. 82-83° (45 mm.) n_D^{20} 1.3168, was obtained.

ψ'-Amyl hexafluoroacetone hemiketal sodium salt, prepared from 39.8 g. (0.10 mole) of ψ'-amyl hexafluoroacetone hemiketal and 2.5 g. (0.105 mole) of sodium hydride, in 100 ml. of toluene was treated with 12.6 g. (0.10 mole) of dimethyl sulfate. After the mixture was refluxed for 6.0 hr., cooled, and filtered, the filtrate was washed with a 200-ml. portion of water, dried over anhydrous calcium sulfate, and the solvent removed. Fractional distillation of the residue afforded 11.5 g. (28%) of methyl ψ'-amyl hexafluoroacetone ketal, b.p. 76-80° (45 mm.), n_D^{20} 1.3179, infrared spectrum, Figure 38, n.m.r. peaks (CCl₄) at τ 6.11 (singlet, CH₃O), τ 5.82 (triplet, J = 13, CF₂CH₂O), and τ 4.00 (triplet, J = 6, HCF₂). The infrared spectra of the two products were the same in all essential details.

8. Bis(ψ'-amyl) hexafluoroacetone ketal (attempted): ψ'-Amyl hexafluoroacetone hemiketal sodium salt, prepared from 39.8 g. (0.10 mole) of ψ'-amyl hexafluoroacetone hemiketal and 2.4 g. (0.10 mole) of sodium hydride, in 100 ml. of ether was treated with 38.6 g. (0.10 mole) of ψ'-pentanol p-toluenesulfonate and refluxed for 5.0 hr. After the mixture was filtered, the filtrate washed with two 100-ml. portions of water, dried over anhydrous calcium sulfate, and the solvent was evaporated. Fractional distillation recovered 42.0 g. (92%) of ψ'-pentanol p-toluenesulfonate, b.p. 112-115° (0.10 mm.), n_D^{20} 1.4312, and 7.1 g. of ψ'-propyl alcohol, b.p. 38-40° (0.28 mm.), n_D^{20} 1.3188.

9. ψ-Propionic acid: The procedure described by Pierce[26] was followed. A solution of 814 ml. of concentrated sulfuric acid in 3 liters of water was cooled to 35° and mixed with 264 g. (2.0 moles) of ψ'-propyl alcohol. Subsequently, 474 g. (3.0 moles) of solid potassium permanganate was added at a rate that maintained the reaction temperature between 40-50°. After the mixture was stirred overnight, solid sodium bisulfite was added until the manganese dioxide just dissolved. The solution was saturated with sodium chloride and extracted several times with ether. The combined ether extracts were dried over anhydrous sodium sulfate, concentrated on a rotary evaporator, and distilled to obtain 248.0 g. (85%) of ψ-propionic acid, b.p. 130-134°. Similar results were obtained in a repetition of the experiment.

10. Ethyl ψ-propionate: The compound was prepared by Faurote[12] method. A mixture of 248 g. (1.7 moles) ψ-propionic acid, 200 ml. of chloroform, and 117 g. (2.6 moles) of ethyl alcohol was refluxed for 25 hr. After the mixture was cooled to 25°, the chloroform phase was separated and dried over anhydrous sodium sulfate. Distillation gave 139.8 g. (43%) of ethyl ψ-propionate, b.p. 105-106°, n_D^{20} 1.3296, infrared spectrum, Figure 39 (reported, b.p. 106-107°, n_D^{23} 1.3268).[27] Similar results were obtained in a repetition of the experiment.

11. 1,1,2,2,4,4,5,5-Octafluoropentan-3-one (attempted):
The procedures described by Simmons[13] and Hauptschein[14] were followed. In an atmosphere of dry nitrogen, 139.0 g. (0.73 mole) of ethyl ψ-propionate, was added dropwise to a stirred solution of 16.9 g. (0.73 g-atom) of sodium shot in 250 ml. of anhydrous diethyl ether. Reaction at room temperature was indicated by a color change from colorless to light yellow and gradually to a deep red-brown. After being stirred overnight at room temperature, the mixture was acidified with 26 ml. of 3N sulfuric acid. The ether layer was separated, combined with five 100-ml. extracts of the aqueous phase, dried over magnesium sulfate, and evaporated on a rotary evaporator. Distillation at atmospheric pressure afforded 42.9 g. of a mixture of ψ-propionic acid and unchanged ethyl ψ-propionate, boiling range 100-134°.

In a second experiment 25.5 g. (1.110 g-atoms) of sodium cut into small pieces covered with 300 ml. of ether was treated with 193.1 g. (1.110 moles) of ethyl β-propionate over a period of 4 hr. The mixture which turned yellow, orange, and then deep red, was stirred at 25° for 28 hr. and allowed to stand 64 hr. Filtration gave 18.0 g. (70% recovery) of sodium. The filtrate was neutralized with concentrated sulfuric acid and filtered to remove some salts. Distillation gave 8.0 g. of a mixture of ethanol and ethyl β-propionate boiling at 73-98°, n_D^{25} 1.3453, infrared bands at 3350 cm^{-1} (OH) and 1770 cm^{-1} (ester C=O); and 133.0 g. (69%) of unchanged ethyl β-propionate boiling at 106-109° n_D^{20} 1.3291.

H. Miscellaneous Fluid Properties

1. Hydrolytic stability: The procedure described by Gamrath[5] was followed in studying the hydrolytic stability of phosphate esters. A weighed sample (0.0050 or 0.01 mole) 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. The data and results are recorded in Table XIV.

TABLE XIV

HYDROLYTIC STABILITY OF ESTERS

Ester	Wt. (moles)	Ml. H_2O	Ml. 1N NaOH/mole
Tricresyl phosphate	3.68 g. (0.010)	50	1.3[a]
Tricresyl phosphate	3.684 g. (0.010)	50	0.67
Triphenyl phosphate	3.263 g. (0.010)	50	0.37
Triphenyl phosphate	3.26 g. (0.010)	50	0.25
Triphenyl phosphate	6.52 g. (0.020)	100	0.28
Bis(β'-amyl) benzenephosphonate	2.93 g. (0.005)	25	1.04
Bis(β'-amyl) benzenephosphonate	5.86 g. (0.010)	50	1.19
Tris(β'-amyl)phosphate .	3.70 g. (0.0050)	25	1,159.8
Tris(β'-heptyl) phosphate	5.20 g. (0.0050)	25	1,323.8
Bis(β'-heptyl) 3-methylglutarate	7.74 g. (0.010)	50	0.29
Bis(β'-heptyl) 3-methylglutarate	7.74 g. (0.010)	50	0.34

[a] Gamrath reports 1.2.[5]

2. Viscometric properties of some polyfluoroalkylester fluids:
The viscosity, ASTM slope, and ASTM viscosity index were determined for
six fluoroester fluids. The data and results are recorded in Table XV.

3. Weight percent evaporation of some fluoroesters: The fluoro-
ester fluid was placed in an aluminum dish, 60 mm. in diameter by 18 mm.
deep, and weighed. The dish containing the fluid was then set on a hot
plate and a thermocouple inserted into the fluid so that the silver bead of
the thermocouple was approximately half way between the bottom of the dish
and the surface of the fluid. This test was conducted in a well-ventilated
hood to provide a circulating atmosphere above the sample surface. The
desired temperature was maintained for 1 hr., then the sample was removed
from the hot plate and allowed to cool to room temperature. The sample
and dish were reweighed and the weight percent evaporation calculated.
Data and results are recorded in Table XVI and plotted in Figures 40, 41, 42
and 43.

TABLE XVI

WEIGHT PERCENT EVAPORATION OF SOME FLUOROESTERS

Fluoroester	Wt. % Evaporation After 1 Hr.		
	200°F	300°F	400°F
Bis(ᵩ'-amyl) 3-Methylglutarate	0.56	23.31	--
Bis(ᵩ'-heptyl) 3-Methylglutarate	0.17	5.75	78.70
Bis(ᵩ'-heptyl) 2-Methylglutarate	0.09	5.87	--
Tris(ᵩ'-amyl) Tricarballylate	0.03	2.42	42.31

TABLE XV

VISCOMETRIC PROPERTIES OF SOME FLUOROESTER FLUIDS

Fluoroester	Viscosity[a] Cs 210°F Found	Reported[b]	100°F Found	Reported[b]	68°F Found	Reported[b,d]	ASTM Slope 68-210°F[e]	ASTM Visc. Index[f]
Bis(β'-amyl) 3-Methylglutarate	2.78	2.79	16.27	15.9	36.75	33	0.88	-59
Bis(β'-heptyl) 3-Methylglutarate	3.57	3.70	26.11	26.4	62.62	66	0.88	-80
Bis(β'-heptyl) 2-Methylglutarate	3.31	--	22.76	--	52.50	--	0.88	-77.5
Bis(β'-heptyl) 2,2'-Dimethylglutarate	3.36	--	22.82	--	58.23	--	0.90	-65.5
Bis(β'-heptyl) 3,3-Dimethylglutarate	3.78	3.87[c]	29.26	28.36[c]	71.63	--	0.88	-87
Tris(β'-amyl) Tricarballylate	6.78	6.74	86.23	79.3	267.55	240	0.85	-25

a/ ASTM D445-65.
b/ Reference 12.
c/ Reference 13.
d/ All values interpolated or extrapolated.
e/ From ASTM D341-43, Chart E.
f/ ASTM D2270-64.

Figure 41 - Temperature-Evaporation Curve for Tris(ψ'-amyl) Tricarballylate

Figure 40 - Temperature-Evaporation Curve for Bis(ψ'-amyl) 3-Methylglutarate

Figure 43 — Temperature-Evaporation Curve for
Bis(ψ'-heptyl) 2-Methylglutarate

Weight Percent Evaporation After 1 Hr.

$1/t + 230 \times 10^{-3}$

Figure 42 — Temperature-Evaporation Curve for
Bis(ψ'-heptyl) 3-Methylglutarate

Weight Percent Evaporation After 1 Hr.

