To the Graduate Council:

I am submitting herewith a dissertation written by Myron Lee Cherry entitled "Aerosol Direct Fluorination: Syntheses of Perfluoroethers and Perfluoroesters." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

James L. Adcock, Major Professor

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AEROSOL DIRECT FLUORINATION: SYNTHESES OF PERFLUOROETHERS AND PERFLUOROESTERS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Myron Lee Cherry

March 1986

DEDICATION

To Ann for all the years of patience and support. "For her price is far above rubies."

ACKNOWLEDGMENTS

I am deeply indebted to my research director, Dr. James L. Adcock, without whose guidance and patience this dissertation would not have been possible. I also wish to thank Maxine Martin for typing the dissertation.

The financial assistance from 3M Corporation and the Department of Chemistry in the form of a teaching stipend is gratefully acknowledged.

I also wish to thank Dr. Richard M. Pagni for his support and his assistance in the writing of this dissertation.

ABSTRACT

A series of perfluoroesters and perfluoroethers has been synthesized utilizing the aerosol direct fluorination technique. In all cases the starting material was the hydrocarbon analog. The following perfluorinated esters and ethers were synthesized: F-1,2-dimethoxyethane, F-bis-2-methoxyethyl ether, F-triethylene glycol dimethyl ether, F-tetraethylene glycol dimethyl ether, F-bornyl methyl ether, F-methyl 2-methoxypropanoate, F-methyl 2,2-dimethylpropanoate, F-methyl 2-methylpropanoate, F-methyl propanoate, F-ethyl propanoate, F-isopropyl propanoate and F-tert-butyl propanoate. In the case of the fluorination of methyl 2-methoxypropanoate the major product was F-2-methoxypropanoyl fluoride, which is a result of ester cleavage. However ester cleavage was not a major problem in the other perfluoro ester syntheses. The purpose of the study of the perfluorinated ester synthesis was to determine what effects different groups attached to the ester linkage would have on cleavage. A one-step synthesis by aerosol direct fluorination producing monofluorobenzene from benzene was carried out. To determine the limitations of aerosol direct fluorination, a compound containing highly hindered hydrogens, 2,4-dimethylpentane, was fluorinated and this resulted in a mixture of mono- and dihydryl isomers where the remaining hydrogens are those that are highly hindered. This technique was also shown to produce a perfluorinated epoxide, F-cyclohexene oxide, from its hydrocarbon analog. All compounds

were characterized by infrared spectroscopy, electron-impact and chemical ionization mass spectrometry and both ^{19}F and ^{1}H nuclear magnetic resonance spectroscopy.

While effluent concentrations of the desired products were usually high, the throughput yields based on hydrocarbon injected into the reactor system were often low. A series of experiments was conducted to determine where losses in the system occur. A series of modifications and improvements were made to enhance throughput yields.

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CHAPTER I

INTRODUCTION

A. Fluorination Methods

The high exothermicity of fluorination reactions has somewhat retarded the development of this branch of chemistry over the years. In order to fluorinate successfully a hydrocarbon such factors as rates of reaction, safe operation and minimal fragmentation of the hydrocarbon must all be dealt with. Fluorine is the most electronegative and reactive of all elements. In fact to date fluorine is known to react with every element except helium, neon, and argon. Moissan[1] reported the first fluorocarbon compound, carbon tetrafluoride, just four years after the discovery of fluorine. However, the discovery by Lebeau and Damiens[2,3] many years later is generally accepted as the first isolation of carbon tetrafluoride because Moissan's data could not be reproduced.

Fluorocarbon chemistry began to progress in the 1930's. Swarts[4] in 1930, for example, produced hexafluoroethane from the electrolysis of aqueous trifluoroacetic acid. In 1933 tetrafluoroethylene was discovered as a by-product of the decomposition products of carbon tetrafluoride in an electric arc.[5] Even though in the next few years other methods were found to synthesize CF_4, C_2F_6 and C_2F_4[6-8] the first fifty years after the discovery of fluorine were generally uneventful. However, in 1937 the discovery of

hexafluoropropane, decafluorobutane, decafluorocyclopentane, dodecafluorocyclohexane and tetradecafluorocycloheptane[9,10] slowly opened up the field of perfluorination syntheses.

The gaseous diffusion process for separating uranium isotopes which was developed in the early 1940's required coolants, lubricants, buffer gases and sealants that were inert to uranium hexafluoride. This directed research efforts towards the synthesis of new perfluorinated compounds that possessed these characteristics. Since that time many techniques for synthesizing perfluorinated compounds have been attempted. The greatest problem encountered in these reactions has always been reaction control because the exothermicity is so high. Until the recent advent of modern flow technology, practical direct fluorinations were not feasible. In fact many perfluorinated compounds are still produced today from procedures based on the Swarts' reaction. This process involves a nucleophilic displacement of another halogen by fluoride. To enhance the halogen removal, a metal fluoride, behaving as a Lewis acid, is used, with antimony fluoride being the most extensively used fluoride in the process.

$$\text{C-Cl} + MF_x \longrightarrow \text{C}^+[MF_x Cl]^- \xrightarrow[(HF)]{F} \text{C-F}$$

Until recently the reaction of elemental fluorine with reagents has not been easily controlled. Direct fluorination of hydrocarbons probably proceeds by the following radical chain mechanism.

