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PART 2

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**INVESTIGATION OF CONDENSATION
TYPE ELASTOMERS**

GEORGE C. SCHWEIKER

RUSSELL R. WHITE

RUDOLPH N. DELEO

HOOKER ELECTROCHEMICAL COMPANY

MAY 1956

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INVESTIGATION OF CONDENSATION TYPE ELASTOMERS

GEORGE C. SCHWEIKER

RUSSELL R. WHITE

RUDOLPH N. DELEO

HOOKER ELECTROCHEMICAL COMPANY

MAY 1956

MATERIALS LABORATORY

CONTRACT No. AF 33(616)-2421

PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This second summary report was prepared by the Hooker Electrochemical Company under USAF Contract No. AF 33(616)-2421. The contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center with Lt E. C. Stump as project engineer.

The personnel of the Hooker Electrochemical Company assigned to the project were Dr. George C. Schweiker, Mr. R. R. White, Mr. R. N. Deleo, with Mr. P. Robitschek acting as director. This report covers the period of work from 1 June 1955 to 1 December 1955.

ABSTRACT

The ultimate goal of the exploratory investigations described is the development of a rubber for special Air Force applications. High thermal stability (350°F or higher); resistance to aromatic fuels, synthetic ester-base oils and hydraulic fluids; resistance to ozone and to weathering oxidation effects; resistance to acids, bases, and salts; resistance to abrasion; and satisfactory performance at -65°F or lower are major requirements for such an elastomer.

To this end, a number of linear polyesters have been prepared from fluorine-containing diols and various dicarboxylic acid chlorides, and their properties determined. Hexafluoropentylene adipate (made from adipyl chloride and 2,2,3,3,4,4-hexafluoropentanediol) is a rubber-like gum when of sufficiently high molecular weight, and this polyester has been cross-linked to evaluate the properties of the elastomer in the light of Air Force requirements.

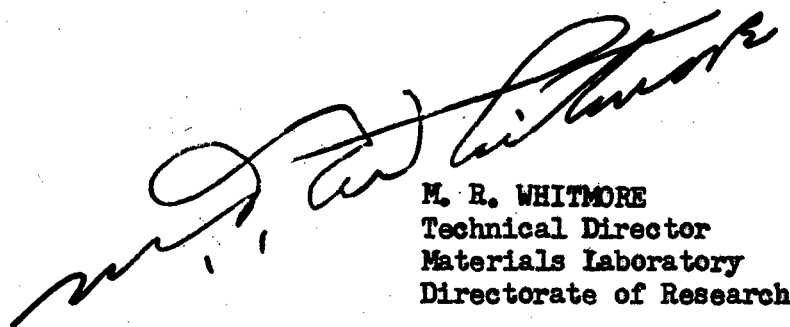
When reinforced with carbon black, the polymer exhibits very good physical properties (tensile strengths above 2600 psi with corresponding elongations above 300%, at the present stage of development). Preliminary evaluations show that this elastomer is thermally stable (serviceable for extended periods to 350°F or higher in air); very resistant to aromatic fuels, synthetic ester-base oils and hydraulic fluids, and acid and salt solutions at room temperature; and not brittle at -65°F or lower. It is not long resistant at the present stage of development to diester fluids at 350°F, however, or to base solutions at room temperature.

It is believed that this rubber is the first example of a fuel resistant, thermally stable elastomer which does not become brittle at low temperatures.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

WADC TR 55-221 Pt 2

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I. INTRODUCTION

The ultimate goal of the exploratory work being performed by Hooker Electrochemical Company under contract with Wright Air Development Center is the development of a rubber for special Air Force applications to possess a superior balance of properties. High thermal stability (350°F. or higher); resistance to aromatic fuels, synthetic ester-base oils and hydraulic fluids; resistance to ozone and to weathering oxidation effects; resistance to acids, bases and salts; resistance to abrasion; and satisfactory performance at -65°F. or lower are major requirements for such an elastomer.

Presently available elastomers do not offer the combination of these desirable properties. One or more attributes have been attained only at the expense of some other equally important quality. For example, solvent resistant addition polymers made by copolymerization with highly polar monomers lack good low temperature flexibility and do not have really high heat stability; organic polysulfide elastomers which show good resistance to fuels and which retain good low temperature flexibility are very poor in heat resistance and also exhibit inadequate mechanical properties. The silicone rubbers offer a very wide range of temperature usefulness, but are not resistant to fuels and solvents and also exhibit poor mechanical properties.

Recently, high heat stability and resistance to various solvents have been obtained in addition polymers containing perfluorocarbon moieties^{1,2}. Low temperature flexibility of these elastomers is poor, however, presumably because of restricted rotation about the perfluorocarbon bonds.

It is logical to expect only marginal improvements through physical changes in molecular structures, additives, etc., with all these types of elastomers. However, major modifications in chemical structure can be expected to increase thermal stability and resistance to solvents (as in the case of the fluorocarbon addition compounds) and yet retain low temperature flexibility.

An ideal method of interpolating atoms which allows free rotation along a fluorocarbon chain is through the use of difunctional intermediates which form polycondensation polymers. The number of methylene fluoride groups in the backbone chain, and/or in a pendent chain, can be varied at will by the proper choice of the starting materials, the remainder of the polymer being composed of flexible units connecting the fluorocarbon moieties. This type of polymer would more closely satisfy the first and second conditions for high elasticity, and the third condition could be met in a variety of ways. These conditions are as follows:

1. Long polymeric chains capable of free-rotation so that a large number of alternative configurations are possible.
2. Only weak secondary forces between the essentially linear chains so that formation of ordered crystalline regions is avoided up to high elongations.

3. Some connecting links between the chains so that permanent plastic flow does not occur upon the application of an extending force.

Some hydrocarbon polycondensation elastomers have been made which, in general, exhibit very good physical properties³⁻⁵. High temperature stability, however, in most cases is not good. In those polymers which are extended and cross-linked with diisocyanates⁴⁻⁵, part of the high temperature instability is probably due to the many polyurethane bonds present; in those polyesters which do not contain diisocyanates³, the ester linkages may be a principal weak point. In this connection, simple esters made from alcohols which do not contain hydrogen on the beta carbon atom - such as those containing fluorine in that position⁶ - are considerably more heat stable than corresponding esters which do contain hydrogen on the beta carbon of the alcohol.

In June of 1954, research on condensation type elastomers was started at Hooker Electrochemical Company under Contract AF 33 (616)-2421 with Wright Air Development Center. A summary report⁷ of the year's work was written in May 1955, which describes the research to that time in detail; the present report covers the research performed from June to December, 1955. During this period of time, emphasis has centered on the preparation of intermediate fluorine-containing diols and dicarboxylic acid chlorides; polymerization of these intermediates into high molecular weight polyesters; cross-linking and testing of these polymers; and the collection of preliminary data. In general, research on the more novel or unusual intermediates considered desirable for use in this project was performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company. Details of the syntheses performed at Purdue appear in Appendix I of this report.

II. SUMMARY AND CONCLUSIONS

A number of fluorine-containing difunctional compounds for use in polyester synthesis have been made in high purity.

Linear polyesters have been prepared from the fluorine-containing diols and various dicarboxylic acid chlorides, some of the polyesters exhibiting rubber-like properties and not becoming brittle at low temperatures. Solubility data suggest that as far as rough solubility characteristics are concerned, it does not make much difference whether additional fluorine (i.e., via the diacid chloride) is incorporated in the backbone chain or in the side chain of these polyesters. The data confirm the fact that increased fluorine content of the polyesters increases hydrocarbon insolubility and raises second order transition temperature.

Change in viscosity (η) with temperature was measured for hexafluoropentylene adipate of various molecular weights (Fig. 1) and constants for the equation¹⁰ $\log \eta = A + \frac{B}{T} + C \frac{Z}{T^2}$ were determined. These data now allow the

calculation of molecular weights (M_n) of those polyesters above 15,000 whose viscosities were unobtainable at 110°C, but which were measured at higher temperatures. The quantity B in the above equation has been related^{10,11} to activation energy for viscous flow, and in the case of hexafluoropentylene adipate the value of 9.39 kcal. is somewhat higher than that of hydrocarbon polyesters.

A series of hexafluoropentylene adipate polymers were made with progressively increasing mol ratio of diol to diacid chloride and progressively increasing mol ratio of diacid chloride to diol. In the former case, fairly good agreement is indicated by comparison with M_n theoretically possible (Fig. 2); in the latter series, the polyesters become increasingly darker with larger excesses of adipyl chloride, indicating a deleterious side reaction with the higher ratios of diacid chloride to diol.

Polyesters of moderate molecular weight have been extended with diisocyanates and cross-linked with either peroxides or diisocyanates. The high molecular weight polyesters (M_n above 15,000) are ideally suited for milling on conventional rubber rollers and were cross-linked with dicumyl peroxide.

Tensile strength of gum vulcanizates of hexafluoropentylene adipate increases markedly with increasing molecular weight; and tensile strength, modulus, and hardness are improved greatly with carbon black reinforcement. At present, tensiles of around 2,000 psi or higher are achieved with from 10 to 30 parts of HAF black-reinforced hexafluoropentylene adipate of M_n 17,100. With 20 parts of Philblack O, tensile strength of this polymer exceeds 2,600 psi.

Preliminary evaluations show that this elastomer is thermally stable (serviceable for extended periods to 350°F or higher in air); very resistant to aromatic fuels, synthetic ester-base oils and hydraulic fluids, and acid and salt solutions at room temperature; and not brittle at -65°F or lower. It is not long resistant at the present stage of development to diester fluids at 350°F, however, or to base solutions at room temperature.

III. DISCUSSION

A. RAW MATERIALS

In keeping with the aims of the contract, and guided by past experimental work⁷, emphasis has been centered on obtaining and using fluorine-containing diols with a variety of dicarboxylic acid chlorides as starting materials for polyester syntheses. The more readily available compounds of these classes are made in the laboratories of the Hooker Electrochemical Company, and a few hydrocarbon compounds are bought, with particular care placed on their purity. In general, investigations on the synthesis of novel or unusual intermediates considered desirable for use in this project are performed at Purdue University under subcontract to Hooker Electrochemical Company. In this connection, various novel fluorine-containing compounds prepared during the period of time covered by this report were synthesized at Purdue University in the manner described in Appendix I of this report. The following list of intermediate chemicals was prepared in the Hooker laboratories.

1. Perfluoroglutaric acid (FGA)
2. Diethyl perfluoroglutarate
3. 2,2,3,3,4,4-Hexafluoropentenediol (HFPD)
4. 1,2-Dichlorooctafluorocyclohexene
5. Perfluoroadipic acid (FAA)
6. Perfluoroadipyl chloride (FAC)
7. Diethyl perfluoroadipate
8. 2,2,3,3,4,4,5,5-Octafluorohexanediol (OFHD)
9. Glutaryl chloride (GC)
10. Adipyl chloride (AC)

Perfluoroglutaric acid (FGA) was prepared by aqueous permanganate oxidation of 1,2-dichlorohexafluorocyclopentene (Hooker Electrochemical Company) in 63-66% yield according to the method described by McBee, Wiseman and Bachmann⁸. Esterification with excess ethanol, distilling off water of reaction as an azeotrope with benzene, gave diethyl perfluoroglutarate⁸ in 85-90% yield. Reduction with lithium aluminum hydride (Metal Hydride, Inc.) as described by McBee, Marzluff and Pierce⁹ resulted in 90-95% yield of 2,2,3,3,4,4-hexafluoropentenediol (HFPD). Cryoscopic measurements performed by the personnel of the analytical laboratories of Hooker Electrochemical Company indicated a purity of 99.8 mol % for HFPD prepared in this manner after three or four recrystallizations from benzene.

A modification of the method used by McBee, Wiseman and Bachmann⁸ for the synthesis of 1,2-dichlorooctafluorocyclohexene gave a 50% yield of the compound from hexachlorobenzene and antimony pentafluoride (General Chemical Div.). Oxidation, esterification, and reduction were performed in a manner

similar to that outlined above for 1,2-dichlorohexafluorocyclopentene. Perfluoroadipyl chloride (FAC) was made in much smaller yield (35%) by the reaction of phosphorus pentachloride (Mallinckrodt Chemical Works) on anhydrous perfluoroadipic acid (FAA) than by the reaction previously reported⁷ of thionyl chloride on FAA.

Glutaryl chloride (GC) was prepared in 78% yield from glutaric acid and phosphorus pentachloride; and some adipyl chloride (AC) was made in 72% yield from adipic acid and thionyl chloride.

The remainder of the adipyl chloride (AC) and the following other raw materials used in this study were purchased in highest grade purity available from the indicated companies, and carefully purified by redistillations when used in the synthesis of the linear polyesters. Glutaric acid (GA; Distillation Products), adipic acid (AA; DuPont), adipyl chloride (AC; Genesee Research), fumaryl chloride (FC; Fisher), dicumyl peroxide on calcium carbonate (DI-CUP 40C; Hercules), methylene bis(4-phenylisocyanate) (MDI; DuPont), and an epoxy reaction product of bisphenol-epichlorohydrin (A-5; Carbide and Carbon).

B. LINEAR POLYESTERS

1. Properties of Linear Polyesters Synthesized from Fluorine-Containing Diols and Various Dicarboxylic Acid Chlorides. Previous work⁷ has shown that the best method of preparing high molecular weight polyesters from fluorine containing diols is through the use of dicarboxylic acid chlorides and the diols. Accordingly, several new polyesters were synthesized by this method, and some of their properties were investigated. Also prepared were several batches of high molecular weight hexafluoropentylene adipate, and some partly unsaturated polyesters.

Table I summarizes the data on the syntheses and properties of the linear polyesters. After the experiment identification number, the second column lists the starting materials followed by the mol ratio of diol to diacid chloride(s). Where two diacid chlorides were utilized, the mol per cent of the diacid chloride used in the smallest amount precedes its abbreviated name, and the mol per cent of the other diacid chloride may be found by subtracting from 100. The length of reaction time is given in hours, and was measured from the start of heating above room temperature until the apparatus was removed from the heating bath at 200°C. Viscosities (η) measured at 110°C when practical are melt viscosities obtained by applying the methods described by Flory¹⁰ for hydrocarbon polyesters. The various functions of the viscosities were calculated from Flory's equations, used by him in the hydrocarbon polyester series. The constants A and B in the equation¹⁰ $\log \eta = A + \frac{B}{CZ^2}$ were determined for hexafluoropentylene adipate at 110°C and the various functions of the viscosities are subject to the limitations previously discussed⁷.

As outlined in Table I, there was no marked difference in the properties of the two polyesters made with glutaryl chloride (GC) and 2,2,3,3,4,4-hexafluoropentanediol (HFPD) and 2,2,3,3,4,4,5,5-octafluorohexanediol (OFHD), respectively. Similarly, there was no marked difference caused by the additional difluoromethylene moiety contained in the six-carbon diol OFHD, as compared with the five-carbon diol HFPD, in the polyesters made with 3-perfluoropropylglutaryl chloride (FPGC) and the diols. This is in contrast to the data found for the reaction between adipyl chloride and these diols. The melting point ($\sim 67^\circ\text{C}$) and solubility characteristics (see below) of octafluorohexylene adipate (AC-OFHD) are definitely different than the melting point ($\sim 30^\circ\text{C}$) and solubility characteristics of hexafluoropentylene adipate (AC-HFPD).