$1/t + 230 \times 10^{-3}$

4. Corrosiveness of bis(ψ'-heptyl) 3-methylglutarate to aluminum and steel: The corrosiveness of a bis(ψ'-heptyl) 3-methylglutarate fluid to 52100 tool steel and 6061-T aluminum was tested in the following manner. The surfaces of the test metals were polished to a mirror finish with 600 grit silicon carbide paper which had been moistened with petroleum ether. After the test pieces had been boiled in benzene and then acetone, they were dried with absorbent cotton, weighed and placed into 50 ml. flasks. Each flask was equipped with a thermometer, reflux condenser, and calcium sulfate drying tube. Bis(ψ'-heptyl) 3-methylglutarate, 15 ml., was added to each flask and then heated at a temperature of 200°F ($\pm$ 5°) for a period of 31 days. Then each individual metal specimen was washed with boiling reagent grade benzene, boiling acetone, air dried, and examined. None of the samples exhibited any evidence of corrosion (pitting and/or staining). The metal test specimens were reweighed and the weight change per unit area calculated. These data are summarized in Table XVII.

TABLE XVII

CORROSION DATA FOR BIS(ψ'-HEPTYL) 3-METHYLGLUTARATE

Sample	Weight (g.) Before	After	Surface Area (sq. cm.)	Weight Change (g.)	Weight Change (g.)/sq. cm.
52100 Tool steel	2.9197	2.9211	4.83	+ 0.0014	+ 0.0003
52100 Tool steel	2.8603	2.8609	4.87	+ 0.0006	+ 0.0001
6061 T Aluminum	0.7828	0.7840	3.51	+ 0.0012	+ 0.0003
6061 T Aluminum	0.7862	0.7858	3.56	+ 0.0004	+ 0.0001

5. LOX compatibility: LOX compatibility data were determined at Marshall Space Flight Center according to MSFC-SPEC-106B and are summarized in Table I, p. 5.

6. Pour points and boiling points: Pour points, reported elsewhere in this report, were determined by ASTM Method D-97-57. Boiling points were determined at atmospheric pressure with a du Pont 900 Differential Thermal Analyzer at a heating rate of 15°/min under an atmosphere of nitrogen.

I. Miscellaneous Grease Properties

1. Preparation of a Vydax 1000 - bis(ϕ'-heptyl) 3-methylglutarate grease and other fluoroester greases: A grease (540 g.) containing 16 weight percent of a fluorocarbon telomer thickener (Vydax 1000) and bis(ϕ'-heptyl) 3-methylglutarate was prepared in the following manner. Vydax 1000 (1,122 g.) was added to a beaker containing 453.6 g. of the base fluid, and the mixture was stirred and heated on a hot plate. The temperature was maintained in the range of 50-55° while the telomer dispersion vehicle, trichlorotrifluoroethane, evaporated. The grease was cooled and then stored under a vacuum to remove the last trace of trichlorotrifluoroethane.

Penetrations of greases containing various amounts of thickener are reported in Table XVIII. The penetrations, worked and unworked, were obtained with a one-quarter scale cone in accordance with ASTM D1403-62.

TABLE XVIII

BIS(ϕ'-HEPTYL) 3-METHYLGLUTARATE GREASES

Wt. % of Fluorocarbon Telomer Thickener	Penetration	
	Unworked	Worked[a]
13	373	361
15	341	333
16	276	312

a/ Sixty reciprocal strokes.

The compositions of other fluoroester greases that were similarly prepared are described in Table XIX.

TABLE XIX

OTHER FLUOROESTER GREASES

Base Fluid		Weight of	Weight of
Fluoroester	Weight (g.)	Vydax 1000 (g.)	Grease (g.)
Bis(t'-amyl) 3-Methylglutarate	84	208	100
Tris(t'-amyl) Tricarballylate	84	208	100

2. **Weight percent oil separation of some fluoroester greases:**
The weight percent oil separations of three fluoroester greases as determined
by Federal Test Method Standard No. 791a, Method 321.2, are reported in
Table XX.

TABLE XX

OIL SEPARATION OF SOME FLUOROESTER GREASES

Grease Type[a]	Weight Percent Oil Separation	
	212°F	300°F
Bis(t'-heptyl) 3-Methylglutarate	4.65	8.16
Bis(t'-amyl) 3-Methylglutarate	5.00	11.82
Tris(t'-amyl) Tricarballylate	4.15	7.50

[a] All greases were thickened with 16% of a fluorocarbon telomer.

3. **Dropping points of some fluoroester greases:** The dropping
points of three fluoroester greases as determined by ASTM 566-64 are reported
in Table XXI.

TABLE XXI

DROPPING POINTS OF SOME FLUOROESTER GREASES

Grease Type[a]	Dropping Point (°F)
Bis(t'-heptyl) 3-Methylglutarate	365
Bis(t'-amyl) 3-Methylglutarate	347
Tris(t'-amyl) Tricarballylate	346

a/ All greases were thickened with 16% of a fluorocarbon telomer.

4. Aluminum shear reactivity of some fluoroester greases: The aluminum shear reactivities of three fluoroester greases were determined in the following manner. A sample of the candidate grease ($\sim$ 3 g.) was placed in a cylindrical hole in a block of 6061 T aluminum. A dowel of the same metal was rotated into the block at 1500 rpm under a load of 1000 psi for 1 min. The results are recorded in Table XXII.

TABLE XXII

ALUMINUM SHEAR REACTION OF SOME FLUOROESTER GREASES

Grease Type[a]	Explosive Reactions/ No. of Trials
Bis(t'-heptyl) 3-Methylglutarate	0/6
Bis(t'-amyl 3-Methylglutarate	0/6
Tris(t'-amyl Tricarballylate	0/6

a/ All greases were thickened with 16% of a fluorocarbon telomer.

5. Other tests: Samples totaling 810 g. of Vydax 1000 thickened bis(t'-heptyl) 3-methylglutarate grease was forwarded to Marshall Space Flight Center for evaluation with a Shell Four Ball Wear Tester and for other performance tests.