Melting points of the glutarate and adipate polyesters made with fluorine-containing diols are from 5° to 12°C higher than corresponding hydrocarbon polyesters, except for the special case of hexafluoropentylene adipate. This polyester melts about 10°C lower than pentamethylene adipate. The AC-HFPD polyester is also very slow to crystallize, in contrast to the other adipate and to the glutarates made with the fluorine-containing diols. The polyesters made from these diols and 3-perfluoropropylglutaryl chloride (FPGC), on the other

TABLE I

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE-CONTAINING DIOLS

Identification Number	Starting Materials	Mol Ratio of Diol to Diacid Chloride(s)	Reaction Time (Hrs)	η (at 110°C)	(Using constants obtained from AA-HFPD polyester)			Comments
					M_n	x_n	Z_n	
GH, 1, 100	GC HFPD	1.000	12	60.7	6,020	39.1	463	waxy solid; m.p. 39-42°C; brittle ~-50°C
GO, 1, 100	GC OFHD	1.000	13	17.2	6,600	25.1	322	waxy solid; m.p. ~40°C brittle ~-50°C
FH, 1, 100	FPGC HFPD	1.000	8	24.6	7,240	30.4	360	viscous liquid; brittle ~-28°C
FH, 1, 100, 2	FPGC HFPD	1.000	22	33.0	7,900	33.2	392	viscous liquid; brittle ~-28°C
FO, 1, 100	FPGC OFHD	1.000	8	45.0	8,770	33.3	426	viscous liquid; brittle ~-25°C
AH, 1, 100	AC HFPD	1.000	9	1370 at 205°C	17,400	108	1400	clear; rubberlike; brittle below -60°C; crystallized very slowly; m.p. ~30°C
AH, 1, 100, 2	AC HFPD	1.000	10	7400	15,430	95.9	1240	
AH, 1, 100, 3	AC HFPD	1.000	7	8400	15,740	97.8	1260	
AH, 1, 1002	AC HFPD	1.002	9	2455 at 173°C	17,100	106	1380	
AO, 1, 100	AC OFHD	1.000	5	1200 at 205°C	18,300	98.6	1372	white, waxy solid; m.p. ~67°C
FAO, 1, 100	FAC OFHD	1.000	13	11.3	5,260	20.4	281	waxy solid; m.p. 65°C
AFH, 95, 5, 100	AC, 5%FC HFPD	1.000	11	97	6,590	40.9	522	
AFH, 90, 10, 100	AC, 10%FC HFPD	1.000	11	60	5,840	36.3	462	brittle ~-55°C
AFH, 90, 10, 100, 2	AC, 10%FC HFPD	1.000	12	153	7,320	45.6	581	
AFH, 85, 15, 100	AC, 15%FC OFHD	1.000	12	133	7,100	44.1	562	

hand, are very viscous liquids which could not be induced to crystallize at all. This property is to be expected in those polyesters which have side groups appended to the linear chain, because the side groups act to either prevent normal packing or to increase vibration interaction of interlocking molecules. The fluorine-containing side chain of FPGC also raises the brittle temperature of the polyesters and increases their hydrocarbon insolubility, as can be seen from comparing the properties of these polyesters with the same unit chain length glutarates. Additional fluorine introduced into the backbone chain of these polyesters via perfluoroadipyl chloride (FAC) raises second-order transition temperature a lesser amount⁷ and increases hydrocarbon insolubility in accord with total fluorine content. Replacement of some adipyl chloride (AC) by fumaryl chloride (FC) also raises brittle temperature slightly. The glutarates exhibit a somewhat higher brittle temperature than does hexafluoropentylene adipate.

In the matter of solubility of the fluorine-containing polyesters to common hydrocarbon solvents, rough solubility data show that increased fluorine content decreases solubility. Thus, the solubility characteristics of the glutarates (GC-HFPD containing 37.0% F and GC-OFHD containing 41.4% F) are very similar to the AC-HFPD polyester⁷ (containing 35.4% F). Solubilities of FPGC polyesters (FPGC-HFPD containing 51.9% F and FPGC-OFHD containing 54.0% F) are closer to the perfluoroadipates (FAC-HFPD previously reported⁷ containing 57.1% F and FAC-OFHD containing 58.9% F and which has the same solubility characteristics as FAC-HFPD⁷). The FPGC polyesters are soluble in acetone, ether, and ethyl acetate; insoluble in benzene, toluene, isooctane, Plexol 201 and water; dispersed by pyridine and chloroform. On the basis of these data, then, as far as rough solubility characteristics are concerned, it does not make much difference whether additional fluorine is incorporated in the backbone chain or in the side groups of these polyesters. The solubility characteristics of octafluorohexylene adipate (AC-OFHD containing 40.6% F) are somewhat anomalous in that this polyester is more resistant to solvents than would be predicted on the basis of total fluorine content. This may perhaps be due to its increased intermolecular order as evidenced by high degree of crystallinity and high melting point. The polyester is soluble in acetone, chloroform, and pyridine; insoluble in benzene, toluene, isooctane, Plexol 201, ether, carbon tetrachloride, and water.

As noted in Table I, the highest molecular weights (M_n), degree of polymerization (x_n), and chain lengths (Z_w) were obtained with adipyl chloride (AC) and the fluorine-containing diols (HFPD and OFHD). Using data on temperature-viscosity relationships described in the following section of this report, the number average molecular weight (M_n) of the highest M_n hexafluoropentylene adipate yet prepared is 17,400; degree of polymerization (x_n) is 108; weight average chain length (Z_w) is 1380. For octafluorohexylene adipate, M_n is 18,300; x_n is 98.6; Z_w is 1372. The other diacid chlorides so far investigated give much lower values for these properties with the fluorine-containing diols. Also, where part of the adipyl chloride (AC) is replaced by equivalent amounts

of fumaryl chloride (FC) in reactions with these diols, M_n , x_n , and Z_w of the resulting polyesters are lower. Since the boiling point of adipyl chloride is higher than that of the other diacid chlorides, it suggests that some diacid chloride may be preferentially leaving the scene of reaction, thereby reducing M_n , x_n , and Z_w .

2. Melt Viscosity - Temperature - Chain Length Relationship. When polyesters of very high molecular weight (above about 15,000) are made, their melt viscosities become impractical to measure at 110°C with the apparatus used throughout this study, mainly because of entrapped air bubbles. However, the values found for hexafluoropentylene adipate⁷ for A and C in the equation¹⁰ $\log \eta = A + CZ_w^{\frac{1}{2}}$ are valid only at 110°C. It was necessary, therefore, to either

determine new values for the constants at some other higher fixed temperature or to relate change in melt viscosity with temperature. The equation of Flory¹⁰ $\log \eta = A + \frac{B}{T} + CZ_w^{\frac{1}{2}}$ (where A and B are new constants, and C is the same as in

the above equation; Z_w is weight average chain length) used in the hydrocarbon polyester series appeared to offer the most practical solution to this problem, even though it is not strictly accurate over a wide temperature range.

Measurements of melt viscosities (η) at different temperatures were performed on several hexafluoropentylene adipate polyesters of different molecular weights (M_n). As illustrated in Fig. 1, plots of $\log \eta$ vs. $1/T$ are not straight lines, in agreement with Flory's results¹⁰ on hydrocarbon polyesters. However, to utilize values of viscosities of polyesters measured at various temperatures, the average slope of $\log \eta$ vs. $1/T$ in the temperature range 110° to 205°C was used to evaluate the constants A and B. The values found for A and B with hexafluoropentylene adipate are: A = -6.88, B = 2050 ($C = 0.153^7$).

In connection with these data, the quantity B has been related^{10,11} to activation energy for viscous flow, i.e., activation energy for viscous flow = (B) (2.3) (R). In the case of hexafluoropentylene adipate the value of 9.39 kcal. is somewhat higher than that of hydrocarbon polyesters.

3. Effect of Varying Mol Ratio of Reactants for Hexafluoropentylene Adipate. Table II gives information on a series of hexafluoropentylene adipate polyesters made with progressively increasing mol ratio of diol (HFPD) to dicarboxylic acid chloride (AC). As theory predicts, the melt viscosities (η) progressively decrease. Fig. 2 illustrates how number average molecular weight (M_n) as calculated from η decreases with increasing mol ratio of diol to diacid chloride (solid curve) in comparison to increasing mol ratio of diacid chloride to diol (broken curve) and to theoretically possible values (dotted curve). Although the values of M_n measured are not as high as theoretically possible for a given excess of diol, the two curves follow each other in general shape.

On the other hand, the curve in Fig. 2 for increasing mol ratio of diacid chloride to diol is somewhat anomalous compared to the theoretically possible curve. The data on this series of experiments are incorporated in Table III. As the ratio of diacid chloride to diol increases, the resulting polyester

TABLE II

INCREASING MOL RATIO OF FLUORINE-CONTAINING DIOL TO DIACID CHLORIDE

Identification Number	Starting Materials	Mol Ratio of Diol to Acid Chloride	Reaction Time (Hrs.)	η (at 110°C)	(Using constants obtained from AA-HFPD polyester)			Comments
					M_n	x_n	Z_w	
AH, 1, 1005	AC HFPD	1.005	7	2440	12,800	79.2	1012	Brittle below -60°C
AH, 1, 1010	AC HFPD	1.010	6	832	10,480	65.0	840	
AH, 1, 1014	AC HFPD	1.014	12	219	7,940	49.3	632	
AH, 1, 1017	AC HFPD	1.017	6	152	7,300	45.3	582	
AH, 1, 102	AC HFPD	1.020	6	128	7,030	43.6	560	
AH, 1, 103	AC HFPD	1.030	6	67.8	6,000	37.2	476	
AH, 1, 104	AC HFPD	1.040	6	40.0	5,210	32.3	414	
AH, 1, 105	AC HFPD	1.050	5	21.3	4,350	27.0	345	
AH, 1, 110	AC HFPD	1.110	5	5.7	2,790	17.3	220	

TABLE III

INCREASING MOL RATIO OF DIACID CHLORIDE TO FLUORINE-CONTAINING DIOL

Identification Number	Starting Materials	Mol Ratio of Acid Chloride to Diol	Reaction Time (Hrs.)	η (at 173°C)	(Using constants obtained from AA-HFPD polyester)			Comments
					M_n	x_n	Z_w	
AH, 1005, 1	AC HFPD	1.005	7	1655	16,100	100	1295	Color increasingly darker
AH, 1010, 1	AC HFPD	1.010	7	680	13,900	86.5	1118	
AH, 1015, 1	AC HFPD	1.015	7	530	13,300	82.6	1070	
AH, 1020, 1	AC HFPD	1.020	7	300	12,050	74.8	968	
AH, 1025, 1	AC HFPD	1.025	7	147	10,600	65.3	847	
AH, 1030, 1	AC HFPD	1.030	9	400 at 110°C	9,040	56.1	721	

becomes increasingly darker. Above a mol ratio of diacid chloride to diol of 1.030, the polyester is quite dark and melt viscosity was impossible to measure accurately with the apparatus used. It is inferred from this behaviour that a deleterious side reaction is occurring at the higher ratios of diacid chloride to diol, which may help to explain the somewhat anomalous shape of the curve illustrated in Fig. 2 for this series. The values and shapes of the experimental curves are also consistent with the assumption that a small amount of diacid chloride may be preferentially leaving the scene of reaction during these experiments.

4. Chain Extension. The higher molecular weight polyesters studied here are well suited for processing on conventional rubber equipment. Hexafluoropentylene adipate of molecular weights around 15,000 or above mills very well on conventional rubber rollers and may be milled conveniently with cooled rollers at molecular weights down to around 12,000. However, when lower molecular weight polyesters are obtained, processing in such a manner is impractical. Also, physical properties of vulcanizates decrease with decreasing molecular weight as shown in Section C of this report. For those polyesters of low or moderate molecular weight, therefore, it is necessary to extend the chains. Of the various methods by which chain extension could be performed (diisocyanates, diepoxides, diketenes, diacid chlorides, etc.), reactions of diisocyanate with hydrocarbon polyesters are best known.

Chain extension with diisocyanates, or with diisocyanates and small amounts of diamines, at 130-160°C was performed with the fluorine-containing polyesters in the manner described for hydrocarbon polyesters^{12,13}. The lower or moderate molecular weight viscous liquid polyesters were transformed by this process into tough, rubberlike gums suitable for milling. Methylene bis(4-phenylisocyanate) (MDI) gave generally better results than 2,4-tolylene diisocyanate (TDI) and was used predominately in these reactions. The polyesters chain-extended in this manner included hexafluoropentylene adipate of various molecular weights, partly unsaturated (i.e. by replacement of some adipyl chloride with fumaryl chloride) hexafluoropentylene adipate-fumarate polyesters, and polyester FH,1,100,2 (Table I) made from 3-perfluoropropylglutaryl chloride (FPGC) and 2,2,3,3,4,4-hexafluoropentanediol (HFPD). In the subsequent cross-linking step (Section C) with diisocyanates, it was found that those diisocyanate-modified polyesters whose original molecular weights were between 4,000 and 10,000 gave the best results in this method of curing.

A preliminary experiment utilizing a typical epoxy monomer (A-5; product of bisphenol A and epichlorohydrin) with hexafluoropentylene adipate of M_n 7300, catalyzed with 5% quinoline, gave some chain extension as evidenced by viscosity increase after heating overnight at 160°C. Further increase in viscosity was obtained by heating for an additional 18 hours at 160°C, but the resulting product was very dark and weak.

C. CROSS-LINKING, REINFORCING, AND PROPERTIES OF VULCANIZATES

Cross-linking of the high molecular weight linear polyesters was accomplished by reaction with peroxide, or with diisocyanate or peroxide in the case of the diisocyanate extended polyesters.

Table IV illustrates how tensile strength of gum vulcanizates of hexafluoropentylene adipate increases with increasing molecular weight (M_n). At the lowest M_n studied (12,200), 8% DI-CUP 40C, which represents 3.2% active dicumyl peroxide was about the optimum amount of curing agent, giving a tensile of 250 psi. As M_n of the linear polyester increases, the amount of curing agent for optimum tensile strength decreases very slightly, and tensile increases very markedly. At M_n of 17,100, tensiles of 800 psi were achieved with 6% and with 7% DI-CUP 40C.

Table V includes data on a sample of a diisocyanate-extended hexafluoropentylene adipate of original M_n 6840, which was cross-linked with 0.5 mol (based on original polyester) methylene bis(4-phenylisocyanate) (MDI) and 1% quinoline. This sample exhibited a tensile of 634 psi. A sample of AFH, 85, 15,100 (see Table I) which had been extended with MDI and cross-linked with DI-CUP 40C exhibited a tensile of 276 psi as shown in Table V. Table VI includes data on a hexafluoropentylene adipate polyester of M_n 6840 extended with MDI and cross-linked with 5% DI-CUP 40C (AH-MDI-5DI); a polyester prepared from 3-perfluoropropylglutaryl chloride (FPGC) and 2,2,3,3,4,4-hexafluoropentanediol (HFPD), chain-extended with MDI and cross-linked with 5% DI-CUP 40C (FH-MDI-5DI); and a hexafluoropentylene adipate polyester of M_n 15,000 cross-linked with 10% DI-CUP 40C (AH-10DI). The tensile of 1410 psi for a gum vulcanizate (AH-MDI-5DI) is the highest value yet attained for these fluorine-containing polyesters (not reinforced). It should be stated that curing with peroxides is much simpler and gives much more consistent results than curing with diisocyanates.