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APPENDIX A

INFRARED SPECTRA OF FLUIDS AND INTERMEDIATES
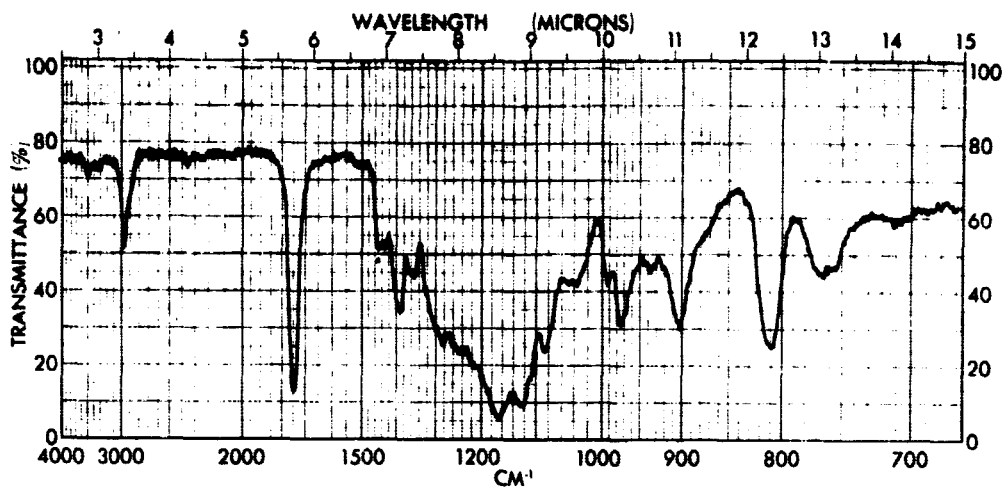
Figure 1 - Infrared Spectrum of Bis(ψ'-amyl) 3-Methylglutarate
(liquid)
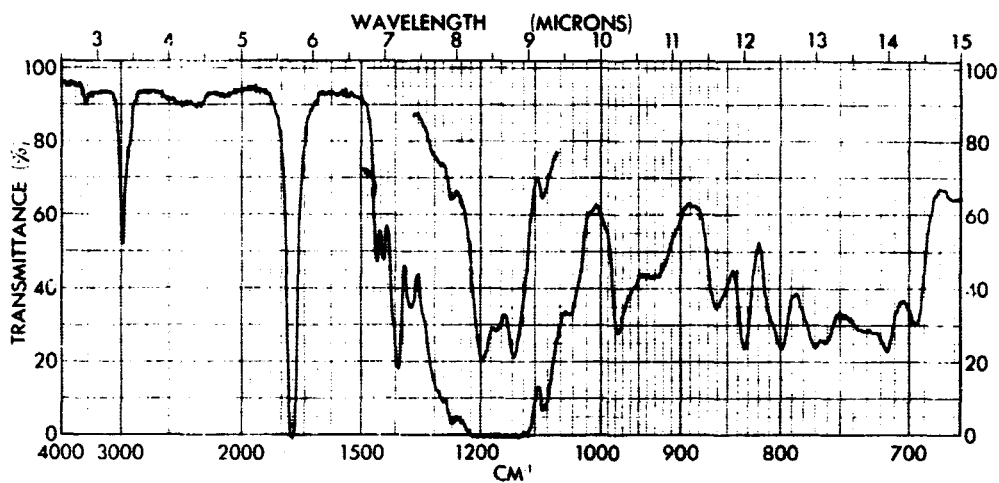
Figure 2 - Infrared Spectrum of Bis(ψ'-heptyl) 3-Methylglutarate
(liquid)
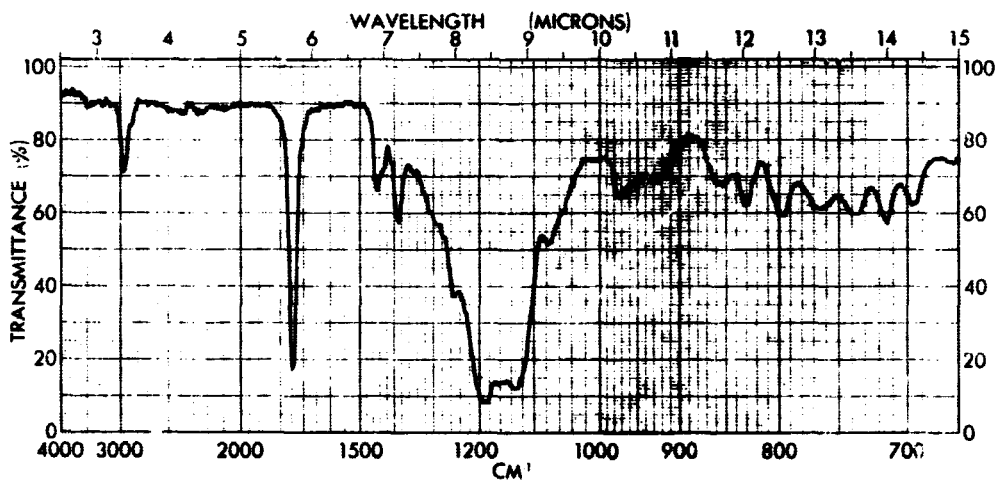
Figure 3 - Infrared Spectrum of Bis(ψ'-heptyl) 2-Methylglutarate
(liquid)
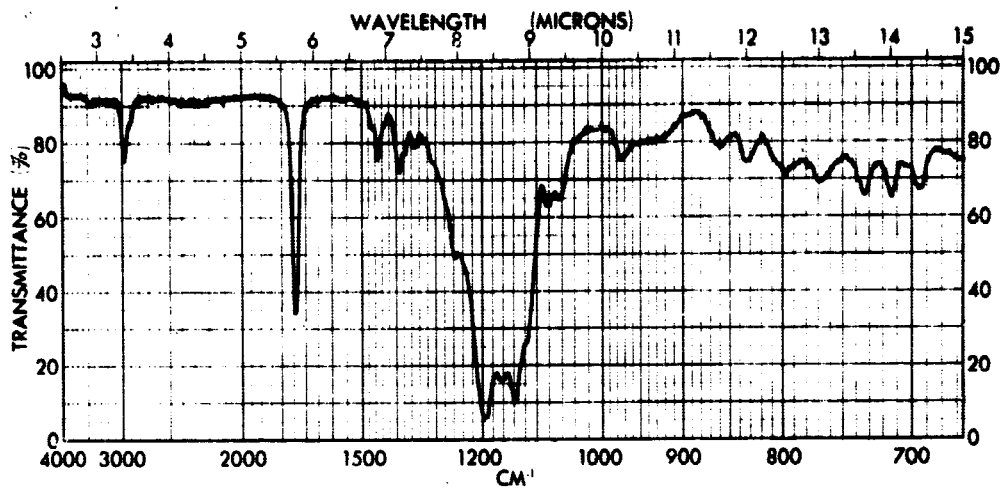
Figure 4 - Infrared Spectrum of Bis(∮'-heptyl) Camphorate
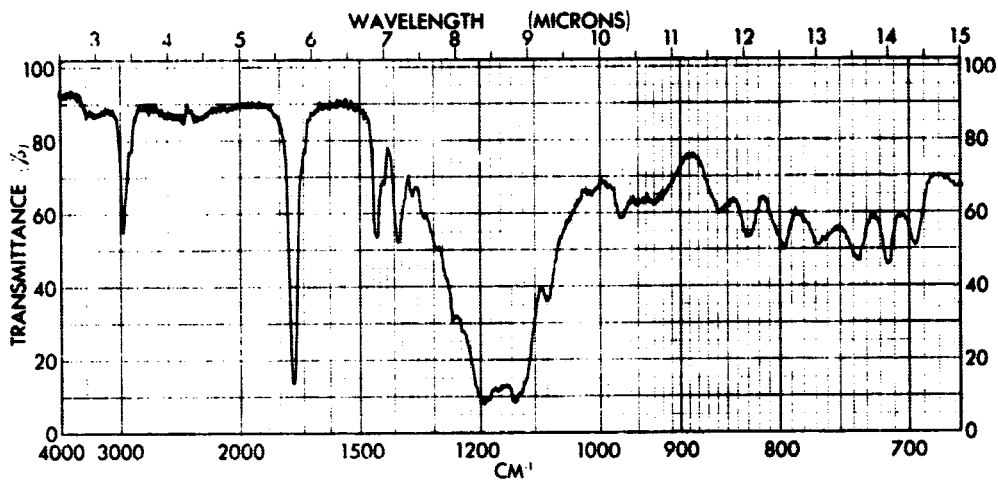
Figure 5 - Infrared Spectrum of Bis(∮'-heptyl) 2,2'-Dimethylglu-
tarate (liquid)
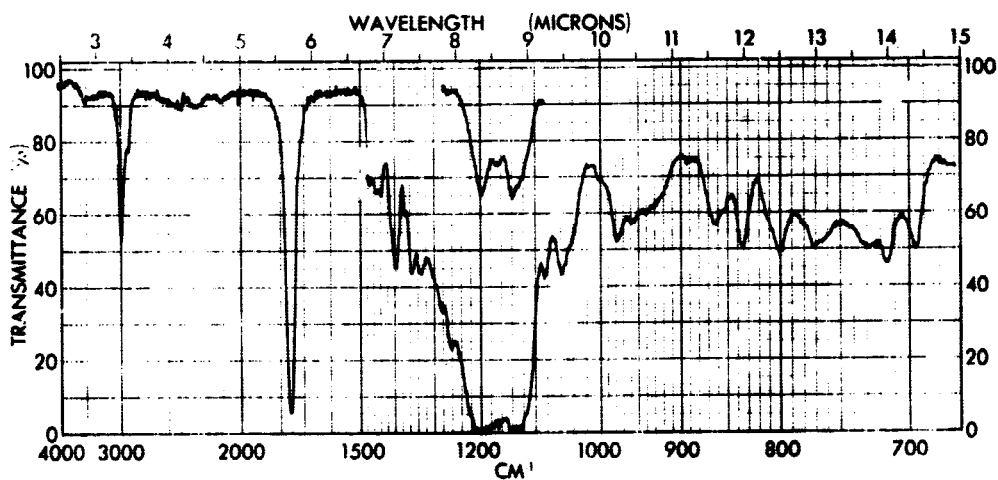
Figure 6 - Infrared Spectrum of Bis(∮'-heptyl) 3,3-Dimethyl-
glutarate (liquid)
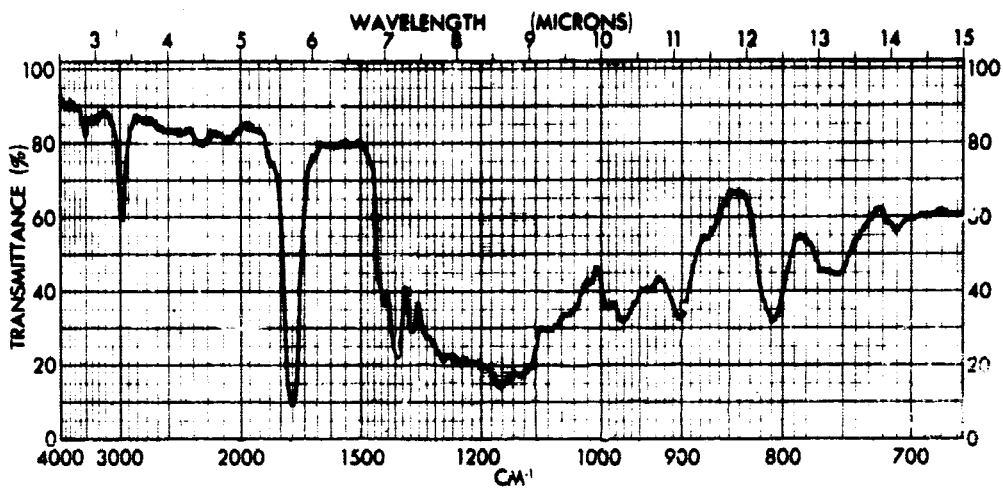
Figure 7 - Infrared Spectrum of Tris(ψ'-amyl) Tricarballylate (liquid)
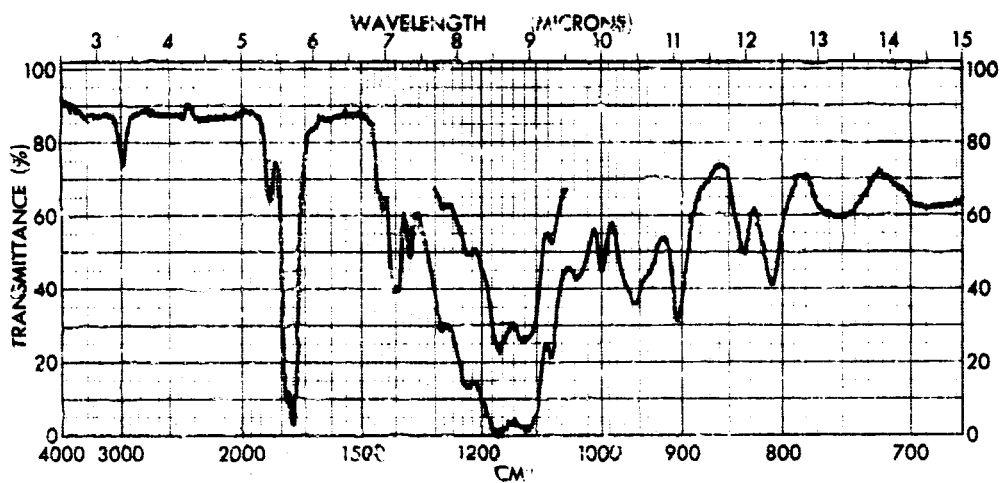
Figure 8 - Infrared Spectrum of Mixed ψ'-Propyl and ψ'-Amyl Tricarballylates (liquid)
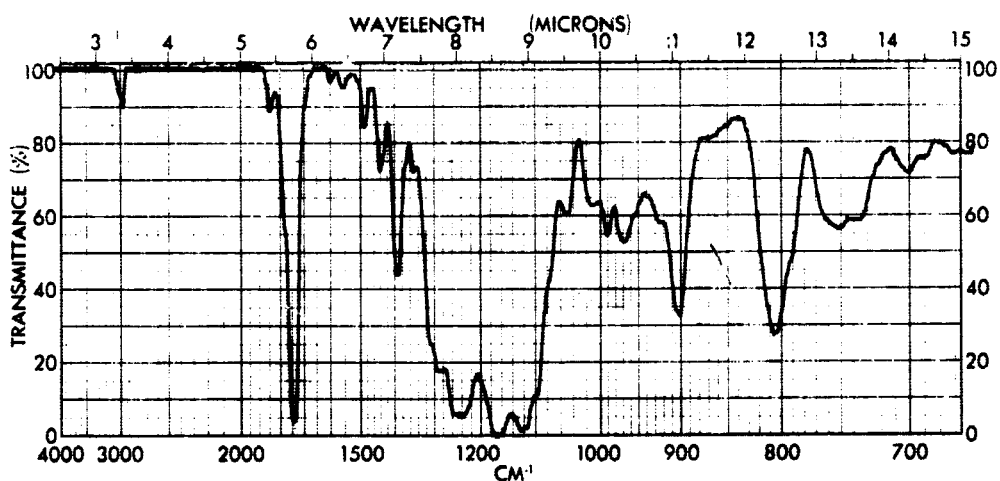
Figure 9 - Infrared Spectrum of 1,2,4,5 Tetrakis(ψ'-amyl) Pyromellitate (liquid)
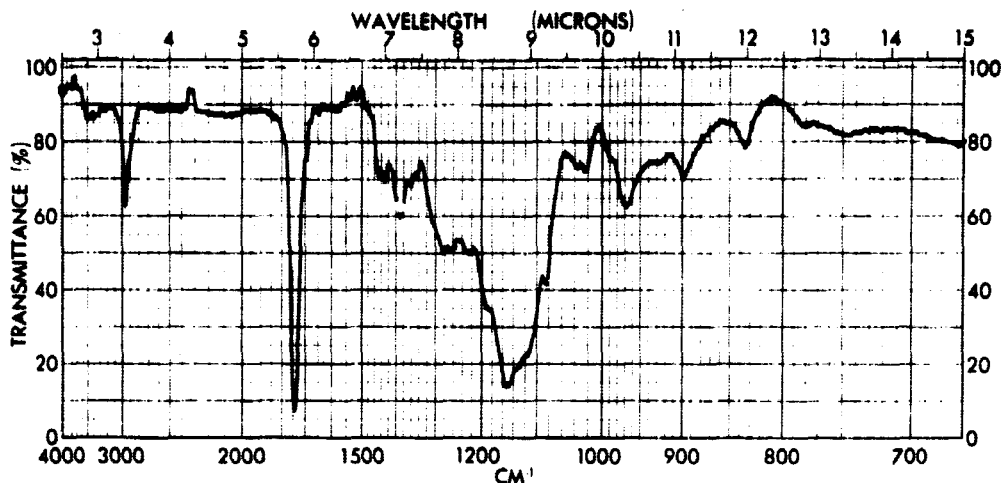
Figure 10 - Infrared Spectrum of the Ester of 3-Methylglutaric Acid ψ'-Propyl alcohol, and 2,2,3,3,4,4-Hexafluoropentane-1,5-diol (liquid)
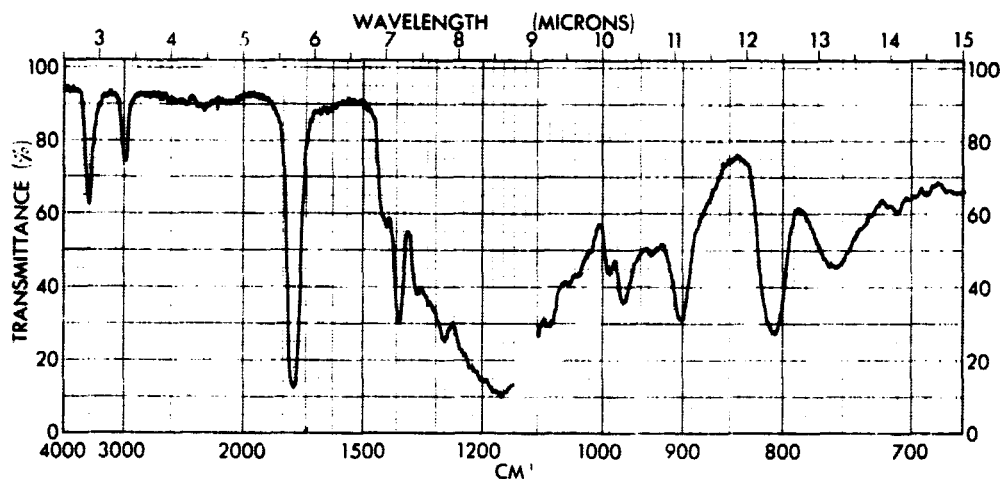
Figure 11 - Infrared Spectrum of Tris(ψ'-amyl) Citrate (liquid)
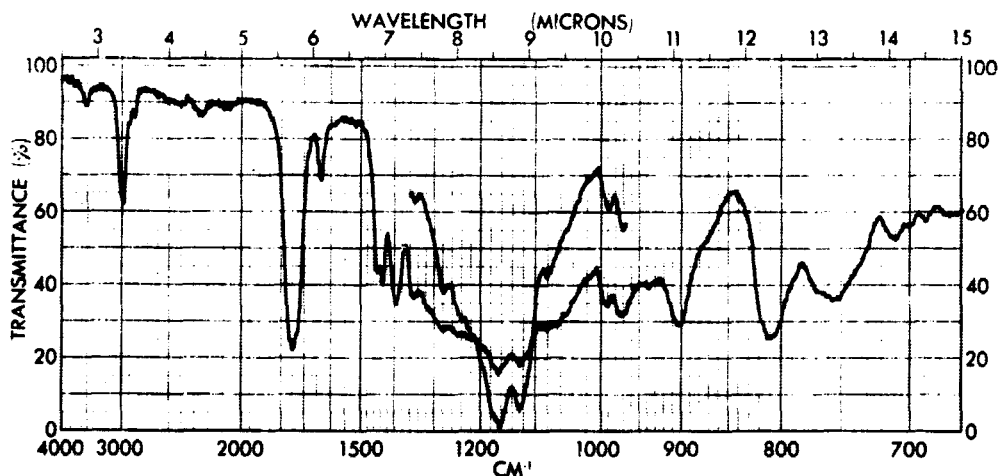
Figure 12 - Infrared Spectrum of Tris(ψ'-amyl) 3-Methoxytricar-ballylate (liquid)
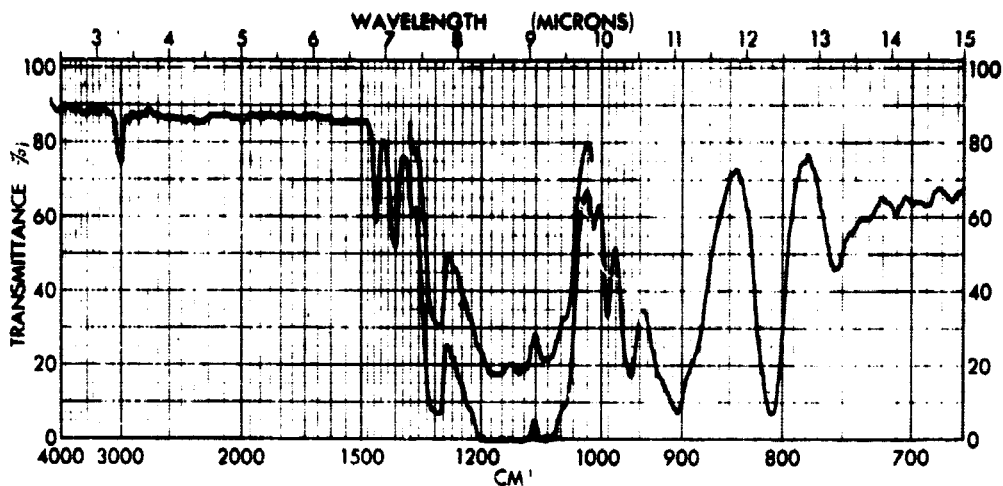
Figure 13 - Infrared Spectrum of Tris(ᵧ'-amyl) Phosphate (liquid)
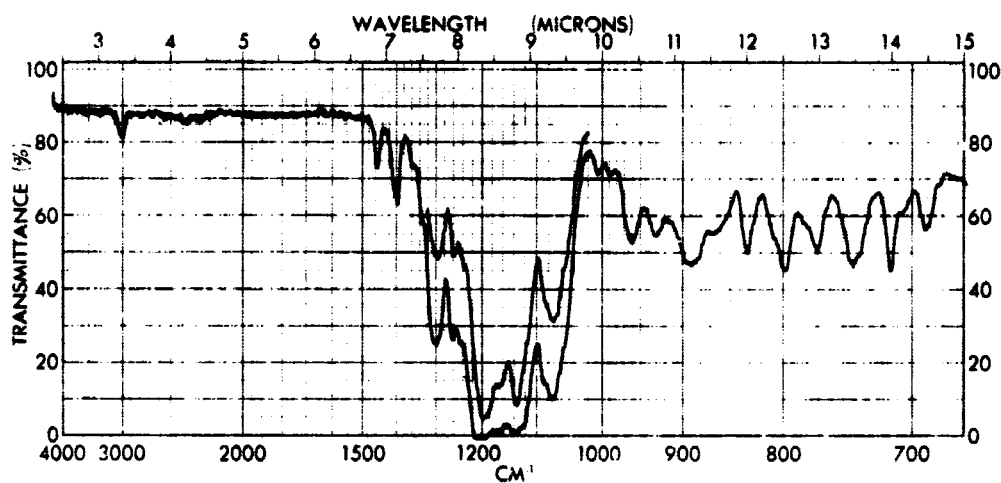
Figure 14 - Infrared Spectrum of Tris(ᵧ'-heptyl) Phosphate (liquid)
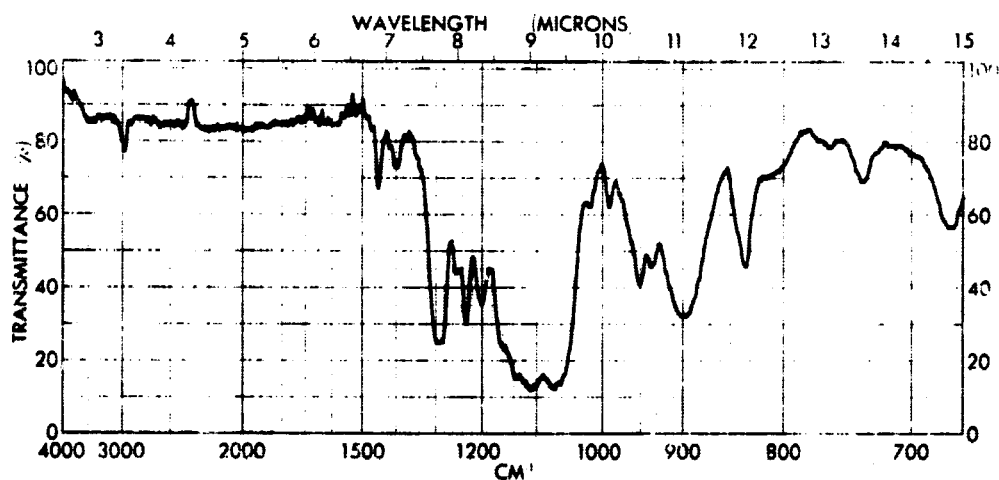
Figure 15 - Infrared Spectrum of Bis(di ᵧ'-propylphosphonyloxy)-
2,2,3,3,4,4-hexafluoropentane (liquid)
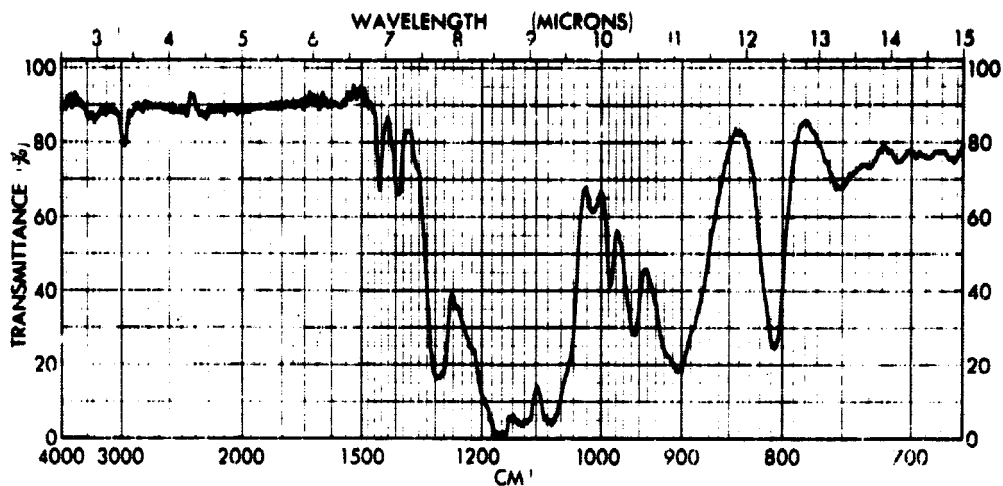
Figure 16 - Infrared Spectrum of Bis(di-ψ'-amylphosphonyloxy-2,2,-3,3,4,4-hexafluoropentane (liquid)
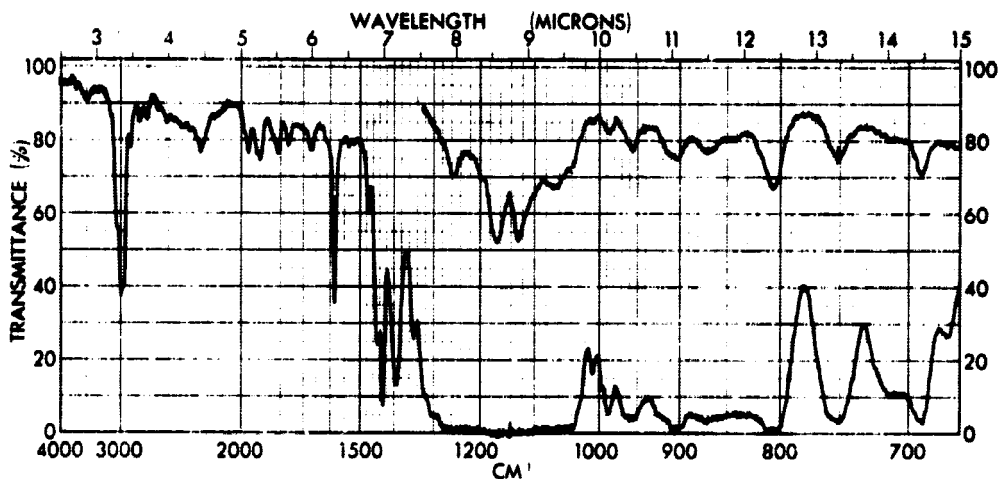
Figure 17 - Infrared Spectrum of Bis(ψ'-amyl) Benzenephosphonate (liquid)
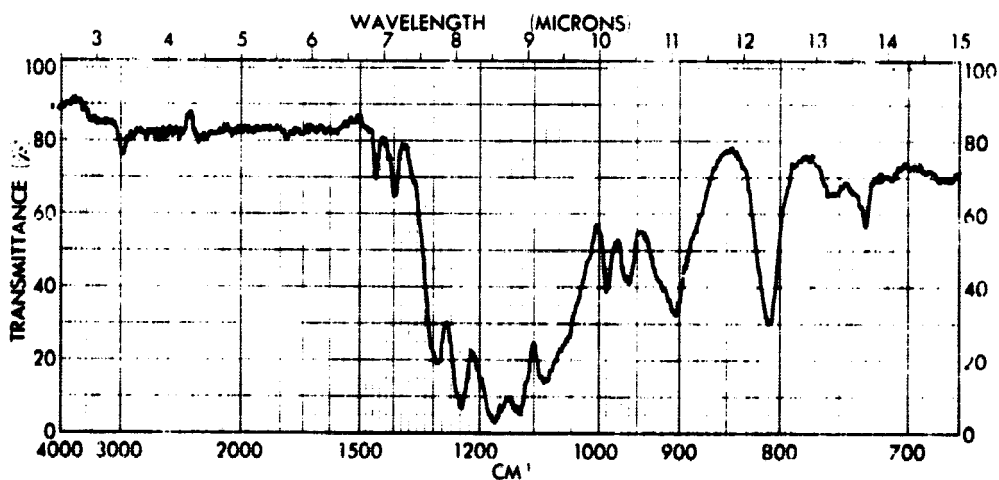
Figure 18 - Infrared Spectrum of Tris[2,2-bis(trifluoromethyl)-5,5,6,6-7,7,8,8-octafluoro-1,3-dioxa-n-octyl] Phosphate (liquid)
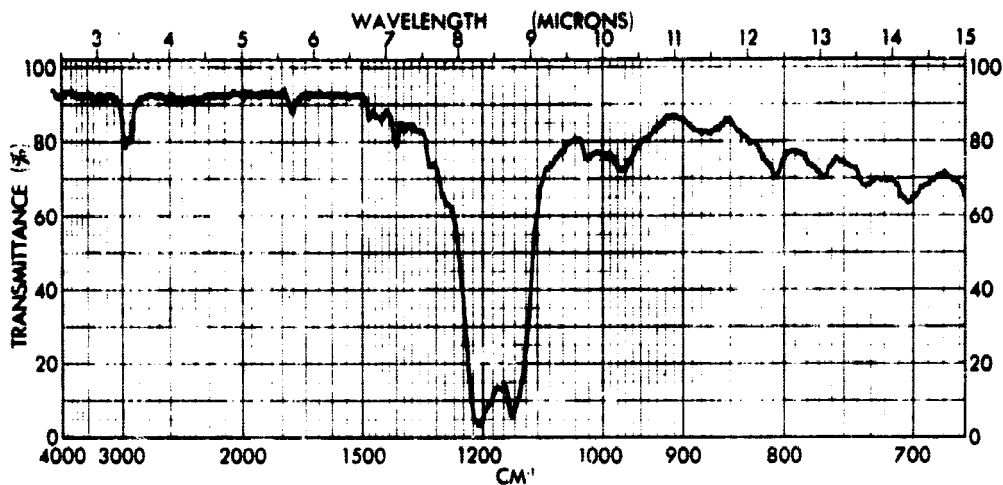
Figure 19 - Infrared Spectrum of 1,4-Bis(ψ'-nonyloxy)butane
(liquid)
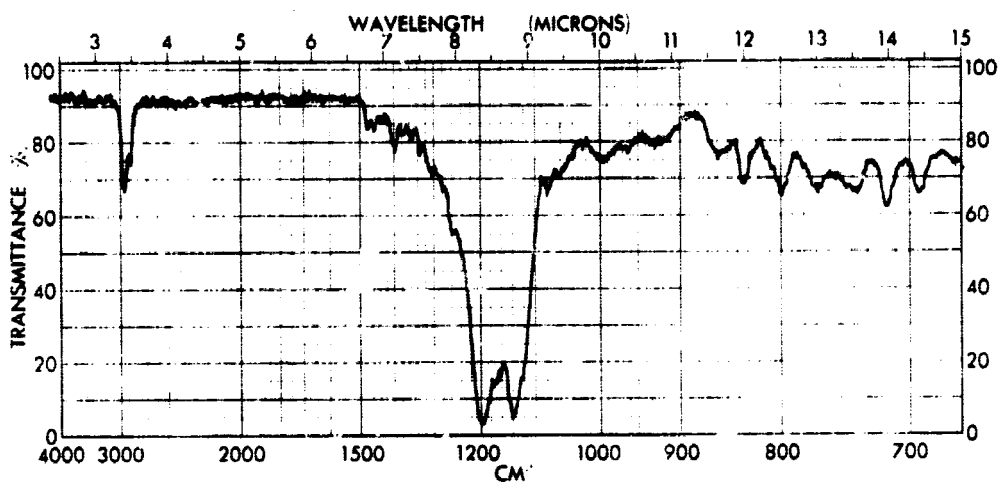
Figure 20 - Infrared Spectrum of 1,6-Bis(ψ'-heptyloxy)hexane
(liquid)
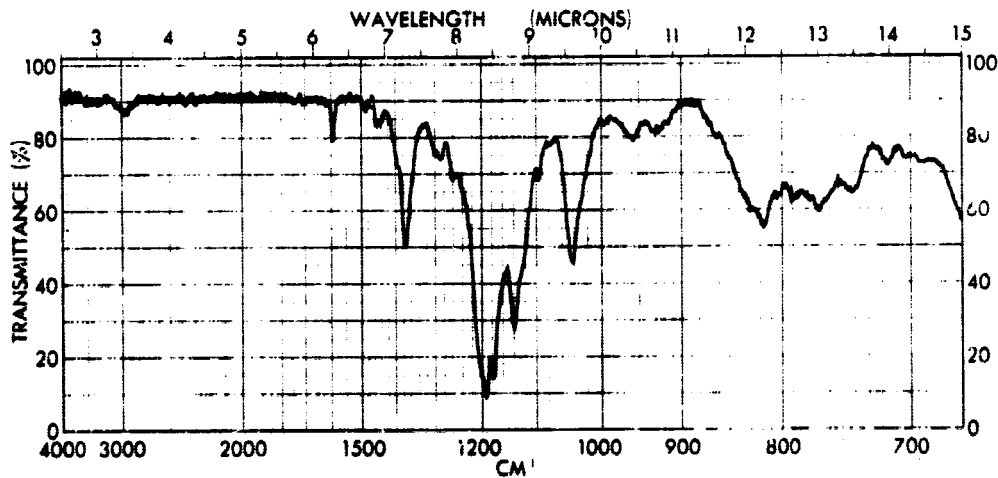
Figure 21 - Infrared Spectrum of 1,5-Bis(ψ'-heptyloxy)hexafluoropentane
(liquid)
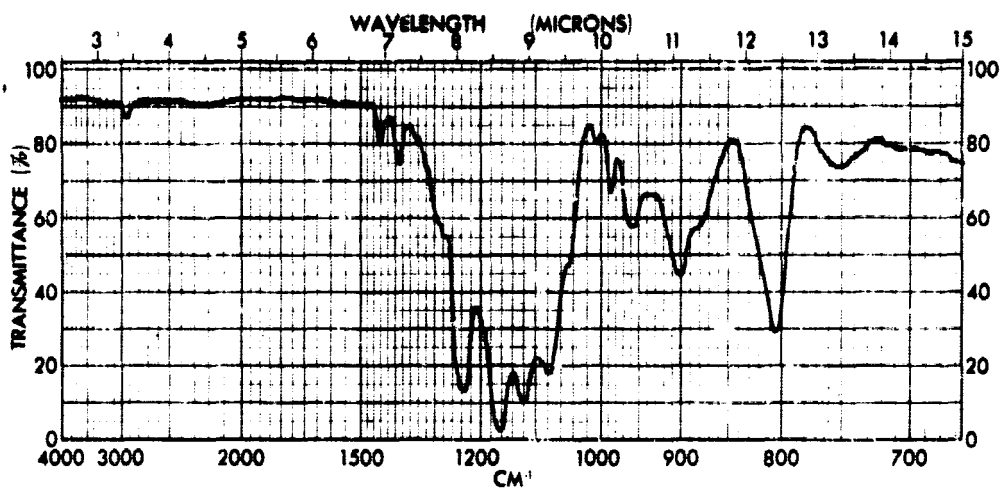
Figure 22 - Infrared Spectrum of Bis(ψ'-amyl) Phosphonitrilate Trimer
(liquid)
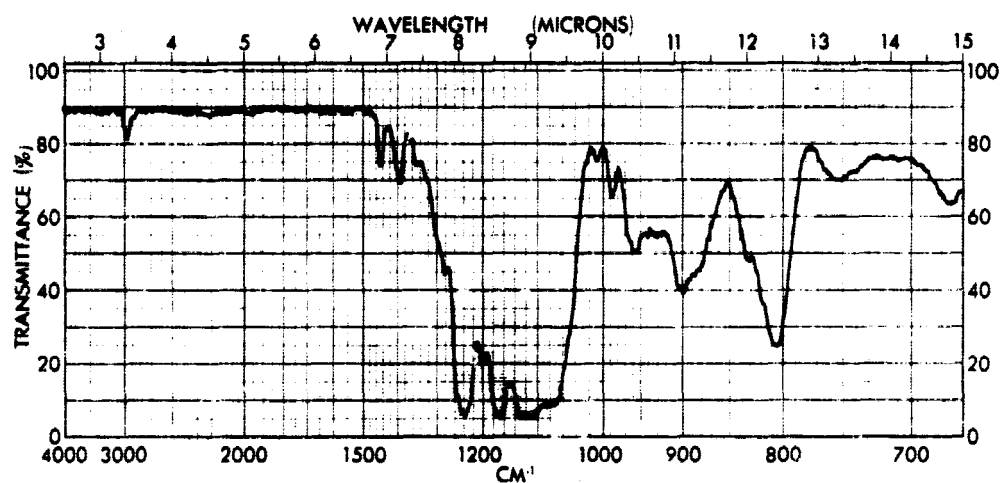
Figure 23 - Infrared Spectrum of (ψ'-Propyl) (ψ'-Amyl) Phosphonitrilate
Trimer (liquid)
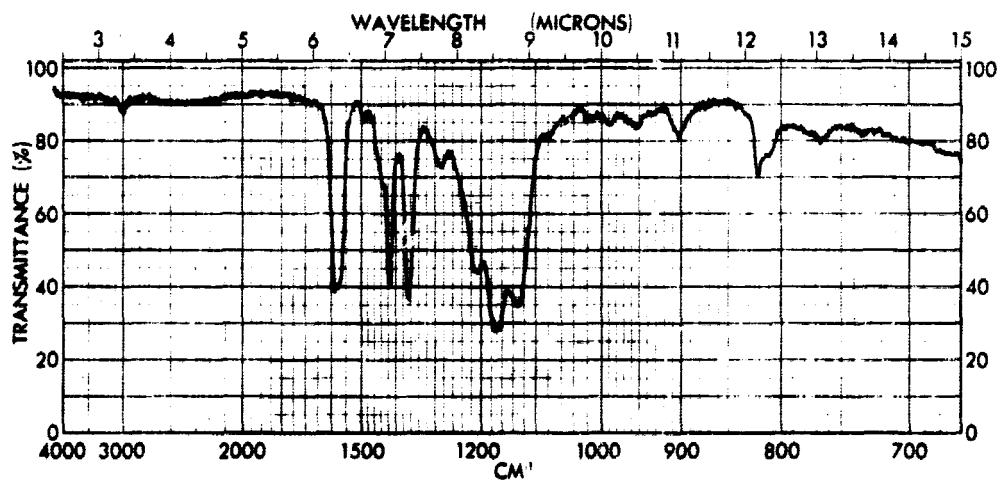