Preliminary experiments on reinforcing hexafluoropentylene adipate have been started. An HAF black (Philblack O) shows a tendency to inhibit peroxide cure which may be overcome by using increasing amounts of peroxide with increasing amounts of black. Table VII lists the first results obtained with Philblack O and Hi-Sil 233. The polyester was hexafluoropentylene adipate of M_n 17,100; curing was effected at 165°C for 1 hour. As expected, tensile strength is increased greatly with the use of carbon black, and modulus and hardness increase with increasing amounts of black. (The results with H-Sil 233 were variable and more data are required for final evaluation.) Tensile strength of around 2000 psi or higher are achieved with from 10 to 30 parts of Philblack O.

Table VII also includes the effect of various amounts of peroxide (DI-CUP 40C) on hexafluoropentylene adipate of M_n 17,100 reinforced with 20 parts of Philblack O. Tensile strength, modulus and hardness increase with increasing amount of peroxide (maximum tensile achieved with 10-12% DI-CUP 40C) while elongation decreases. Amounts of from 10% to 12% DI-CUP 40C produced tensiles of over 2600 psi.

TABLE IV

CROSS-LINKING OF HEXAFLUOROPENTYLENE ADIPATE

	<u>For M_n 12,200</u>				
% DI-CUP 40C	<u>6</u>	<u>7</u>	<u>8</u>	<u>2</u>	<u>10</u>
Tensile strength (psi)	80	87	250	160	74
Elongation (%)	700	600	675	425	175
Set at break (%)	10	5	1-2	0	0
Hardness (Shore A)	35-40	40-45	40-45	40-45	40-45

	<u>For M_n 13,200</u>		<u>For M_n 15,000</u>
% DI-CUP 40C	<u>7</u>	<u>8</u>	<u>6</u>
Tensile strength (psi)	260	420	650
Elongation (%)	620	600	700
Set at break (%)	0-2	0-2	1-2
Hardness (Shore A)	40-45	40-45	47-52

	<u>For M_n 17,100</u>		
% DI-CUP 40C	<u>6</u>	<u>7</u>	<u>8</u>
Tensile strength (psi)	800	800	600
Elongation (%)	560	525	500
Modulus (300%)	176	160	190
Set at break (%)	1-2	1-2	0-1
Hardness (Shore A)	48-53	50-55	45-50
Brittle point (°F)	below -65°	below -65°	below -65°

TABLE V

PHYSICAL PROPERTIES OF GUM VULCANIZATES

	Tensile strength (psi)	Elongation (%)	Set at break (%)	Hardness (Shore A)	Brittle Point (°C)	Volume increase (%)
AC-HFPD (M_n 6840) extended and cross-linked with MDI	634	360	5	65	below -65°	
After 7 days in 70 isooctane: 30 toluene fuel	350	360	5	63	----	10-20
AFH, 85, 15, 100 extended with MDI cross-linked with DI-CUP 40C	276	65	0	70	below -65°	
After 7 days in 70 isooctane: 30 toluene fuel	200	60	0	70	----	0-10

TABLE VI
GUM VULCANIZATES

<u>Elastomer</u>	<u>Original Properties</u>		
	<u>AH - IODI</u>	<u>AH - MDI - 5DI</u>	<u>FH - MDI - 5DI</u>
Tensile strength (psi)	200	1410	585
Elongation (%)	280	375	420
Modulus (300%)	-	600	270
Set at break (%)	0	1-2	1-2
Hardness (Shore A)	45-50	50-55	45-50
<u>After 250 Hours in Air at 350°F</u>			
Weight loss (%)	6.3	4.3	4.5
Wt. Loss corrected for dicumyl peroxide content (%)	2.7	2.4	2.6
Tensile strength (psi)	175 (-13%)	51 (-97%)	77 (-87%)
Elongation (%)	530 (+89%)	280 (-26%)	250 (-40%)
Modulus (300%)	144	-	-
Set at break (%)	7	-	-
Hardness (Shore A)	47-52 (+4%)	42-47 (-15%)	38-43 (-15%)
<u>After 72 Hours in Flexol 201 at 350°F</u>			
Weight loss (%)	30	25	32
Tensile strength (psi)	100 (-50%)	103 (-93%)	80 (-86%)
Elongation (%)	340 (+22%)	360 (+4%)	320 (-24%)
Set at break (%)	0-1	1-2	1-2
Hardness (Shore A)	47-52 (+4%)	43-48 (-13%)	42-47 (-6%)

TABLE VII
REINFORCING OF HEXAFLUOROPENTYLENE ADIPATE (M_n 17,100)

	Philblack O						Hi-Sil 233		
	10	15	20	25	30	40	20	20(u)	30
% Reinforcing agent									
% DI-CUP 40C	7	7.5	8	8.5	9	10	8	8	9
Tensile strength (psi)	1968	2353	2100	2150	1808	1538	497	724	309
Elongation (%)	500	475	425	400	360	350	575	575	490
Modulus (300%)	240	692	917	1200	1280	1230	129	34	155
Set at break (%)	1-2	1-2	1-2	1-2	2-3	5-6	37	31	69
Hardness (Shore A)	55-60	57-62	55-60	56-61	60-65	63-68	42-47	45-50	47-51
Brittle point (°F.)	----- all below -65° -----								
	With 20 Parts Philblack O								
% DI-CUP 40C	7	8	9	10	11	12	13	14	
Tensile strength (psi)	1670	2208	2221	2640	2632	2656	2530	2120	
Elongation (%)	425	450	430	375	325	310	250	225	
Modulus (300%)	777	834	1167	1600	2247	2380	-	-	
Set at break (%)	1-2	1-2	1-2	1-2	1-2	0-1	0-1	0-1	
Hardness (Shore A)	56-60	56-60	58-62	60-64	64-68	65-69	69-73	70-74	

The effect of heat aging in air and in Plexol 201 at 350°F on several gum vulcanizates is shown in Table VI. The two elastomers that were chain-extended with diisocyanate before cross-linking with peroxide (AH-MDI-5DI and FH-MDI-5DI) exhibited about the same weight loss (2.4% and 2.6% corrected for dicumyl peroxide content) as the rubber which did not contain diisocyanate (2.7% corrected, AH-LODI) after 250 hours at 350°F. However, tensile strength of the former samples deteriorated 87-97%, while the latter only decreased 13% in tensile. Similar results were obtained on specimens aged in Plexol 201 at 350°F for 72 hours, but weight and tensile losses were much greater. Since AH-LODI is overcured, the better retention of properties after aging compared to AH-MDI-5DI and FH-MDI-5DI is probably due to both the fact that the former gum vulcanizate did not contain any diisocyanate and that it had a relatively denser cross-linking than the latter. Table V includes data on resistance of gum vulcanizates to 70/30: isooctane/toluene. Tensile after 1 week aging is decreased somewhat with volume swell of 0 to 20% exhibited, depending on the base polyester and type and amount of cross-linking.

Table VIII gives the properties of hexafluoropentylene adipate (M_n 17,100) reinforced with varying amounts of Philblack O and Hi-Sil 233 after aging at 350°F in air and in Plexol 201 (original properties in Table VII). Table IX gives results on hexafluoropentylene adipate (M_n 17,100) reinforced with 20 parts Philblack O and cured with varying amounts of DI-CUP 40C after the same tests (350°F). Consideration of these tables shows that the more highly cross-linked samples (i.e. those containing 11% and 12% DI-CUP 40C with 20 parts black, in Table IX) retain their tensile strength and other properties best during the aging tests at 350°F. Although a drop in tensile of 52% was exhibited by the sample of hexafluoropentylene adipate (M_n 17,100) containing 20 parts black and cured with 11% DI-CUP 40C after 257 hours at 350°F, the tensile strength of 1265 psi remaining after the heat aging test indicates that this elastomer offers much promise. The results of aging in Plexol 201 at 350°F for 72 hours are not as good. The same sample as above lost 76% of its original tensile strength, exhibiting a tensile of 663 psi after the test. Weight losses in air and in Plexol 201 at 350°F indicate that at 350°F in Plexol 201, some solvating or other action is taking place. After 257 hours in air at 350°F, weight losses are from 3% to 4%, and when the weight per cent of dicumyl peroxide is subtracted, weight losses are very negligible. After 72 hours in Plexol 201 at 350°F weight losses are higher (5.78% for the best sample, or 2.14% when corrected for dicumyl peroxide content).

In Plexol 201 at room temperature, reduction of tensile strength and weight loss is very small. As shown in Table X, a sample of hexafluoropentylene adipate with 20 parts black, cross-linked with 8% DI-CUP 40C, exhibited a tensile of 1888 psi (-14%) and weight loss of 0.16% after 1 week in Plexol 201 at room temperature. Data in Table X show, also, that these elastomers are very resistant to the effect of 70/30: isooctane/toluene and to 10% solutions of hydrochloric acid and sodium chloride (1 week at room temperature). They are not stable after 1 week in 10% sodium hydroxide solution.

TABLE VIII

HEAT AGING OF REINFORCED HEXAFLUOROPENTYLENE ADIPATE (M_n 17,100) FOR 257 HOURS IN AIR AT 350°F.

	Phillblack 0			Hi-Sil 233		
	20	30	40	20	30	40
% Reinforcing Agent	20	30	40	20	30	40
% DI-CUP 40C	8	9	10	8	9	10
Weight loss % 24 hrs.	2.35	2.03	1.89	2.68	2.14	1.89
120 hrs.	3.06	2.82	2.98	5.60	8.13	8.13
194 hrs.	3.45	3.38	3.84	7.55	11.3	11.3
257 hrs.	3.70	3.59	4.23	8.87	13.0	13.0
Wt. loss corrected for dicumyl peroxide content (%)	1.20	1.00	1.56	6.37	10.4	10.4
Tensile strength (psi)	400 (-81%)	400 (-78%)	338 (-78%)	194 (-61%)	136 (-56%)	136 (-56%)
Elongation (%)	425 (same)	450 (+25%)	325 (-7.1%)	575 (same)	375 (-23%)	375 (-23%)
Modulus (300%)	166 (-82%)	190 (-91%)	307 (-75%)	65 (-50%)	109 (-30%)	109 (-30%)
Set at break (%)	1-2	20	50	31	38	38
Hardness (Shore A)	50-55 (-8.8%)	55-60 (-8.1%)	59-64 (-6.2%)	42-47 (same)	55-60 (+16%)	55-60 (+16%)

Heat Aging For 72 Hours in Plexol 201 at 350°F.

Weight loss %	8.8	19
Tensile strength (psi)	650 (-69%)	258 (-48%)
Elongation (%)	350 (-18%)	300 (-48%)
Modulus (300%)	500 (-45%)	-
Set at break (%)	1-2	2-3
Hardness (Shore A)	50-55 (-8.8%)	54-59 (+27%)

TABLE IX

HEAT AGING OF HEXAFLUOROPENTYLENE ADIPATE (M_n 17,100) REINFORCED
WITH 20 PARTS PHLEBLACK O FOR 257 HOURS IN AIR AT 350°F.

% DI-CUP 40C	7	8	9	10	11	12
Weight loss % 24 hrs.	1.87	1.38	1.53	1.54	1.58	2.44
168 hrs.	2.72	2.35	2.46	2.48	2.62	3.52
257 hrs.	3.12	2.81	2.92	3.00	3.04	4.05
Wt. loss corrected for dicumyl peroxide content (%)	0.92	0.31	0.13	(+0.08)	(+0.32)	0.41
Tensile strength (psi)	560 (-66%)	624 (-72%)	800 (-64%)	1088 (-58%)	1265 (-52%)	1168 (-56%)
Elongation (%)	425 (same)	400 (-11%)	430 (same)	425 (+13%)	400 (+23%)	375 (+21%)
Modulus (300%)	288 (-63%)	320 (-62%)	416 (-64%)	560 (-65%)	750 (-67%)	800 (-66%)
Set at break (%)	5	5-6	5	4-5	2-3	1-2
Hardness (Shore A)	56-60 (same)	56-60 (same)	58-62 (same)	61-65 (+1.6%)	63-67 (-1.5%)	59-63 (-9.0%)

Heat Aging For 72 Hours in Plexol 201 at 350°F.

Weight loss %	11.6	7.72	5.78	5.78
Wt. loss corrected for dicumyl peroxide content (%)	9.4	4.64	2.42	2.14
Tensile strength (psi)	304 (-82%)	448 (-83%)	663 (-76%)	720 (-73%)
Elongation (%)	325 (-31%)	350 (-6.6%)	350 (+7.7%)	330 (+6.5%)
Modulus (300%)	240 (-69%)	320 (-81%)	417 (-81%)	640 (-73%)
Set at break (%)	0-1	1-2	1-2	3-4
Hardness (Shore A)	56-60 (same)	54-58 (-9.7%)	56-60 (-12%)	57-61 (-12%)

TABLE X

RESISTANCE OF REINFORCED HEXAFLUOROPENTYLENE ADIPATE (M_n 17,100) TO SOLVENTS AT ROOM TEMPERATURE

	Plexol 201	70/30 : isooctane/toluene	10% HCl	10% NaCl	10% NaOH
Parts Philblack 0	20	10	15	10	25
% DI-CUP 40C	8	7	7.5	7	8.5
Hours in fluid	168	168	168	168	168
Weight change (%)	-0.16	+11.9	-1.0	-0.13	-35
Tensile strength (psi)	1888 (-11%)	2156 (+9.6%)	2700 (+15%)	1756 (-10.8%)	445 (-79%)
Elongation (%)	425 (-5.6%)	510 (+2.0%)	500 (+5.3%)	500 (same)	350 (-12.5%)
Modulus (300%)	-	452 (+88%)	750 (+8.1%)	574 (+140%)	-
Set at break (%)	1-2	1-2	1-2	1-2	0-1
Hardness (Shore A)	54-58 (-3.1%)	50-55 (-9.1%)	57-62 (same)	54-59 (-1.9%)	56-61 (same)

IV. EXPERIMENTAL

A. PREPARATION OF RAW MATERIALS

In general, research on the preparation of novel or unusual intermediates for use in this project was performed at Purdue Research Foundation, and details of that work are included in Appendix I of this report. The intermediates described below were prepared at Hooker Electrochemical Company, and further details of known compounds may be found in the literature references cited.

Perfluoroglutaric Acid (FGA) was prepared by aqueous permanganate oxidation of 1,2-dichlorohexafluorocyclopentene (Hooker Electrochemical Co.) according to the method described by McBee, Wiseman and Bachmann⁸. Yields of white crystalline FGA, purified by vacuum distillation, were 63-66%; b.p. 116°-121°C at 0.5 mm.

Diethyl Perfluoroglutarate⁸ was prepared by refluxing a mixture of FGA and 100% excess ethanol with a small amount of sodium bisulfate in benzene. After the water of reaction had been azeotroped off and the benzene removed, the crude ester was washed with 5% sodium bicarbonate, water, dried and distilled. Colorless diethyl perfluoroglutarate was obtained in 85-90% yields; b.p. 56°C at 0.5 mm.