Figure 24 - Infrared Spectrum of 2,4-Bis(ψ'-amyloxy)-6-(ψ'-nonyloxy)-
s-triazine
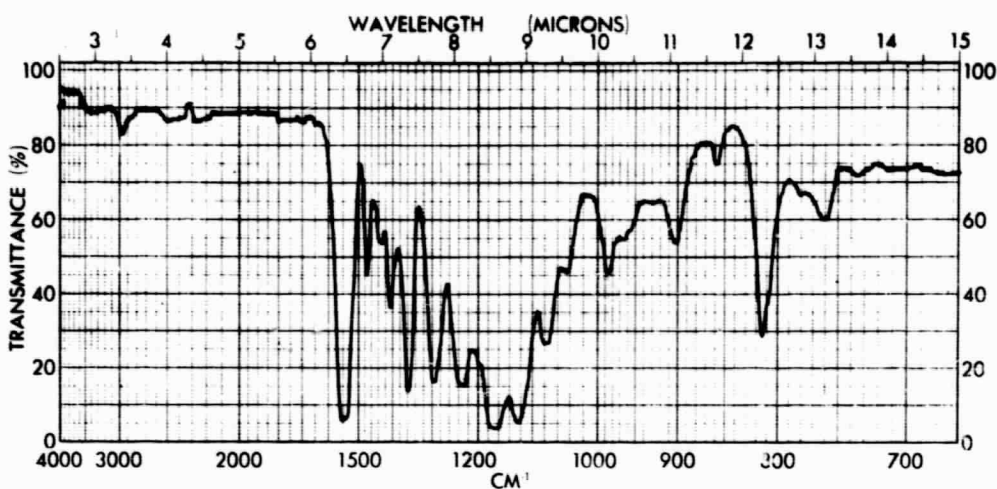
Figure 25 - Infrared Spectrum of The Product Obtained in the Attempt to Prepare
2,4,6-Tris[2,2-bis(trifluoromethyl)-5,5,6,6,7,7,8,8-octafluoro-1,3-
dioxa-n-octyl]-s-triazine (liquid)
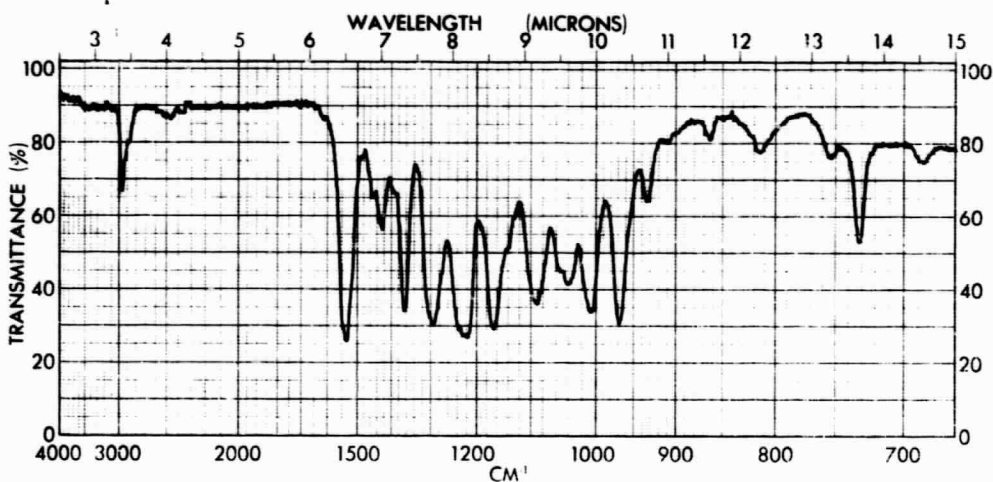
Figure 26 - Infrared Spectrum of the Product Obtained in the Attempt to Prepare
2,4,6-Tris[2,2-bis(trifluoromethyl)-1,3-dioxa-n-hexyl]-s-triazine
(liquid)
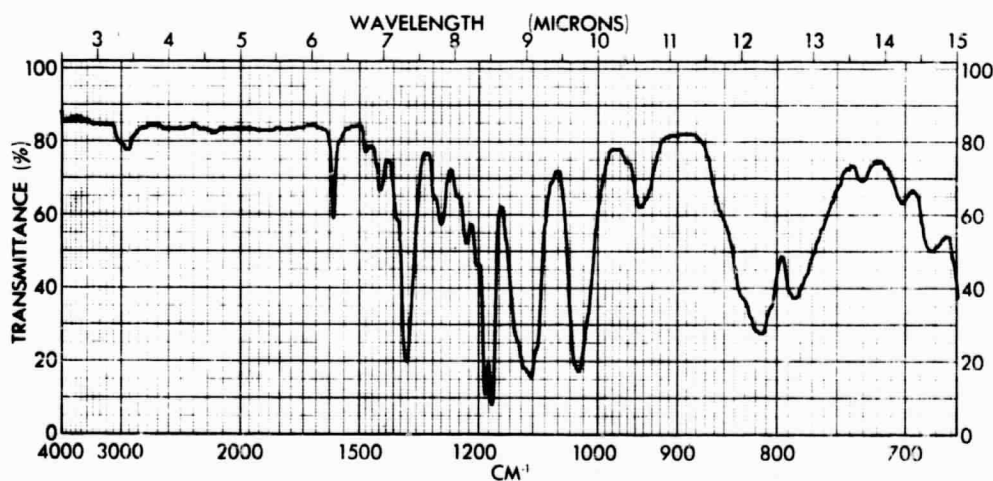
Figure 27 - Infrared Spectrum of ψ'-Propanol p-Toluenesulfonate
(liquid)
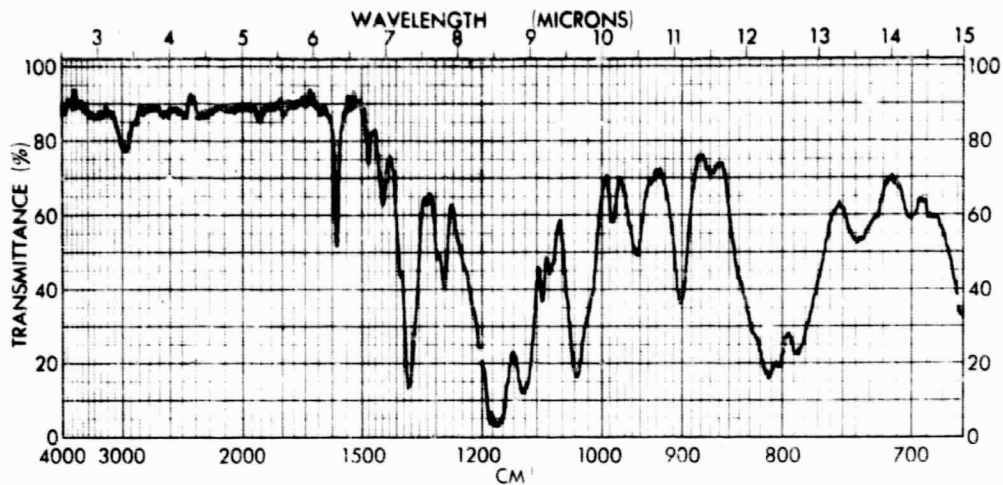
Figure 28 - Infrared Spectrum of ψ'-Pentanol p-Toluenesulfonate
(liquid)
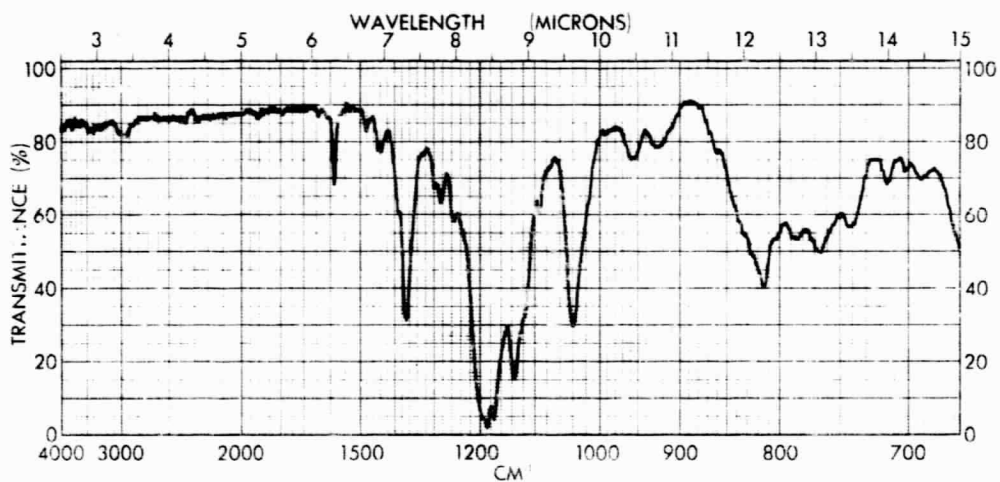
Figure 29 - Infrared Spectrum of ψ'-Heptanol p-Toluenesulfonate
(liquid)
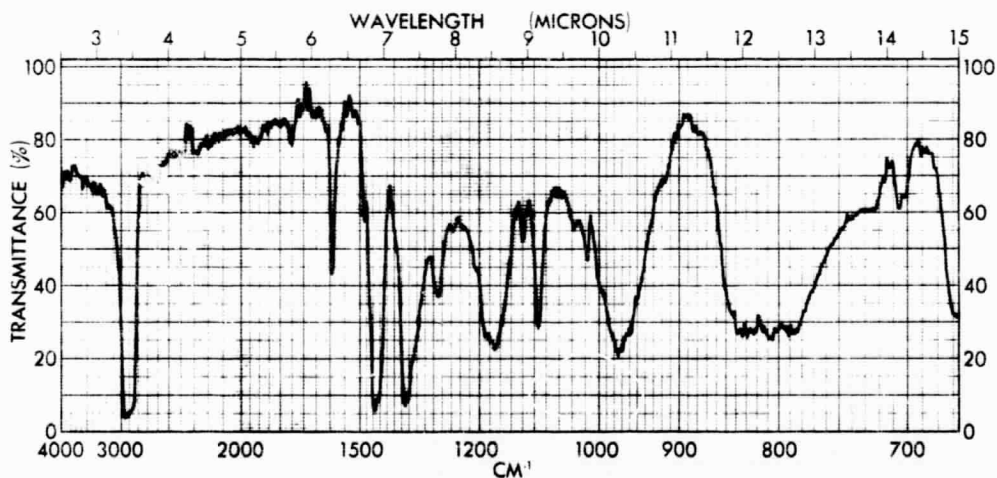
Figure 30 - Infrared Spectrum of Pentaerythritol Tetra-p-toluene-
sulfonate (Nujol)
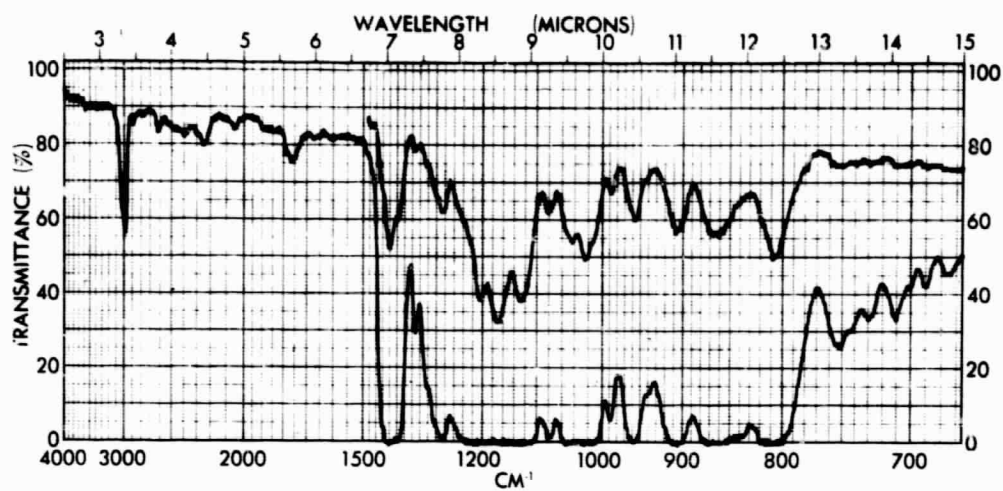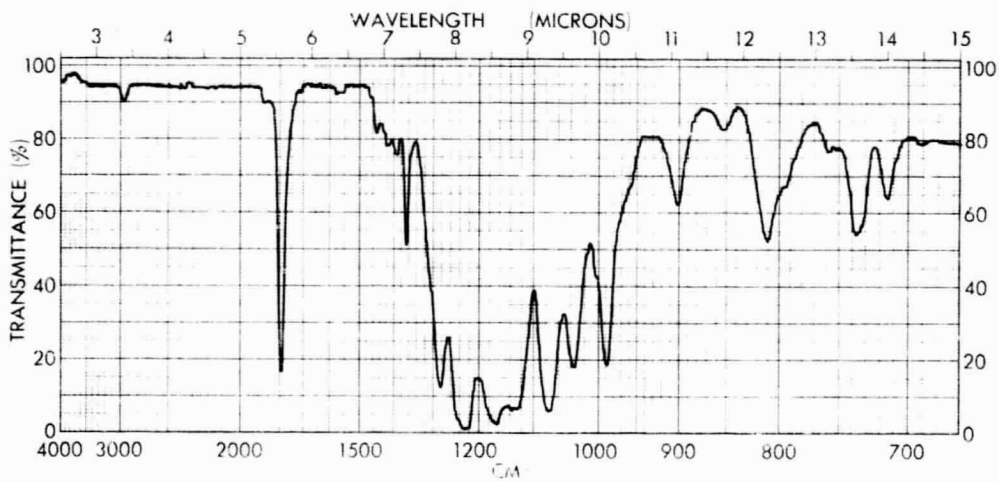
Figure 31 - Infrared Spectrum of Bis(ψ'-amyl) Sulfate (liquid)
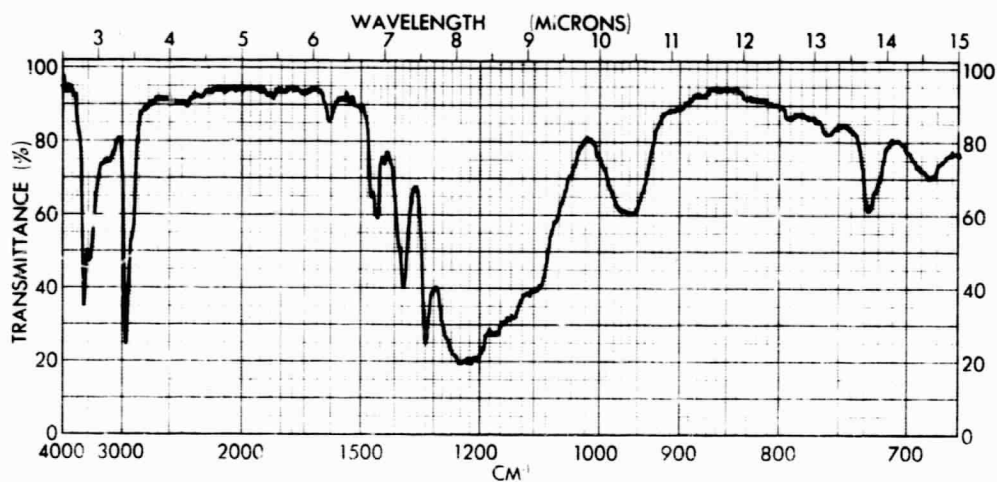
Figure 32 - Infrared Spectrum of n-Propyl Hexafluoroacetone Hemiketal
(liquid)
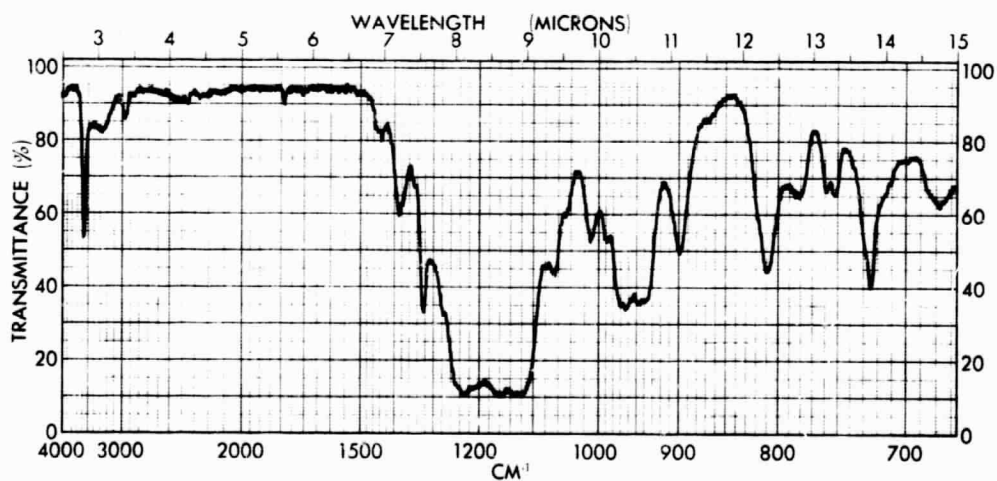
Figure 33 - Infrared Spectrum of ψ'-Amyl Hexafluoroacetone Hemiketal
(liquid)
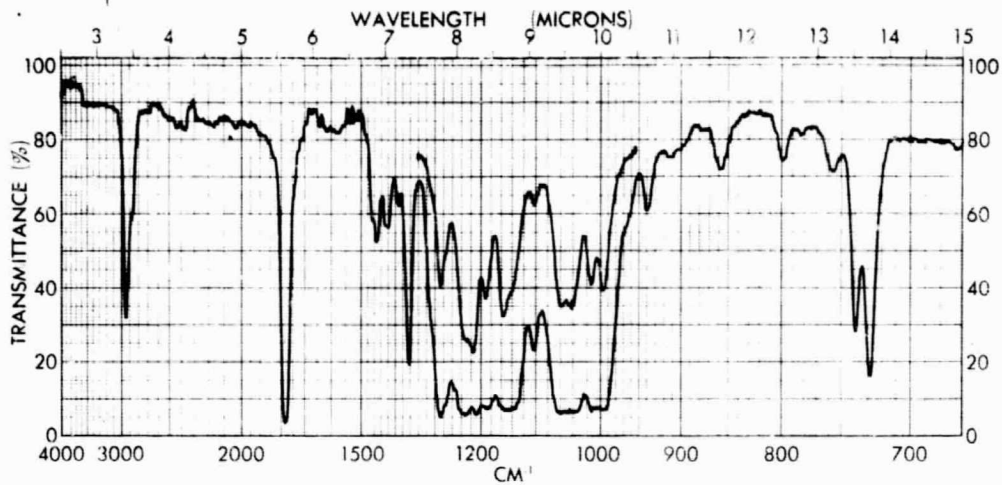
Figure 34 - Infrared Spectrum of n-Propyl Hexafluoroacetone Hemiketal Acetate (liquid)

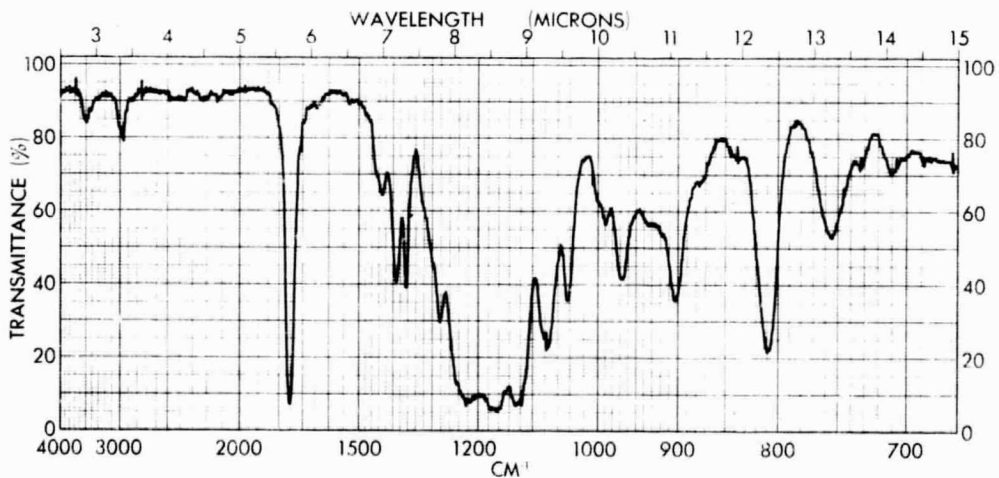Figure 35 - Infrared Spectrum of ψ'-Amyl Hexafluoroacetone Hemiketal Acetate (liquid)