2,2,3,3,4,4-Hexafluoropentenediol (HFPD) was prepared by reduction of diethyl perfluoroglutarate with lithium aluminum hydride (Metal Hydride, Inc.) according to the method reported by McBee, Marzluff and Pierce⁹. Yields of 90-95% white crystalline HFPD were obtained after three or four recrystallizations from benzene; m.p. 77.5°-79.5°C.

A purity of 99.8 mol % for HFPD prepared in this manner is indicated from cryoscopic measurements performed by the personnel of the analytical laboratories of Hooker Electrochemical Company.

1,2-Dichlorooctafluorocyclohexene was prepared from hexachlorobenzene and antimony pentafluoride (General Chemical Div.) by a modification of the method used by McBee, Wiseman and Bachmann⁸. In this procedure, antimony pentafluoride was added gradually to a slurry of the hexachlorobenzene in mixed chloro-fluoro-antimony salts maintained at 125-135°C. The heat of reaction is more easily controlled by this method, and the yield was increased by 10%. Distillation of the reaction mixture gave crude product which was washed with 17% hydrochloric acid, 10% potassium hydroxide, and water and dried. Fractional distillation gave colorless 1,2-dichlorooctafluorocyclohexene in 50% yield; b.p. 111°-114°C at 750 mm.

Perfluoroadipic Acid⁸ (FAA), Diethyl Perfluoroadipate⁸, and 2,2,3,3,4,4,5,5-Octafluorohexanediol⁹ (OFHD) were prepared in a manner similar to that outlined above for the perfluoroglutarate series, and as also described in reference 7.

Perfluoroadipyl Chloride⁷ (FAC) was made by reacting together equivalent amounts of FAA and phosphorus pentachloride (Mallinckrodt Chemical Works). A 35% yield of colorless FAC was obtained after several fractional distillations; b.p. 132.5°-133°C at 751 mm. (The action of thionyl chloride on FAA previously reported⁷ gave 75-80% yields.)

Glutaryl Chloride (GC) was prepared by the action of phosphorus pentachloride on an equivalent amount of glutaric acid (Distillation Products). A yield of 89% colorless GC was obtained from distillation of the reaction mixture; b.p. 106°-107°C at 13 mm. Redistillation gave 78.1% colorless GC; b.p. 106°-106.5°C 13 mm.

Adipyl Chloride (AC) was prepared from 50% excess thionyl chloride (Hooker Electrochemical Co.) and adipic acid (DuPont). Distillation gave 72% colorless AC; b.p. 124°C at 13 mm.

B. PREPARATION OF LINEAR POLYESTERS

The preparation and characterization of the linear polyesters described in Tables I, II, and III, with the exception of polyester AH,1,1002 (Table I), were performed in the manner and apparatus described in reference 7. Polyester AH,1,1002 was made in a conventional 500 cc. resin pot fitted with a high speed stirrer, thermometer, nitrogen inlet tube, and outlet connected to atmosphere or vacuum.

Viscometer tubes and methods described by Flory¹⁰ for the determination of melt viscosities (η) and molecular weights (M_n) of hydrocarbon polyesters were applied in this work to the fluorine-containing polyesters.

Chain extension of lower or moderate molecular weight linear polyesters with diisocyanates, or with diisocyanates and small amounts of diamines, at 130-160°C was performed in the manner described for hydrocarbon polyesters^{12,13}. Since the lower molecular weight fluorine-containing polyesters contain very predominately hydroxyl end groups (as discussed in reference 7), 1.00 mol of diisocyanate was used in chain extension, based on the molecular weight of the polyester as determined from melt viscosity measurements. In those cases where diamines were also used, 1.10 mol diisocyanate and 0.10 mol of diamine were customarily used. The reactants were mixed together at 120°-130°C for about 15-30 minutes, transferred into a greased or waxed tray and heated at 130°-160°C overnight in an oven. This treatment transformed the lower molecular weight viscous liquid polyesters into tough, rubberlike gums suitable for milling.

C. CROSS-LINKING AND TESTING OF VULCANIZATES

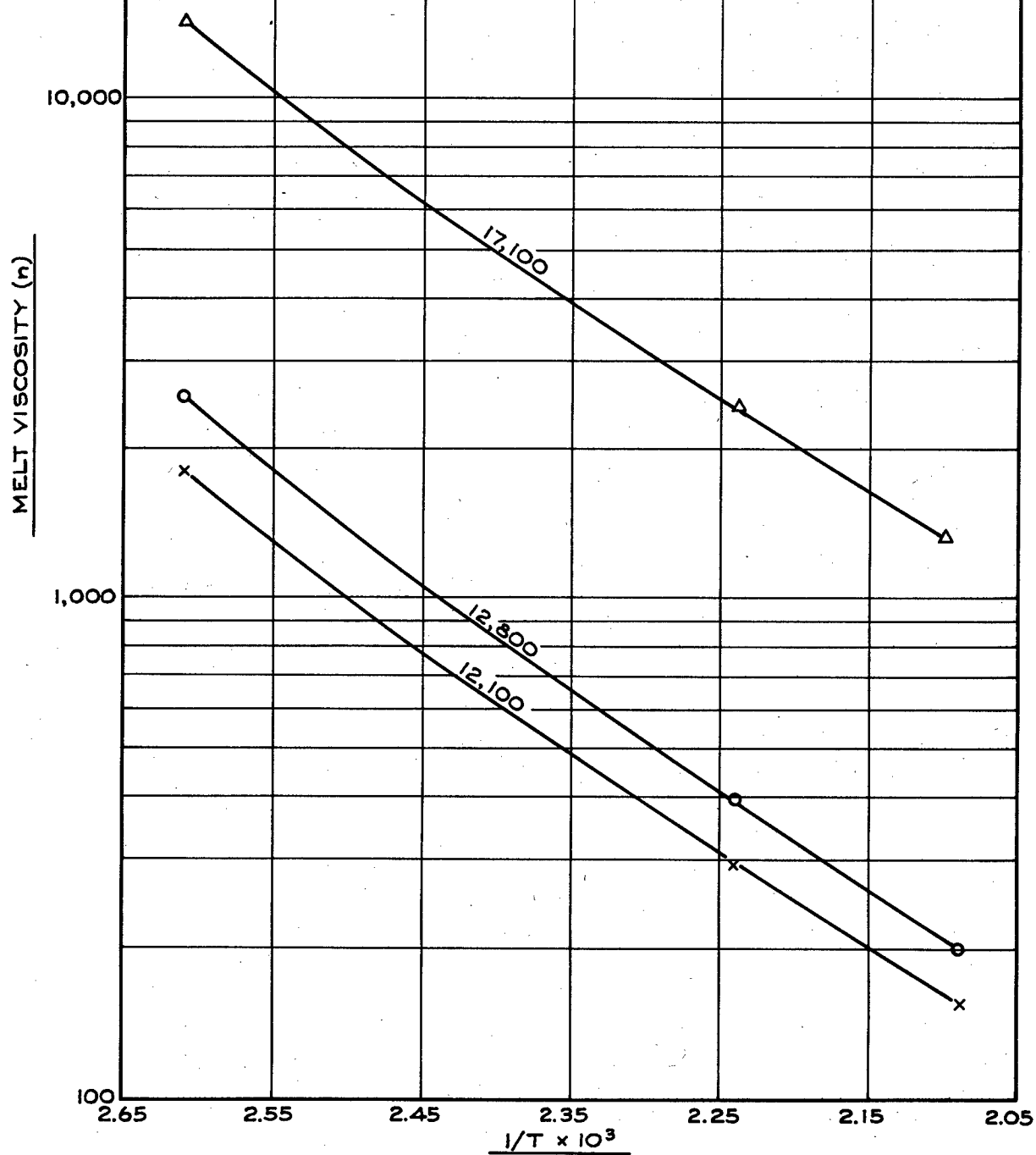
The higher molecular weight (M_n) polyesters are well suited for processing on conventional rubber equipment, and milling in the specified amounts of reinforcing agent (if any), followed by the curing agent, was accomplished on water-cooled or on slightly-warmed rollers, depending on M_n of the polymers.

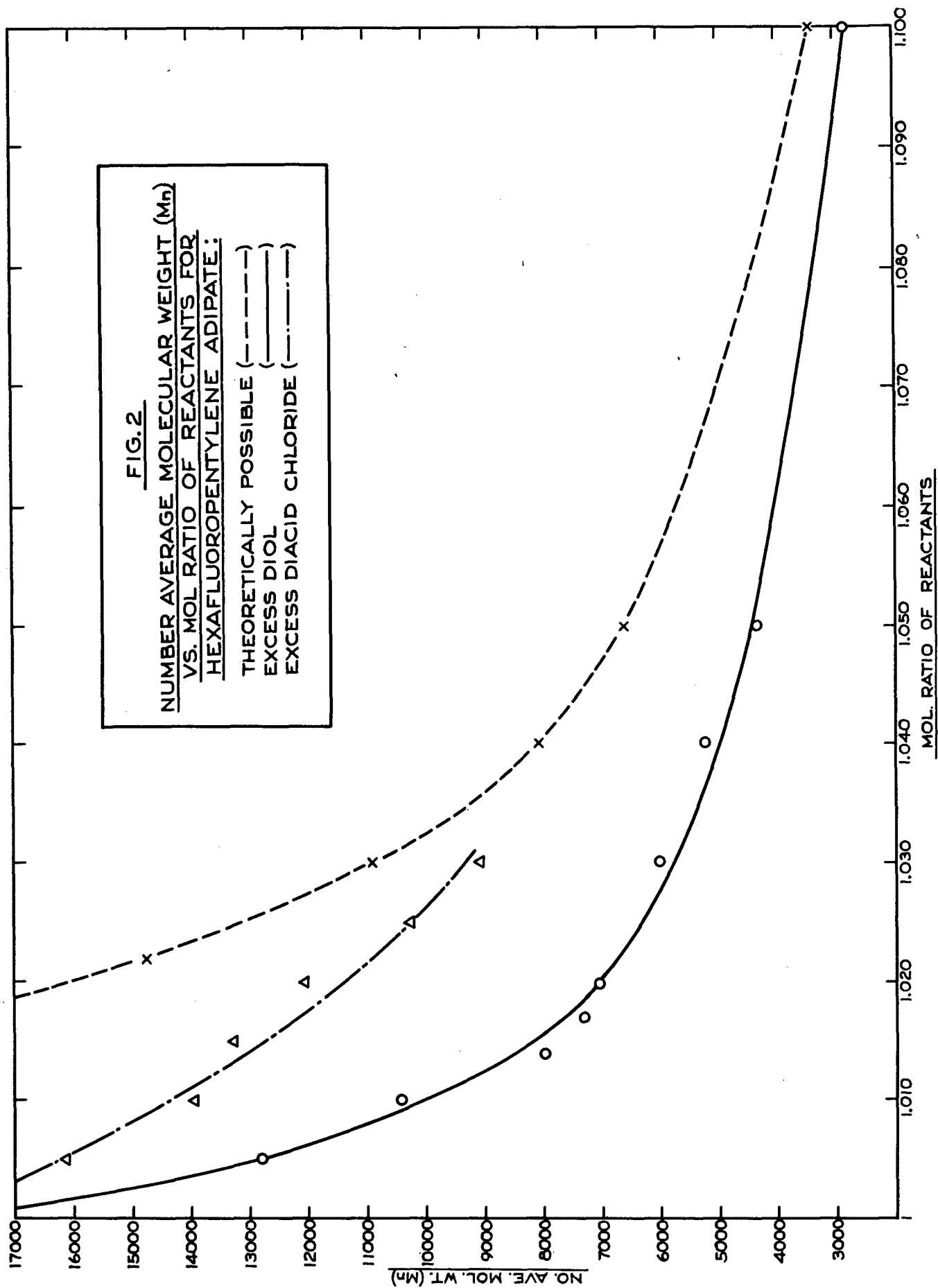
Curing with diisocyanate was accomplished by milling in the specified amount of diisocyanate (usually 0.50 mol methylene bis(4-phenylisocyanate) based on the molecular weight of the original polyester as determined from melt viscosity measurements) and 1% quinoline (based on total weight of material) and molding at 150°C for 90 minutes. Post-curing at room or at elevated temperatures increases the tensile strength, etc., of the polymers prepared in this manner.

Curing with peroxide was effected by heating the mixture, after milling, in a stainless steel mold (4" x 4" x 0.025") at 165°C for 60 minutes.

Dumbbell specimens cut from the moldings were tested on a Scott Tester, Model L-6, for tensile strength and elongation, before and after aging tests. The aging tests are thus seen to be more severe than usual, because of the high surface to weight ratio of the very thin (0.025") specimens. The specimens were suspended from wires attached to the tops of jars containing the test medium in the case of solvent aging tests, or to a rack in the oven in the case of heat aging tests. After completion of aging, the specimens were weighed and allowed to rest at $23^\circ \pm 1^\circ\text{C}$ for at least four hours before testing.

FIG. 1
MELT VISCOSITY (η) VS. $1/T \times 10^3$
FOR HEXAFLUOROPENTYLENE
ADIPATE OF INDICATED MOL. WT.





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13. T. Mastin and N. Seeger, U.S. Patent 2,625,535 (1953).

APPENDIX I

SUBCONTRACT WORK PERFORMED AT PURDUE UNIVERSITY

Research on the syntheses of certain intermediate difunctional chemicals containing fluorine, or fluorine in combination with certain hetero atoms interspersed in the carbon chain, such as sulfur, oxygen, and nitrogen, has been performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company. In general, fluorocarbon compounds considered desirable as intermediates for this project at the present stage consist of dicarboxylic acids from which the corresponding dicarboxylic acid chlorides can be made, with less emphasis being placed on the corresponding diols. It was considered particularly important to investigate such compounds possessing perfluoroalkyl pendent groups attached to the linear hydrocarbon difunctional chain.

This appendix consists of a summary report on the work performed at Purdue University under the subcontract. With the exception of 3-perfluoropropylglutaryl chloride, the compounds described herein have not yet been made into polyesters.

Second Summary Progress Report

FLUORINE CONTAINING MONOMERS
FOR CONDENSATION POLYMERS

Earl T. McBee

Carleton W. Roberts

Department of Chemistry and the Purdue Research Foundation

PURDUE UNIVERSITY

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Subcontract with the
HOOKER ELECTROCHEMICAL COMPANY
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on

Contract AF 33(616)-2421 RDO NO. 617-11 SR-3N
Task Number 73404

WADC TR 55-221 Pt 2

FOREWORD

This is the second summary progress report prepared by the Department of Chemistry, Purdue University on work concerned with the investigation and development of new fluorine-containing monomers suitable for condensation type polymers. This work was performed on a subcontract with the Hooker Electrochemical Company as part of Contract AF 33(616)-2421 RDO No. 617-11 SR-3N, Task Number 73404.

The personnel assigned to this project were Mr. Gordon Wilson, Jr. under the direct supervision of Dr. E.T. McBee and Dr. Carlton W. Roberts.

ABSTRACT

1. The methyl and ethyl esters of perfluorooctanoic acid were made in 78 and 70% yield respectively.
2. Perfluorooctanoyl aldehyde was prepared in 78% yield by the lithium aluminum hydride reduction of either the methyl or ethyl ester of perfluorooctanoic acid.
3. Perfluorooctanoyl aldehyde was condensed with ethyl bromoacetate to give ethyl 3-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecenoate in 39% yield.
4. Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate was prepared in 66% yield from the 3-hydroxy compound by phosphorus pentoxide dehydration.
5. Condensation of ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate with ethyl malonate and subsequent hydrolysis and decarboxylation gave 3-perfluoroheptylglutaric acid.
6. 3-Perfluoroheptylglutaryl chloride was prepared in 73% yield from the corresponding acid.
7. Hydrogen sulfide was added to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate to give a 66.6% yield of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate and a lower boiling substance that may be ethyl 3-thiohydroxy-4,4,5,5,6,6,6-heptafluorohexanoate. This preparation was repeated several times.
8. Hydrolysis of ethyl 3,5-bis(perfluoropropyl)-4-thiapimelate has been investigated under basic and acidic conditions. Alkaline hydrolysis is not a satisfactory method and acid hydrolysis gives a 50 to 60% yield of 3,5-bis(perfluoropropyl)-4-thiapimelic acid. This acid is obtained as a mixture of meso and racemic compounds.
9. The conversion of 3,5-bis(perfluoropropyl)-4-thiapimelic acid to the diacid chloride has been effected in 85% yield using thionyl chloride; phosphorus pentachloride does not give a clean product.
10. The lithium aluminum hydride reduction of ethyl 3,5-bis(perfluoropropyl)-4-thiapimelate gave the 3,5-bis(perfluoropropyl)-4-thiaheptane-1,7-diol in 86% yield.
11. Extensive investigations of the oxidation of 3,5-bis(perfluoropropyl)-4-thiapimelic acid and its derivatives to the corresponding sulfones have given compounds believed to have arisen from cleavage of a carbon-sulfur bond.

12. Several attempts to prepare di(1-carbethoxymethyl-2,2,3,3,4,4,4-heptafluorobutyl) ether have failed.
13. The reaction of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate with n-butylamine gave ethyl 3-butylamino-4,4,5,5,6,6,6-heptafluorohexanoate in 76% yield.
14. Reaction of ethyl 3-butylamino-4,4,5,5,6,6,6-heptafluoro-2-hexenoate with an additional mole of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate does not proceed to give the tertiary amine.
15. Ammonia does not add to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate under the condition tried, anhydrous ammonia in ethyl ether.
16. Several repetitions were made of the preparative scheme - ethyl heptafluorobutyrate, heptafluorobutanoyl aldehyde, ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate, ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, 3-perfluoropropylglutaric acid, 3-perfluoropropylglutaryl chloride.

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SUMMARY AND CONCLUSIONS

Satisfactory methods have been devised for the preparation of 3-perfluoropropylglutaric acid and 3-perfluoroheptylglutaric acid and their derivatives.

Satisfactory methods have been devised for the preparation of 3,5-bis(perfluoropropyl)-4-thiapimelic acid and its derivatives.

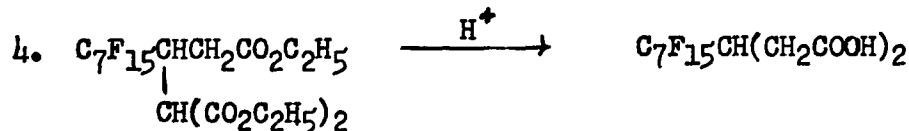
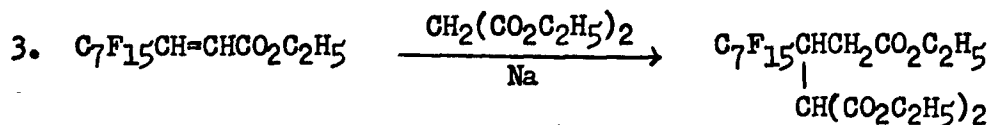
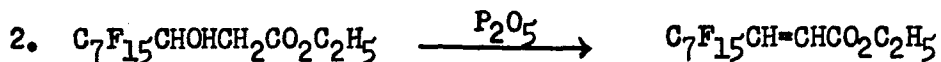
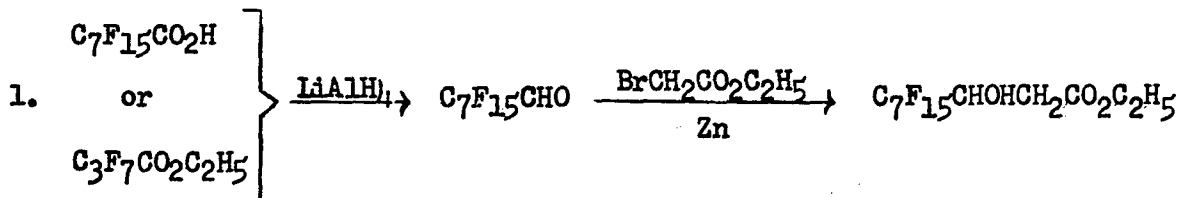
Investigation is underway into satisfactory preparative methods for oxygen-, nitrogen- and other sulfur-containing difunctional compounds suitable for polymerization studies.

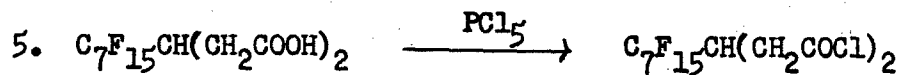
DISCUSSION

A. PREPARATION OF 3-PERFLUOROHEPTYLGLUTARIC ACID AND DERIVATIVES

For possible use in the synthesis of polyesters, the monomers 3-perfluoropropylglutaryl chloride, 3-perfluoropropyl-1,5-pentanediol and diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate have been prepared from the intermediate, ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate (1). The analogous compounds containing a perfluoroheptyl group instead of the perfluoropropyl group were to be synthesized from the corresponding intermediate. Therefore, the preparation of this intermediate from the commercially available perfluorooctanoic acid was initiated.

Pierce and Kane (2) have prepared perfluorooctanoyl aldehyde from methyl perfluorooctanoate in 70% yield by reduction with lithium aluminum hydride at -70°C . It was decided to use their procedure and thus perfluorooctanoic acid was esterified by the procedure recommended by the Fluorochemicals Department of Minnesota Mining and Manufacturing Company for the esterification of perfluorobutyric acid. The yield of methyl perfluorocaprylate on a preliminary 0.2 mole run was 77.7%. However, when 1.5 moles of the acid were esterified a yield of only 70% was obtained. Since the reduction of the ester to the aldehyde may not give more than about a 70% yield, the preparation of the aldehyde from the acid via the ester can be expected to give only a 49-55% overall yield. It was therefore decided to investigate the direct reduction of the acid to the aldehyde by an inverse addition of lithium aluminum hydride at -5 to 0°C (3).





The crude aldehydrol was isolated in the usual manner. When this crude aldehydrol was added to a mixture of sulfuric acid and phosphorous pentoxide, the distillate appeared to be a mixture of compounds and very little material was collected near the reported boiling point of the aldehyde. A large part of the acid apparently was not reduced since one-third of the distillate collected boiled above 160°C. Redistillation of lower boiling fractions through a short column did not prove satisfactory since fractions containing both solid and liquid were again obtained, with the temperature steadily climbing throughout the distillation. The combined fractions were then esterified with ethyl alcohol. The separation of the products from this procedure has not been accomplished as yet.

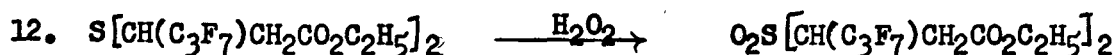
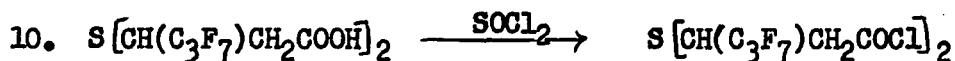
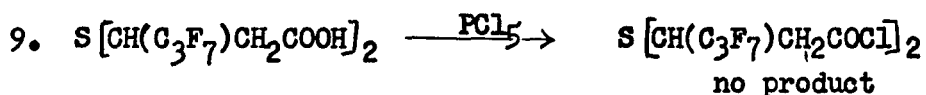
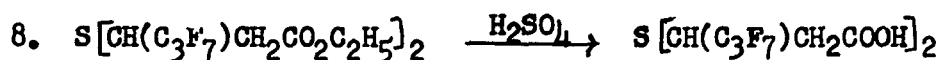
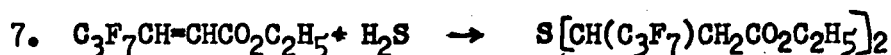
An additional quantity of ethyl perfluorooctanoate was prepared and the ethyl ester was reduced to perfluorooctanoyl aldehyde with lithium aluminum hydride at -70°C. The final step in the preparation, distillation of the aldehyde, b.p. 122°C, from concentrated sulfuric acid, gave a fraction b.p. 121-124°C, representing a 78.5% yield (Equation 1). However, on standing in a stoppered flask for two days, the product turned milky. The finely divided white solid present in the flask did not appear the same as the aldehydrol and when the product was again distilled from sulfuric acid the white solid was left as an insoluble residue in the acid. The aldehyde obtained from the second distillation from sulfuric acid was used immediately for condensation with ethyl bromoacetate (Equation 1).

From the Reformatsky reaction was obtained only a 39% yield of ethyl 3-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoate. At the end of refluxing the reactants, there was a scum on top of the reaction mixture. The scum is thought to be polymerized aldehyde and has been encountered before. When the reaction mixture had been washed and the ether-benzene solution dried, the solvents were removed by distillation. At 80°C a solid distilled along with the benzene. This was retained for future investigation. The product from the Reformatsky reaction was dehydrated with phosphorous pentoxide to gave a 66% yield of ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate (Equation 2).

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate was subjected to a Michael condensation with diethyl malonate followed by hydrolysis and decarboxylation to yield 3-perfluoroheptylglutaric acid in 52.8% overall yield (Equation 4). 3-Perfluoroheptylglutaryl chloride was then prepared in 73% yield from the corresponding acid by reaction with phosphorous pentachloride (Equation 5). And it is planned to prepare the 3-perfluoroheptyl-1,5-pentanediol by the lithium aluminum hydride reduction of either the diethyl 3-perfluoroheptylglutarate or the free acid (Equation 6).

B. PREPARATION OF SULFUR-CONTAINING DIFUNCTIONAL MONOMERS

In order to obtain more of the 3,5-bis(perfluoropropyl)-4-thiapimelic acid for use in preparation of the acid chloride the following experiments were conducted: two moles of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate were dehydrated to give an 84.1% yield of ethyl 4,4,5,5,6,6,6-heptafluorohexanoate; the hexenoate was reacted with hydrogen sulfide to give a 66.6% yield of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate (1) (Equation 7); and the diethyl thiapimelate was hydrolyzed in sulfuric acid and a 56.2% yield of 3,5-bis(perfluoropropyl)-4-thiapimelic acid was obtained (Equation 8). This hydrolysis gave a yield much lower than expected. Perhaps this was due to the rather drastic conditions of heating the ester with concentrated sulfuric acid at approximately 100°C. It also may be due to the fact that the acid does not seem to be too stable in boiling benzene or toluene although by itself it melts without visible decomposition. When the lower melting acid is recrystallized from benzene small droplets of a purple oil are formed when the solution is heated. These oil droplets adhere to the glass and do not crystallize when the benzene solution is cooled. Evaporations of benzene and toluene solutions were thus carried out on a steam bath with a rapid stream of air playing on the contents of the beakers to minimize the formation of the oil droplets. The hydrocarbon solution was then decanted into a clean beaker to effect crystallization.



An investigation of the hydrolysis of the ester was then undertaken. It was found that 5% sodium hydroxide caused some type of decomposition leading to a dark oil and tar. With a small sample of ester in concentrated sulfuric acid hydrolysis was accomplished yielding, after several recrystallizations, the thiapimelic acid as white plates with a melting point of 156-157°C. The combined crystallization liquors were reduced in volume and

a crop of small crystals was obtained which was thought to be the impure thiapimelic acid. However, when the hydrolysis was repeated on a larger scale it was noted that the thiapimelic acid crystallized out of toluene first but the second crop obtained was some other compound. The thiapimelic acid obtained accounts for only about one-third of the ester used. The melting range of the second crop of crystals was 108-116°C and recrystallization from toluene or benzene did not seem to give any purification. It appeared that the acid hydrolysis of the thiapimelic ester would have to be done under less vigorous conditions to obtain a better yield of the desired acid.

The lower-melting substance is insoluble in hot and cold water but is soluble in cold 5% sodium hydroxide solution. As with the diethylpimelate, a dark red color is formed when the alkaline solution is warmed. Acidification of the colored solution causes a black, sticky tar to separate as a second phase. The substance also dissolves in sodium bicarbonate solution with the evolution of carbon dioxide. It was therefore felt that the substance could be the half ester, monoethyl 3,5-diperfluoropropyl-4-thiapimelate. However, attempts at further hydrolysis in acidic medium have in all cases yielded starting material. Also, while the neutral equivalent of the monoethyl pimelate should be 542, the value determined experimentally is 261. The same value was found for the higher melting compound. The molecular weights of both high and low melting compounds were determined by the Rast method and found to be the same for both compounds. The values obtained were low, for the calculated molecular weight of 3,5-bis(perfluoropropyl)-4-thiapimelic acid is 514 and the experimentally determined values were 417 and 420. However, it is felt that the low values were justified by the experimental technique used. When the sample was melted with camphor there was a loss of camphor due to sublimation and evaporation. To keep the loss of camphor approximately equal in each case, the small flasks containing the samples and camphor were immersed in an oil bath maintained at 190°C for approximately the same length of time. They were then stoppered, swirled to mix the contents and set aside to cool. Any loss of camphor during these operations would make the result lower than the true value since the weight of the camphor taken appears in the numerator of the expression used to calculate the molecular weight, i.e.:

$$\text{Molecular Weight} = \frac{39.7 \times \text{Wt. of camphor}}{\text{lowering of the m.p.} \times \text{Wt. of sample}}$$

Since the neutral equivalents and the molecular weights of the high and low melting substances are the same it was thus concluded that they are the same compound. The large difference in melting points may be rationalized by considering the structural formula for the acid. It is noted that there are two similar asymmetric carbons. A meso compound and a racemic mixture should exist if the formation of the ester from the addition of hydrogen sulfide to the trans-hexenoate was in no way stereospecific. This must have been the case for if there had been a stereospecific addition involved, the mixture of D and L acid would not be racemic and an optical rotation

would result from solutions of either the higher or the lower melting substance. However, solutions of these substances showed no rotation when placed in a polarimeter. The higher melting acid is the least soluble and crystallized from toluene in white plates. The lower melting acid was obtained upon concentration of the mother liquor and was recrystallized from benzene. It does not form large crystals but small hard clusters of crystals. The latter have not been obtained in a pure state, judging from the wide melting range of 108-116°C. It seems reasonable to assume that the higher melting acid which forms large plates which give a sharp melting point is the meso acid while the lower melting acid is the racemic mixture contaminated with some of the meso compound. The fact that a mixture of isomers was not noticed when the ester was prepared is not surprising when the boiling points of the ethyl esters of tartaric acid are considered. The ethyl ester of meso tartaric acid boils at 157.5°C/14 mm while the ethyl ester of DL-tartaric acid has a boiling point of 158°C at 14 mm (4). Since the 3,5-bis(perfluoropropyl)-4-thiapimelic acid is only to be used as an intermediate, further work toward obtaining the lower melting isomer in the pure state has been abandoned for the present time.