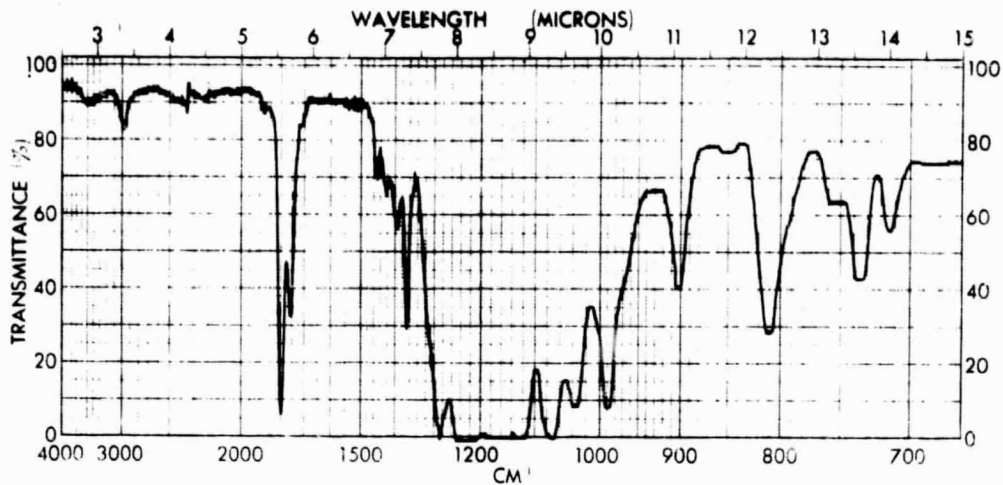Figure 36 - Infrared Spectrum of ψ'-Amyl Acetate (liquid)