A small amount of the pure and anhydrous 4-thiapimelic acid was reacted with phosphorous pentachloride. The small amount of yellow product obtained boiled at 100°C/1 mm. Elementary analysis showed fluorine, chloride and sulfur to be present and the compound gave many tests characteristic of acid chlorides. A ten-gram sample of the pimelic acid was then treated with phosphorous pentachloride, under essentially the same conditions as before. After refluxing the reactants for one hour the phosphorous oxychloride was removed at atmospheric pressure but when a reduced pressure distillation of the residue was attempted a decomposition took place which yielded only tars and a heavy red oil that would not distill below 160°C/1 mm (Equation 9).

Since the reaction of phosphorous pentachloride with 3,5-bis(perfluoropropyl)-4-thiapimelic acid did not produce the desired acid chloride an attempt was made to prepare this substance using thionyl chloride. The initial product isolated was very light yellow in color but redistillation produced an 84.5% yield of colorless product that gave reactions characteristic of acyl halides (Equation 10).

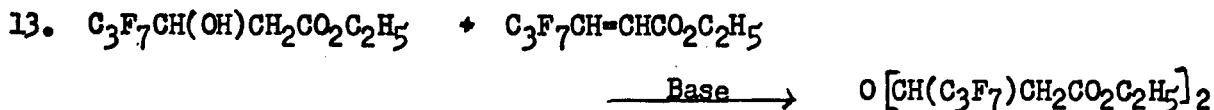
The lithium aluminum hydride reduction of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate to the corresponding glycol has been accomplished. The 3,5-bis(perfluoropropyl)-4-thiaheptane-1,7-diol is a very viscous oil which boils at 103°C/0.1 mm. The first reduction was made on a small amount of ester and did not produce as much product as desired. To obtain a larger sample of the glycol it was first necessary to prepare more of the thiapimelate by the addition of hydrogen sulfide to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. This preparation was performed by the same procedure used in previous preparations except that the temperature was not kept as low as usual during the addition. The crude product (yellow in color) was obtained in 74% yield and the usual forerun of ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate was almost negligible. Reduction of the crude thiapimelate to the glycol produced a product which was slightly yellow after a first

distillation. Redistillation produced a yellow forerun and a colorless product (Equation 11).

The oxidation of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate to the corresponding sulfone has been attempted several times. The substance isolated in each case was a viscous orange oil. Oxidation of the thiapimelic acid produced a similar oil (Equation 12). The thiapimelic ester was oxidized under rather drastic conditions, i.e., refluxing acetic acid, acetic anhydride and 30% aqueous hydrogen peroxide. After removal of the solvents an attempt to distill the viscous residue under reduced pressure resulted in decomposition to tars and a small amount of very hygroscopic white solid. Crystallization of the residue from a similar oxidation produced a similar extremely hygroscopic solid. The latter compound, which contains fluorine and sulfur, melts (open tube) over the range 65-90°C and is quite acidic. The acidic nature of this product may be explained by assuming that the ester was hydrolyzed to the acid under the reaction conditions. Another possibility is that the drastic conditions ruptured the carbon to sulfur bond and a sulfonic acid was produced. This might explain the fact that the product is highly hydroscopic (5). In order to investigate the oxidation of the free thiapimelic acid, a quantity of the acid had to be prepared from the diethyl ester. This was accomplished by an acidic hydrolysis in the same manner as previously reported and oxidation studies are underway.

C. PREPARATION OF OXYGEN-CONTAINING MONOMERS

The preparation of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate and the corresponding acid and acid chloride have been described above. The corresponding compounds with oxygen in place of the sulfur were considered interesting as possible monomers for polyesters. Therefore, attempts have been made to prepare di(1-carbethoxymethyl-2,2,3,3,4,4,4-heptafluorobutyl)-ether by a condensation of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate (Equation 13).



None of the desired product was obtained when the reactants were refluxed with sodium ethoxide, B.T.A. Hydroxide (30% benzyltrimethylammonium hydroxide in methanol) and with some of the gel produced when metallic sodium is dissolved in the β -hydroxy ester. In each case starting material was recovered. When the β -hydroxy ester and the α,β -unsaturated ester were refluxed with B.T.A. hydroxide and piperidine a 39% recovery of the unsaturated ester was obtained. The fraction recovered which included the boiling range of the β -hydroxy ester was large, corresponding to a 119% recovery of this starting material. Obviously the fraction contained some other compound, possibly the adduct of piperidine with the α,β -unsaturated ester.

A subsequent attempt was made to effect the addition using sodium hydride as a catalyst. From the dark brown reaction mixture a solid was obtained. This reaction product is quite polar since it readily dissolves in water and alcohols and is insoluble in hot benzene and toluene. Attempts to recrystallize it from acetone-benzene and acetone-chloroform mixtures produced gels instead of well formed crystals and the product has not been obtained in a pure form. In another attempt to add ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, using benzene as a solvent and sodium hydride as a catalyst, a small amount of the α,β -unsaturated ester was isolated from the reaction products. An acidic white solid which melted at 75-76°C, after recrystallization from benzene, was also isolated. This agrees with the melting point for 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic acid (6). A liquid substance with a boiling point intermediate between these known compounds was also isolated. The identity of this substance has not been completed, but its physical properties are different from those of the known hydroxy and unsaturated heptafluorohexanoic acids and esters.

Another preparatory route to the desired ether was considered. If it were possible to prepare ethyl 3-bromo-4,4,5,5,6,6,6-heptafluorohexanoate and then carry out a Williamson synthesis with the sodium salt of the β -hydroxy ester, an ether should result. The proximity of a perfluoro-alkyl group may first of all prevent the ready addition of hydrogen bromide

to the unsaturated acid or ester and secondly, the β -bromo ester may not be reactive toward alkoxides. However, this possible preparation of the desired ether is under investigation. Toward this end, ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate has been hydrolyzed to the free acid. The addition of hydrogen bromide to this acid is being investigated, first in saturated aqueous solution.

D. PREPARATION OF NITROGEN-CONTAINING MONOMERS

A tertiary amine in which perfluoroalkyl groups are present on all carbons attached to the nitrogen may be a very weak base. If such an amine is a weak enough base it may be possible that the corresponding ammonium chloride may be very unstable or may not exist to any extent at all. Thus the acid chloride of N,N-bis(1-carboxymethyl-2,2,3,3,4,4,4-heptafluorobutyl)-2,2,3,3,4,4,4-heptafluorobutylamine could be used with glycols in the preparation of polyesters, for the hydrogen chloride produced during polymerization would not effect the unreacted amine. Numerous references to the addition of primary alkyl amines to acrylic esters have appeared in the literature. Most of the conditions used are extremely mild, e.g., standing at room temperature for several days. An investigation has been started to determine if a primary amine will add to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. When n-butyl amine was allowed to stand with the α, β -unsaturated ester in ethanol for six days at room temperature a small amount of product, b.p. $87^{\circ}\text{C}/3.5$ mm, $n_D^{20.5}$ 1.3709 to 1.3730 was isolated that contained nitrogen. It did not dissolve in dilute hydrochloric acid and did not give a Hinsberg test for a primary or secondary amine. Assuming this compound is the desired tertiary amine, the yield was 23.5%. The reaction was repeated using no solvent and heating at reflux temperature for three hours. The same product was isolated in this second reaction in a 36% yield, assuming it to be the desired tertiary amine. An analysis for carbon and hydrogen was obtained for this substance. The percentages found for carbon and hydrogen were intermediate between the calculated values for the desired tertiary amine and the secondary amine, (1-carbethoxymethyl-2,2,3,3,4,4,4-heptafluorobutyl)butylamine. The reaction was repeated, using benzene as a solvent. The product obtained has a slightly lower boiling point and a higher index of refraction than the substance isolated before, viz: b.p. $97^{\circ}\text{C}/7.5$ mm, $n_D^{19.5}$ 1.3758. The product, which gave positive tests for nitrogen and fluorine on elementary analysis, did not react with benzene-sulfonyl chloride or acetyl chloride and did not give a positive color test for secondary amines with acetaldehyde and sodium nitroprusside (the Simon test). This reaction product was submitted for ultimate analysis, and the results indicated that the product was the secondary amine, ethyl 3-butyl-amino-4,4,5,5,6,6,6-heptafluorohexanoate (Equation 14). The preparation was repeated exactly as before



(using two moles of the hexenoate for each mole of the butylamine) except that the reactants were refluxed for 75 hours. The yield of secondary amine was 76.2%, based on the butylamine used, and the recovery of the excess hexenoate was approximately 100%. Since the secondary amine did not add to the α, β -unsaturated ester in boiling benzene solution other reaction conditions which will perhaps cause the addition will be investigated in the future.

Since the addition of n-butylamine to the α, β -unsaturated ester in benzene solution gave only the 1:1 adduct, ethyl 3-butylamino-4,4,5,5,6,6,6-heptafluorohexanoate, an attempt was made to effect the addition of the

3-butylamino ester to the heptafluorohexenoate at a higher temperature. The two esters were combined in the absence of any solvent and refluxed for 16 hours. Some of the reactants were decomposed, especially the amine, but no apparent addition was observed.

It was then thought that a smaller amine would be more likely to add to two moles of the heptafluorohexenoate. To investigate this possibility the addition of ammonia to the unsaturated ester was attempted using ether solution at ice bath temperature and a very small amount of sodium amide as catalyst. In the fairly short reaction time used there appeared to be no addition. This reaction will be investigated further using either a longer reaction period or carrying out the reaction at a higher temperature in a pressurized system.

E. REPEATED PREPARATIONS OF SAMPLES FOR POLYMERIZATION

Several of the compounds previously described (1) were prepared again for subsequent conversion to compounds needed in the polymerization studies.

Stobbe condensation of diethylsuccinate with perfluorobutyraldehyde was investigated previously but none of the desired ethyl 2-carboxymethyl-4,4,5,5,6,6,6-heptafluoro-2-hexenoate was produced. It was thought that perhaps a highly fluorinated ketone rather than a perfluoroaldehyde would give a satisfactory reaction. Therefore, this condensation has been attempted using diethylsuccinate and methyl perfluoropropyl ketone. The product, ethyl 2-carboxymethyl-3-methyl-4,4,5,5,6,6,6-heptafluoro-2-hexenoate should be easily reduced to give a substituted 1,4-butanediol with a high percentage of fluorine in the side chain. However, the only isolated product of the reaction was recovered diethylsuccinate.

EXPERIMENTAL

A. PREPARATION OF 3-PERFLUOROHEPTYLGLUTARIC ACID

1. Preparation of Methyl Perfluorooctanoate. Into 12.8 grams (0.40 mole) methyl alcohol were poured (with cooling) 21.6 grams (0.22 mole) concentrated sulfuric acid (1). This ice-cold solution was then added to 82.8 grams (0.20 mole) perfluorooctanoic acid in a 500-ml flask and the flask was stoppered and left overnight. After refluxing for 2 hrs., the contents were distilled through an 8" column packed with glass helices. The product collected consisted of two phases which distilled over the range 90-115°C. The lower phase was separated, dried over anhydrous magnesium sulfate and distilled under reduced pressure. The product collected, b.p. 74.5°C/32 mm to 73°C/29 mm, n_D^{20} 1.3062, amounted to 66.5 grams (77.7%). Using the same procedure, an additional 621 grams (1.50 moles) of perfluorooctanoic acid gave 450 grams (70%) of methyl ester, b.p. 73-75°C mm, n_D^{20} 1.3061.

2. Preparation of Ethyl Perfluorooctanoate. Into a 2000 ml flask were placed 394.5 grams (0.953 mole) perfluorocaprylic acid and 701.5 grams of absolute ethyl alcohol. Hydrogen chloride was bubbled through the solution until 11 grams had been absorbed. The flask was set aside for a day and then the contents were refluxed for 1 hour. The excess ethyl alcohol was removed by distillation at reduced pressure. The residue consisted of two phases which would not separate into layers. This residue was washed with 10% sodium carbonate solution to dissolve unreacted acid and the remaining single organic phase was distilled to yield 201 grams (61%) of ethyl perfluorooctanoate, b.p. 48-50°C/4.6 to 4.8 mm, $n_D^{20.5}$ 1.3098. The sodium carbonate solution was acidified with sulfuric acid and extracted with benzene. From the benzene solution 42 grams of perfluorocaprylic acid and 10 grams of ethyl perfluorooctanoate were obtained. In an additional run 65 grams (70.3%) of ethyl ester was prepared.

3. Preparation of Perfluorooctanoyl Aldehyde. (a) Into a 3-liter 3-necked flask fitted with stirrer, reflux condenser and addition funnel with pressure equalizer side tube were placed 310 grams (0.75 mole) perfluorooctanoic acid dissolved in two pounds of anhydrous ether. The apparatus was swept out with nitrogen while cooled in an ice-salt bath. Then a solution of 16.1 grams (0.42 mole) lithium aluminum hydride in one pound anhydrous ether was transferred under nitrogen to the addition funnel and added during 2 hrs. The reaction mixture was stirred for one hour after addition was complete. Then, 80 ml of 95% ethyl alcohol was added dropwise followed by addition of the reaction mixture to approximately 300 grams of ice and 60 ml of concentrated sulfuric acid in a 4000-ml beaker. The ether layer was removed and the aqueous layer was extracted with three 100-ml portions of ether. The combined ether solutions were dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the residue was added dropwise to a mixture of 32 grams of phosphorus pentoxide and 150 ml concentrated sulfuric acid in a flask equipped with an addition funnel, stirrer and distilling head connected to a downward condenser. Three frac-

tions were collected as follows: I - b.p. 110-130°C, 45 grams; II - b.p. 130-160°C, 102 grams; and III - b.p. 160-188°C, 122 grams. Only fraction I contained any liquid. Redistillation of fractions I and II through a short column (equipped with a simple head so that the solid material would not plug the still) did not accomplish any separation. All fractions were then added to 750 ml of absolute ethyl alcohol and 10 grams of hydrogen chloride were added. The flask was stoppered and left for six days. After refluxing for two hours, the alcohol was removed by reduced pressure and the residue subject to distillation through a 30" column filled with glass helices. The fractions obtained are as follows:

Initial (from Dry Ice trap and up to 84°/80 mm) two phases, 14.2 grams

I 84-86°C/80 mm, one phase, 10.9 grams

II 86°C/80 mm to 95°C/78 mm, two phases, 27.8 grams

III 95-102°C/78 mm, one phase, 34.1 grams

IV 60-64°C/4 mm, one phase, 12.0 grams

(b) A 3-liter, 3-necked flask was placed in a cold temperature bath and fitted with a Hershberg stirrer, an addition funnel with a pressure equalizing arm, and a condenser fitted with a drying tube. Into the flask were placed 428 grams (1.0 mole) methyl perfluorooctanoate and 1200 ml of anhydrous ether. While the solution was cooled to -70°C by adding Dry Ice and trichloroethane to the bath, a slow stream of nitrogen was passed through the apparatus, entering through the addition funnel. When the solution was cooled sufficiently, a lithium aluminum hydride solution was placed in the addition funnel and addition to the cold ester solution was started. The lithium aluminum hydride solution was prepared by adding 10 grams (0.26 mole) of the powdered hydride to 500-ml of anhydrous ether and stirring in a nitrogen atmosphere for 2 hours. The addition of the hydride solution to the ester was completed in 1/2 hour and the reaction mixture was stirred an additional hour before 30 ml of 95% ethyl alcohol were added. At this point a heavy viscous liquid in the bottom of the flask prevented stirring and thus the reaction mixture was hand-stirred until all of the alcohol had reacted. The flask was then removed from the cold temperature bath and allowed to warm to near room temperature. The contents were then poured over a mixture of approximately one kilogram of ice and 90 ml of concentrated sulfuric acid. The ether layer was removed and the aqueous layer extracted three times with 200-ml portions of ether. The combined ether solutions were dried over Drierite and the ether and alcohols removed by distillation at atmospheric pressure. The impure aldehydrol was then placed in a 1-liter three-necked flask fitted with stirrer, addition funnel and distilling head connected to a downward condenser. An equal volume of concentrated sulfuric acid was added slowly with heating and vigorous stirring. The perfluorooctonoyl aldehyde collected amounted to 309.5 grams (78% yield) b.p. 120-125°C. A subsequent run gave 142 grams (78.5%) of aldehyde, b.p. 121-124°C.

4. Preparation of Ethyl 3-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoate. Perfluorooctonoyl aldehyde was treated with ethyl bromoacetate and zinc powder by the procedure given previously (1) for the similar reaction of perfluorobutyraldehyde. A yield of 87 grams (26.5%) of 3-hydroxypentadecafluorodecanoate was obtained from 278 grams (0.7 mole) of perfluorocaprylaldehyde, 117 grams (0.7 mole) ethyl bromoacetate and 45.7 grams (0.7 mole) of zinc dust. The product boiled from 95-99°C (mostly 96-97°C) at approximately 2 mm; n_D^{20} 1.3420. A forerun, b.p. 40-95°C, consisted of 78 grams and the pot residue of 67 grams consisted of a dark red-orange brittle solid.

In a subsequent run 82 grams (39%) of product, b.p. 108°C/5 mm to 97°C/1.8 mm, n_D^{23} 1.3412 was obtained.

5. Preparation of Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-2-decenoate. Into a 500-ml flask were placed 150 grams (0.32 mole) of ethyl 3-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoate and 45 grams of phosphorous pentoxide. After sitting for one day at room temperature the contents were distilled to yield 95 grams (66%) of the α,β -unsaturated ester, b.p. 139.5°C/97 mm, n_D^{20} 1.3379.

6. Preparation of 3-Perfluoroheptylglutaric Acid. To 200 ml of absolute alcohol in a 1000-ml three-necked flask fitted with condenser, stirrer and addition funnel were added 5 grams (0.22 mole) of metallic sodium. Following complete reaction of the sodium, 35.2 grams (0.22 mole) of diethyl malonate were added slowly and the reaction mixture was cooled in an ice bath. During 1/2 hr. 90.4 grams (0.20 mole) of ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate was added. The reaction mixture was slowly brought up to reflux temperature and refluxed for 1 1/2 hrs. The mixture was then poured over approximately 1000 grams of ice and made slightly acidic with hydrochloric acid. The lower (organic) layer was removed and the upper (aqueous) layer was extracted with three 100-ml portions of ether. The ether extracts were combined with the organic layer and dried over magnesium sulfate. The ether was removed by distillation and the crude tricarboxylic ester was placed in a 500-ml three-necked flask fitted with a stirrer, a stopper and a Vigreux column connected to a condenser. One hundred milliliters of concentrated hydrochloric acid and 100-ml of water were added and vigorous stirring was started. The flask was heated so that the vapor at the top of the column was maintained at 75-80°C for 47 hrs. At the end of this time no more carbon dioxide was evolved and the flask contents were foaming badly. The flask contents were poured into an equal volume of ice water but still foamed badly when stirred. Filtration was attempted but the gel only plugged the filters. The aqueous suspension was then extracted with ether and the ether solution was dried. Upon evaporation of the ether a tan-colored solid remained. Part of the solid was recrystallized from toluene, m.p. 123-125°C, and part of it from an alcohol-water mixture, m.p. 125-126°C. Neutral equivalent calculated for 3-perfluorobutylglutaric acid: 250. Found: (run in triplicate) 249.5, 250, 250.5.

7. Preparation of 3-Perfluoroheptylglutaryl Chloride. In a 100-ml round-bottomed flask were placed 25.0 grams (0.05 mole) 3-perfluoroheptylglutaric acid and 20.8 grams (0.10 mole) phosphorous pentachloride. The mixture was hand flamed until the vigorous reaction subsided and was then refluxed for one and three-quarters hours. The phosphorous oxychloride was removed by distillation at atmospheric pressure and the residue was distilled under reduced pressure to yield 19.5 grams (73%) of 3-perfluoroheptylglutaryl chloride, b.p. 88°C/0.7 mm, n_D^{20} 1.3704.

Anal. calculated for $C_{12}H_5F_{15}Cl_2O_2$: C, 26.86; H, 0.93; Cl, 13.20.
Found: C, 26.57; H, 1.10; Cl, 13.44.

B. SULFUR-CONTAINING MONOMERS

1. Preparation of Diethyl 3,5-bis(Perfluoropropyl)-4-thiapimelate.

Hydrogen sulfide was treated with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate using piperidine and Triton B as catalyst as described previously (1). The thiapimelate isolated amounted to 313 grams which corresponds to a 66.6% yield. From the forerun of the distillation of the product, 22.5 grams of a substance boiling at 53°C at approximately 1.5 mm was obtained. The substance contains fluorine and sulfur and forms a precipitate with alcoholic silver nitrate solution. This compound, which may be ethyl 3-thiohydroxy-4,4,5,5,6,6,6-heptafluorohexanoate, has been submitted for ultimate analysis.

A subsequent preparation was conducted in the same manner, except that the temperature was allowed to rise 65 to 70°C during the reaction. From 142 grams (0.53 moles) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate were obtained 112 grams (74.1%) of the thiapimelate, b.p. 100-102°C/0.6 mm, n_D^{20} 1.3767.

2. Hydrolysis of Diethyl 3,5-bis(Perfluoropropyl)-4-thiapimelate. Into a 500-ml three-necked flask fitted with stopper, stirrer and air-cooled reflux condenser were placed 57.0 grams (0.1 mole) of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate and 450 grams of concentrated sulfuric acid. With rapid stirring, the flask was heated at 90-99°C for 2 1/2 hrs. in a water bath. The contents were then cooled slightly and poured over approximately 2000 grams of ice. A sticky mass separated out. The water solution was decanted from this mass and was extracted with ether. The ether solution was dried over magnesium sulfate, the ether removed on the hot plate and the residue taken up in hot toluene. Cooling yielded 6.9 grams of crystals, m.p. 106-114°C. To the sticky mass from which the water had been decanted were added 1000 ml of toluene. The resulting solution was boiled for a few minutes and then cooled. The crystals thus produced weighed 16.7 grams and melted at 147-156°C. Recrystallization three times from toluene resulted in crystals of 3,5-bis(perfluoropropyl)-4-thiapimelic acid, m.p. 156-157°C. Calculated for $C_{12}H_8F_{14}O_4S$: C, 28.02; H, 1.56. Found: C, 27.68; H, 1.85. Reduction in volume of the toluene mother liquor from the first crystallization of this acid produced a second crop of 18.0 grams of crystals, m.p. 108-112°C. Recrystallization from benzene gave crystals with m.p. 108-116°C. Further recrystallizations from benzene and toluene did not alter the melting range. Evaporation of the mother liquor from the second crop of crystals produced 5.2 grams of crystals, m.p. 107-115°C.

In two other preparations a total of 116.5 grams of acid, m.p. 155-157°C was obtained.

Molecular weight determinations by the Rast method were made on both isomers. Duplicate determinations on the lower melting isomer gave the results 415 and 418 while the single determination on the higher melting isomer gave the value of 420. Approximately 10% alcoholic solutions of both isomers showed no rotation when placed in a polarimeter.

(a) Attempted Hydrolysis of Substance with M.P. 108-116°C. Small samples of the lower melting substance from the hydrolysis of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate were added to four test tubes which contained, respectively, concentrated 80% and 50% sulfuric acid and concentrated hydrochloric acid. The test tubes were heated in a boiling water bath for one hour. Starting material was recovered in each case when the acidic solution was poured over ice and the solid recrystallized from benzene. In a similar manner, samples were run in concentrated sulfuric acid at 160°C for one half hour and at room temperature for 15 days. Again only unchanged starting material was recovered.

(b) Determination of Neutral Equivalents. The usual procedure was used with the sodium hydroxide solution having a normality of 0.0960. The results of the duplicate analyses are as follows:

<u>Sample</u>	<u>3,5-bis(perfluoropropyl)- 4-thiapimelic acid</u>	<u>Substance with m.p. 108-116°C</u>
I	263	264
II	263	259

3. Reaction of 3,5-bis(Perfluoropropyl)-4-thiapimelic Acid with Phosphorous Pentachloride. (2) Into a 25 ml flask were placed approximately 2.5 grams (0.005 mole) 3,5-bis(perfluoropropyl)-4-thiapimelic acid and 2.1 grams (0.01 mole) phosphorous pentachloride. After the initial vigorous reaction had subsided the mixture was refluxed for 1/2 hr. The phosphorous oxychloride was then removed by distillation at atmospheric pressure and the residue was distilled under reduced pressure to yield a few drops of yellow liquid, b.p. 100°C/1 mm. Elementary analysis showed the product contained fluorine, sulfur and chlorine. The following tests run on the compound show it to behave like the expected product, 3,5-bis(perfluoropropyl)-4-thiapimelyl chloride:

- Water - insoluble, no visible reaction at room temperature.
- Aqueous Silver Nitrate - no reaction at room temperature, slow reaction at 100°C to give silver chloride precipitate.
- Alcoholic Silver Nitrate - immediate precipitation of silver chloride.
- Aqueous ammonia - insoluble, slow reaction to give a red oil.
- Ammonia in ether - white precipitate formed immediately.
- Aniline - vigorous reaction to give a solid derivative.
- 5% aqueous sodium hydroxide - no reaction at room temperature, when warmed, dark red oil and red solution formed.

(b) Into a 500 ml round-bottomed flask were placed 51.4 grams (0.1 mole) 3,5-bis(perfluoropropyl)-4-thiapimelic acid (mixture of isomers). The flask was connected to a reflux condenser and with cooling in an ice bath a large excess (100 grams, 0.84 mole) of thionyl chloride was added through the condenser. The reaction mixture was hand flamed until it became homogeneous and then heated to reflux for 1 1/2 hrs. The excess thionyl chloride was removed by distillation at approximately 100 mm pressure. The residue was distilled through a 35 cm column and yielded 49.4 grams of very light yellow product, b.p. 90-97°C/1 mm. Redistillation produced 46.6 grams (84.5% yield) of colorless product, b.p. 86-88°C/0.7 to 0.8 mm, n_D^{20} 1.3892. A previous run using 0.015 mole of the thiapimelic acid gave a 72.6% yield of light yellow colored acid chloride.

4. Reactions of Diethyl 3,5-bis(Perfluoropropyl)-4-Thiapimelate with Hydrogen Peroxide. (a) In a 125 ml Erlenmeyer flask the following substances were mixed: 5.7 grams (0.01 mole) diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate, 30 ml glacial acetic acid and 15 ml of 30% hydrogen peroxide. The contents were stirred and allowed to stand at room temperature for four days. The mixture was then poured over 100 grams of ice and neutralized with sodium hydroxide. The aqueous solution was extracted with ether and the ether was removed to yield a very small amount of light yellow oil which could not be crystallized.

(b) Into a 200 ml round-bottomed flask was placed 11.4 grams (0.02 mole) diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate, 100 ml acetic acid and 35 ml 30% hydrogen peroxide solution. The solution was warmed and a vigorous reaction started. After the reaction subsided the mixture was refluxed for 2 hours. Isolation of the reaction product was the same as above and produced only a small amount of yellow-orange oil.

(c) Into a 200-ml round-bottomed flask were placed 11.4 grams (0.02 mole) diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate, 35 ml glacial acetic acid, 35 ml acetic anhydride and 30 ml of 30% hydrogen peroxide. The flask was connected to a reflux condenser and the two-phase mixture was warmed until a vigorous reaction started. It was then cooled in an ice bath until the reaction subsided. This was followed by refluxing for 2 hours.

Manganese dioxide was then carefully added to decompose the excess peroxide, the excess manganese dioxide removed by filtration and the solvents removed by distillation at 35 mm. The residual oil was placed on a fractionating column and a distillation attempted. The oil decomposed at 100-110°C/0.7 mm to give a black charcoal-like residue and a small amount of very hygroscopic white crystals on the thermometer and condenser. The oil from a similar oxidation was not distilled but was crystallized by scratching under a layer of petroleum ether. The crystals thus obtained are very hygroscopic and melt over the range 65-90°C (open tube). Elementary analysis on the acidic compound shows the presence of both fluorine and sulfur.

(d) In a 200-ml round-bottomed flask 7.9 grams (0.015 mole) 3,5-bis(perfluoropropyl)-4-thiapimelic acid, 30 ml acetic anhydride, 30 ml acetic acid and 25 ml 30% hydrogen peroxide were refluxed for two hours. A small amount of manganese dioxide was added to decompose the excess peroxide. Since there was no apparent decomposition the oxide was filtered off and the solvents were removed by distillation at reduced pressure. The residue was a dark brown oil which was taken up in ether and decolorized to some extent with charcoal. On removal of the ether an orange, very viscous oil remained.

5. Preparation of 3,5-bis(Perfluoropropyl)-4-thiaheptane-1,7-diol. A 2-liter flask was fitted with a Hershberg stirrer, a reflux condenser with a drying tube at the open end, and an addition funnel with a pressure-equalizing side arm. After the apparatus was swept out with a stream of dry nitrogen 600 ml of absolute ether and 10 grams of lithium aluminum hydride were placed in the flask. A solution of 114 grams (0.2 mole) of diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate in 200 ml of absolute ether was then added dropwise over a period of one and a half hours. After the addition was complete the reaction mixture was refluxed for 2 hrs. The mixture was then cooled in an ice bath and 200 ml of 95% ethanol were added dropwise. The resulting partially hydrolyzed reaction mixture was then poured into a beaker containing 600 grams of ice and 90 ml of concentrated sulfuric acid. The ether layer was removed and the acidic aqueous solution was extracted with three 100 ml portions of ether. The combined ether solutions were washed with 100 ml of saturated sodium bicarbonate solution and then dried over magnesium sulfate. Removal of the ether and distillation of the residue gave a yield of 83.7 grams (86.1%) of 3,5-bis(perfluoropropyl)-4-thiaheptane-1,7-diol, b.p. 109-112°C at 0.2 to 0.3 mm, n_D^{20} 1.3820. Calculated for $C_{12}H_{12}F_{14}O_2S$: C, 29.65; H, 2.27; F, 54.73. Found: C, 29.68; H, 2.43; F, 54.82.