Figure 37 - Infrared Spectrum of a Mixture of ψ'-Amyl Hexafluoro-
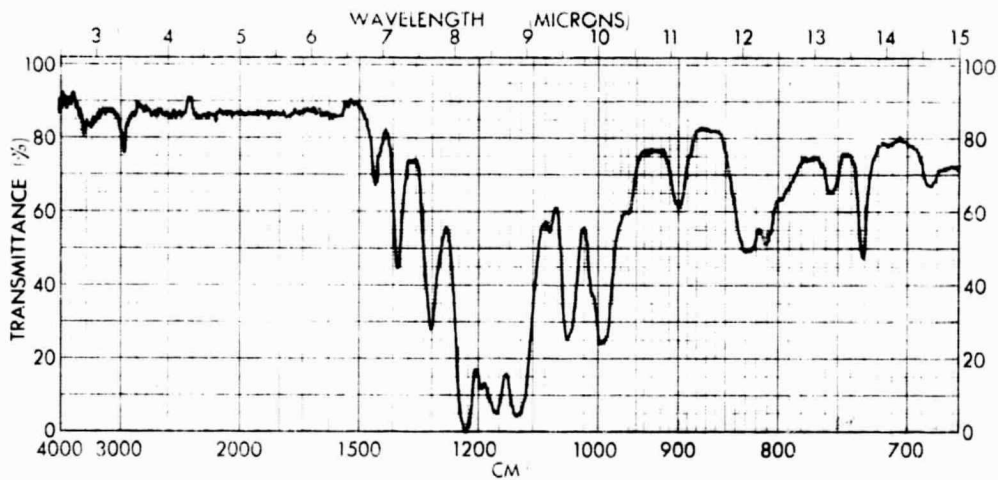acetone Hemiketal and ψ'-Amyl Acetate (liquid)

Figure 38 - Infrared Spectrum of Methyl ψ'-Amyl Hexafluoroacetone
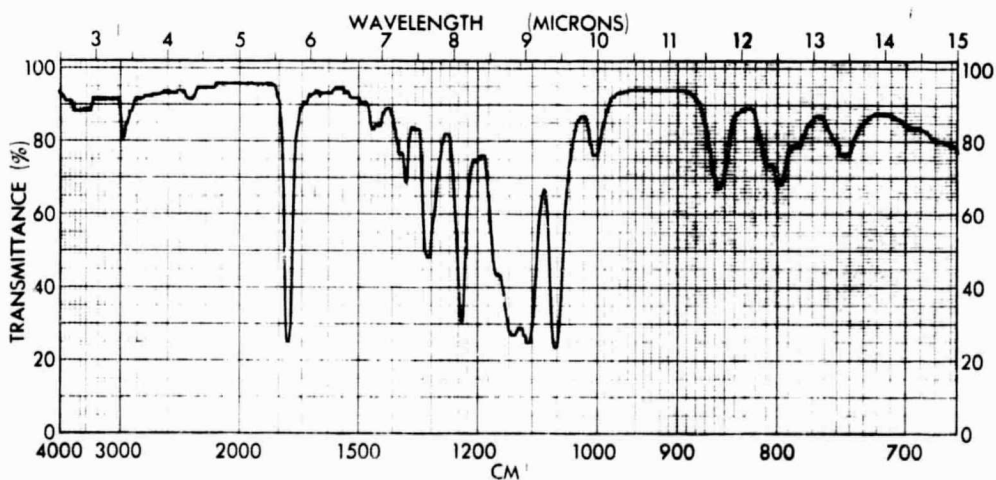Hemiketal (liquid)

Figure 39 - Infrared Spectrum of Ethyl ψ-Propionate (liquid)