C. OXYGEN-CONTAINING MONOMERS

1. Attempted Preparations of di(1-Carbethoxymethyl-2,2,3,3,4,4,4-heptafluorobutyl) Ether. (a) A few small pieces of sodium were added to 5 ml of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate and a yellow gel was soon obtained. Some of this yellow gel was added to a 100 ml round-bottomed flask which contained 18.8 grams (0.07 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 22.5 grams (0.075 mole) of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate and the mixture was refluxed for 3 1/2 hrs. The reaction mixture was then distilled at reduced pressure. The recovery of unsaturated ester was 16.3 grams (86.7%), b.p. 78-80°C/80 mm, and 19.3 grams (85.8%) of the β -hydroxy ester was recovered, b.p. 125-128°C/80 mm.

(b) Into a 100-ml flask were placed 13.4 grams (0.05 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and a small amount of sodium ethoxide. Some of the reaction mixture was spilled and not recovered but the remaining contents of the flask were refluxed for 13 hrs and then poured into 200 ml of cold water. The water layer was slightly acidic to litmus. The organic layer was taken up in 100 ml of ether and the water layer was extracted with two 50-ml portions of ether. The combined ether solutions were dried over magnesium sulfate, the ether removed by distillation at atmospheric pressure and the residue subjected to reduced pressure distillation. The recovery of the unsaturated ester was 7.6 grams, b.p. 88°C/79 mm, n_D^{22} 1.3525 to 1.3527.

(c) This experiment was identical with (b) except instead of sodium ethoxide 2.5 ml of B.T.A. hydroxide was used as catalyst. The unsaturated ester recovered amounted to 10.4 grams (78%), b.p. 82°C/82 mm to 87°C/79 mm, n_D^{20} 1.3440 to 1.3452. There were 9.3 grams (65%) of the β -hydroxy ester recovered, b.p. 133-136°C/78 mm.

(d) Into a 100-ml flask were placed 16.1 grams (0.06 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, 17.2 grams (0.06 mole) of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate, 5 ml of B.T.A. hydroxide and 3 ml of piperidine. The resulting solution was refluxed for 6 hrs and then distilled at reduced pressure. The fraction corresponding to the unsaturated ester, b.p. 72-80°C/77 mm, amounted to 6.2 grams (39% recovery). The fraction which boiled from 118-122°C/75 mm amounted to 20.4 grams which calculated as recovery of the β -hydroxyester is equivalent to 119% recovery. The fraction probably contains not only β -hydroxy ester but also the adduct of piperidine with the unsaturated ester.

(e) Into a 100-ml round-bottomed flask were placed 13.4 grams (0.05 mole) ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 14.3 grams (0.05 mole) ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate. A small amount (approximately 0.2 gram) of sodium hydride was then added in portions. The reaction was vigorous indicating that the reactants were not anhydrous or that they react with the hydride. The reaction mixture was then refluxed for 6 hrs. The resulting dark brown gel was taken up in ether and decolorized to some extent with charcoal. Removal of the ether left a tan-colored solid that was washed with benzene to remove any unreacted ester. Part of the solid material was recrystallized from an acetone-benzene mixture, m.p. 170-180°C.

(f) In a 200-ml three-necked flask fitted with stirrer, reflux condenser and a gas inlet tube were added 13.4 grams (0.05 mole) ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, 14.3 grams (0.05 mole) ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate and 50-ml of benzene (which had been dried over calcium hydride). The flask was swept out with dry nitrogen and approximately 1.2 grams (0.05 mole) sodium hydride was added. A vigorous reaction started and much foaming occurred. After refluxing for 4 hrs the mixture was let stand overnight. The addition of a few milliliters of absolute ethanol produced vast quantities of foam which came out the end of the condenser and were caught in a flask. The entire reaction mixture was then cautiously poured over ice. The alkaline solution was made slightly acidic (pH = 3) by the addition of sulfuric acid and was extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and the ether and benzene were then removed by distillation at atmospheric pressure. Distillation of the residue produced the following fractions:

<u>Fractions</u>	<u>B.P., °C/mm</u>	<u>n_D^{23}</u>	<u>Grams</u>
I	75-109/69	1.3441	1.7
II	109-110/69	1.3500	12.9
III	110-112/69 to 66	1.3468	3.2
IV	112/66 to 112/15	1.3486	3.1

The distillation was stopped since a solid material was plugging the still at this point. The solid material was collected and recrystallized from benzene to give white crystals, m.p. 75-6°C, which were soluble in dilute sodium hydroxide and produced carbon dioxide when added to a carbonate solution. The compound is believed to be 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic acid.

Fractions II, II and IV were combined and redistilled to give the following fractions:

<u>Fractions</u>	<u>B.P., °C/mm</u>	<u>n_D^{20}</u>	<u>Grams</u>
I	106-108/69	1.3510	0.9
II	108-108.5/69	1.3516	2.7
III	108.5-109/69	1.3514	4.6
IV	109-110/69	1.3510	3.6

Elementary analysis on fraction (II) and (III) show fluorine to be present. The substance, d_4^{19} 1.313, is insoluble in water, dilute base, dilute acid and 85% phosphoric acid but is soluble in cold, concentrated sulfuric acid. While it does not decolorize a solution of bromine in carbon tetrachloride it does decolorize cold, dilute, neutral potassium permanganate solution. The substance reacts with metallic sodium and gives negative tests with Tollen's reagent and 2,4-dinitrophenylhydrazine. Acidic hydrolysis of the substance produces a water insoluble acidic liquid.

2. Attempted Preparation of 3-Bromo-4,4,5,5,6,6,6-heptafluoro-hexanoic Acid. Into a 100-ml three-necked flask fitted with a stirrer, reflux condenser and a stopper were placed 7.0 grams of 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid and 50-ml of 48% aqueous hydrobromic acid. With vigorous stirring the reaction mixture was refluxed for 90 hrs and then poured over approximately 250 grams of ice. The solid material was taken up in ether and the aqueous solution extracted twice with 75-ml portions of ether. The combined ether solutions were dried over Drierite. Distillation of the residue after removal of ether gave 5.65 grams (81% recovery) of unchanged acid; b.p. 80-84°C/10 mm, m.p. 47-49°C.

D. NITROGEN-CONTAINING MONOMERS

1. Reaction of n-Butylamine with Ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. Into a 200-ml round-bottomed flask were placed 26.8 grams (0.1 mole) ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, 7.3 grams (0.1 mole) n-butylamine and 100 ml of benzene. The reaction mixture was then refluxed for 4 hrs and an additional 26.8 grams (0.1 mole) ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate were added. Refluxing was then continued for 18 hrs. The benzene and unreacted butylamine were then removed by distillation at atmospheric pressure and the residue was subjected to reduced pressure distillation. The recovery of unreacted α, β -unsaturated ester was 20.8 grams, b.p. 65°C/73 mm to 74°C/78 mm, n_D^{21} 1.3441 to 1.3442. The higher boiling material was collected in five fractions, b.p. 93°C/9 mm to 112°C/8.5 mm, n_D^{21} 1.3742 to 1.3749, and amounted to 21.1 grams. These fractions were combined and redistilled to yield 14.8 grams of colorless liquid, b.p. 97°C/7.5 mm, $n_D^{19.5}$ 1.3758. Elementary analysis by sodium fusion showed the presence of fluorine and nitrogen. The product showed no reaction with benzene sulfonyl chloride or acetyl chloride and did not give any color with acetaldehyde and sodium nitroprusside solutions.

Anal. calculated (for the tert-amine) $C_{20}H_{25}F_{11}O_2N$: C, 39.44; H, 4.14. Calculated (for the sec-amine) $C_{12}H_{18}F_7O_2N$: C, 42.22; H, 5.32. Found: C, 41.55; H, 4.62 [See experiment (c)].

Other preparations attempted are as follows:

(a) Into a 50-ml flask were placed 2.92 grams (0.04 mole) of n-butylamine, 24.1 grams (0.09 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 22 ml of absolute ethyl alcohol. The flask was stoppered and left at room temperature for six days. The contents were then distilled to yield 6.40 grams (26.8% recovery) of the α, β -unsaturated ester, b.p. 65°C/44 mm and 5.74 grams of a substance boiling at 87°C/3.5 mm, n_D^{20} 1.3709 to 1.3730. The product contained fluorine and nitrogen, did not dissolve in dilute hydrochloric acid and did not react with benzene-sulfonyl chloride.

(b) Into a 50-ml round-bottomed flask were placed 10.72 grams (0.04 mole) ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 1.46 grams (0.02 mole) n-butylamine. The mixture was refluxed for three hours and then sat at room temperature for 16 hrs. Distillation at reduced pressure produced 5.03 grams (47% recovery) of the α, β -unsaturated ester, b.p. 41°C/12 mm, to 33°C/6 mm, n_D^{20} 1.3439 to 1.3442 and 4.42 grams of a substance with boiling range 95-97°C/7 mm, n_D^{20} 1.3731.

(c) One-tenth of a mole (7.3 grams) n-butylamine with 53.6 grams (0.20 mole) of the α, β -unsaturated ester gave 26 grams (76.2% based on the butylamine used) of the secondary amine, b.p. 87-9°C at 4 mm, n_D^{19} 1.3759 and 26.5 grams of recovered α, β -unsaturated ester (99% recovery of the excess), b.p. 70-5°C at 70 to 71 mm, n_D^{20} 1.3448.

Anal. Calculated for $C_{12}H_{18}F_7NO_2$: C, 42.23; H, 5.28; F, 39.00; N, 4.11. Found: C, 42.23; H, 5.06; F, "not more than 40.95"; N, 4.63.

2. Reaction of Ethyl 3-Butylamino-4,4,5,5,6,6,6-heptafluorohexenoate with Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate. Into a 50-ml flask were placed 17 grams (0.05 mole) of ethyl 3-butylamino-4,4,5,5,6,6,6-heptafluorohexanoate and 14.1 grams (0.06 mole, 20% excess) ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. A boiling chip was added and the mixture heated to reflux. Refluxing was continued for 16 hrs during which time the temperature within the flask fell from 161°C to 137°C. The reaction mixture was then distilled to give a recovery of 11.6 grams (82.3%) of the α,β -unsaturated ester and 9.75 grams (57%) of the 3-butylamino ester. The residue was a black tar.

3. Reaction of Ammonia with Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate. A three-necked flask of 500-ml capacity was fitted with a sealed stirrer, a gas inlet tube and a reflux condenser. Into the flask were placed 26.8 grams (0.10 mole) ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 200-ml of absolute ether. The apparatus was swept out with dry nitrogen and a very small amount of sodium amide was added. The flask was cooled in an ice bath and with rapid stirring ammonia was admitted to the flask until the ether solution became saturated. The solution was then stirred until the ice melted and the bath and reaction flask came to room temperature. This amounted to approximately 3 hrs. The reaction was then brought to reflux temperature to expel the excess ammonia. The light orange-colored solution was poured over 150 grams of ice, the ether layer removed and dried over anhydrous magnesium sulfate. Upon removing the drying agent, the ether was removed by distillation at atmospheric pressure and the orange-colored residue was distilled under reduced pressure. The recovery of the α,β -unsaturated ester was 20.4 grams (76.2%). No other product was isolated.

E. PREPARATIONS REPEATED FOR ISOLATION OF ADEQUATE AMOUNTS OF INTERMEDIATES AND SAMPLES

1. Dehydration of Ethyl 3-Hydroxy-4,4,5,5,6,6,6-heptafluoro-2-hexanoate. Two moles, 572 grams, of the ester were dehydrated with phosphorous pentoxide by the procedure outlined previously (1). A yield of 451 grams (84.1%) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was obtained.
2. Preparation of Ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. Two moles, 572 grams, of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate were dehydrated with phosphorous pentoxide by the procedure outlined previously (1). A yield of 446.5 grams (83.3%) of the unsaturated ester was obtained.
3. Preparation of 4,4,5,5,6,6,6-Heptafluoro-2-hexenoic Acid. Into a 200-ml flask were placed 40 grams (0.15 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 135 ml of 10% aqueous sodium hydroxide. The mixture was refluxed for five hours, then cooled and extracted with ether to remove any unreacted ester. The basic aqueous solution was brought to a pH of approximately three with dilute sulfuric acid and extracted with three 75-ml portions of ether. The combined ether extracts were dried over Drierite and the ether removed on a steam bath. The residue solidified on cooling to give 20 grams (56%) of 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid, m.p. 47.5-49°C.
4. Preparation of 3-Perfluoropropylglutaryl Chloride. This preparation was carried out in the same manner as previously reported (1). Using 60.0 grams (0.20 mole) of 3-perfluoropropylglutaric acid, a yield of 57 grams (84.5%) of the acid chloride was obtained.
5. Preparation of Ethyl Perfluorobutyrate. A 3-liter 3-necked flask was fitted with a stirrer, addition funnel and a reflux condenser. Into the flask were placed 1070 grams (5.0 moles) perfluorobutyric acid and 345 grams (7.5 moles) absolute ethyl alcohol. With stirring and cooling 613 grams (6.25 moles) of concentrated sulfuric acid were added dropwise from the addition funnel. The resulting mixture was then refluxed overnight. Upon cooling the upper (organic) layer was separated and washed with 150-ml of water, followed by a washing with 150-ml of 5% sodium carbonate. The ester was then set aside to dry over Drierite.

Another five-mole batch was started and treated in the same manner except that the stirrer stopped during the night, allowing the reaction mixture to become super heated. When the stirring motor switch was cut off the stirrer moved enough that an undetermined amount of reaction product boiled out the end of the condenser.

The combined dried crude products from both batches were distilled to yield 1927 grams (80%) of ethyl perfluorobutyrate, b.p. 94-95°C.

6. Preparation of Perfluorobutyraldehyde. Ethyl perfluorobutyrate was reduced with lithium aluminum hydride using the same conditions as used previously (1). From 968 grams (4.0 moles) of the ester there were obtained 620 grams (78.3%) of perfluorobutyraldehyde, b.p. 28-32°C.

7. Attempted Condensation of Diethylsuccinate with Methyl Perfluoropropyl Ketone. The procedure used was identical with that used for the attempted condensation of perfluorobutyraldehyde with diethylsuccinate given previously (1). One-tenth of a mole (21.2 grams) of the ketone was used. The only product isolated was diethylsuccinate.

APPENDIX

Cumulative list of samples submitted to the Hooker Electrochemical Company.

1. $\text{C}_3\text{F}_7\text{CH}(\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$
2. $\text{C}_3\text{F}_7\text{CH}(\text{CH}_2\text{CH}_2\text{OH})_2$
3. $\text{C}_3\text{F}_7\text{CH}(\text{CH}_2\text{COCl})_2$
4. $\text{C}_7\text{F}_{15}\text{CH}(\text{CH}_2\text{COCl})_2$
5. $\text{S}[\text{CH}(\text{C}_3\text{F}_7)\text{CH}_2\text{COCl}]_2$
6. $\text{S}[\text{CH}(\text{C}_3\text{F}_7)\text{CH}_2\text{CH}_2\text{OH}]_2$

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