	ΔH (kcal/mole)	ΔG(kcal/mole)
$F_2 \longrightarrow 2F\cdot$	+37	+30
$F_2 + RH \longrightarrow R\cdot + HF + F\cdot$	+4	-6
$RH + F\cdot \longrightarrow R\cdot + HF$	-34	-36
$R\cdot + F_2 \longrightarrow RF + F\cdot$	-68	-68
$R\cdot + F\cdot \longrightarrow RF$	-107	-98

Bockemuler[11] bubbled a mixture of nitrogen and fluorine through a cold solution of an organic compound in an inert solvent and successfully achieved mono- and difluorination but not perfluorination. The first significant advance in perfluorination synthesis utilizing elemental fluorine was by Bigelow and co-workers.[12] In their process fluorine was diluted in a stream of gaseous nitrogen and then mixed in a steel tube that contained the hydrocarbon and a finely divided metal, usually silver plated copper turnings.[13-16] The mechanism of this reaction is still under question and most believe that the metal turnings serve more for heat dissipation than for catalysis. This reaction worked well with simple hydrocarbons but as the complexity of the hydrocarbon skeleton increased, the degree of fragmentation also increased.

Later Bigelow and co-workers,[17-19] modified their system so that concentric tubes were used to introduce the separate gas streams. This allowed for the quick removal of product from the reaction volume and thus reduced fragmentation. This procedure is often referred to as "Jet Fluorination." Although ethanes and materials

containing up to four carbons could be successfully perfluorinated, the method essentially failed for higher molecular weight substrates.

Fowler and co-workers,[20,21] in 1941 developed a technique whereby the vapor of an aliphatic or an aromatic hydrocarbon was passed over a bed of cobalt trifluoride. Generally this method gave better yields than the Bigelow procedure. However, aromatic hydrocarbons ordinarily lost their aromaticity due to the saturation of the rings with fluorine. Since cobalt difluoride was produced in this reaction, a stream of elemental fluorine was passed over the cobalt difluoride bed to regenerate cobalt trifluoride. Therefore a hydrocarbon stream and a gaseous fluorine stream were allowed to pass alternately over the bed to make the process continuous. This method allowed better control of the reaction since the fluorination of the hydrocarbon with cobalt trifluoride is less exothermic than with elemental fluorine and thus it gave less fragmentation of the carbon skeleton.

Probably the most widely used method of fluorinating organic compounds on the industrial scale is the electrochemical fluorination method.[22-26] By dissolving an organic solute in anhydrous hydrogen fluoride and applying a small electrical potential to the solution, hydrogen is evolved at the cathode and fluorination of the host organic compound takes place at the nickel anode. Low voltages are maintained to avoid producing elemental fluorine. While this method still gives some fragmentation of the carbon skeleton, functional groups are retained to a greater extent than in previous methods.

However, the greatest limitations of electrochemical fluorination are the insolubility of many organic species in liquid hydrogen fluoride and the low yields of the desired product.

The most significant advances in the understanding of the direct fluorination reaction occurred as a result of developments begun by Margrave and continued by Lagow.[27-29] Essentially a finely ground (<100 mesh) hydrocarbon solid is placed in a nickel boat and a premixed volume of fluorine and helium is allowed to pass over the solid. Later this process was further developed into the low temperature gradient ("LTG") method.[30-32] The low temperature reactor was based on the fact that, as a compound became more highly fluorinated, its volatility increased, allowing a more rapid degree of diffusion of the compound through the reaction zone. This cryogenic reactor was designed to have a temperature gradient along the reactor length. Lagow came to the realization that, in order to synthesize perfluorinated compounds from the hydrocarbon analog, the kinetics of the reaction must be controlled so that fragmentation of the carbon skeleton would be retarded. Reaction-limiting initial conditions, maximizing the amount of exposed surface area of the hydrocarbon to elemental fluorine, and the low temperature gradient enhanced fluorination conditions and yet kept the carbon skeleton intact.

Many interesting and unique syntheses of compounds have resulted from the "LTG" technique. Some types of substrates subjected to this technique have been polyethers,[33-35] polyesters,[36]

carboranes,[37,38] metal alkyls,[39-41] aromatics,[42,43] alkanes,[44-47] and ethers and esters.[48-50] Although high yields based on distribution of crude product have been reported, this procedure is slow and is a "batch" process which is not easily scaled up for industrial application. With the exception of speed, the "LTG" method does possess all of the basic attributes necessary for perfluorination of hydrocarbons. This technique does not, however, perfluorinate compounds successfully which have low solid-state volatility, and no crystallinity. Furthermore, the procedure does not expose a large surface area of the substrate to elemental fluorine.

B. Aerosol Direct Fluorination

Aerosol direct fluorination is a radically new approach to the control of reactions involving elemental fluorine and organic substrates containing hydrogens.[51,52] This technique produces perfluorinated compounds directly from an organic precursor. An important advantage of this technique over prior ones is that it is a flow process. This allows the reaction to be run on a large scale for industrial application and uses fluorine efficiently which lowers cost. Yields of the desired product obtained with this system have been reported to be as high as 98 percent.

The success of aerosol direct fluorination depends on many theoretical considerations and empirical rationalizations. Many conditions present in this system contribute to a high yield of desired product and will be discussed in detail.

The fluorination of molecules takes place on a sodium fluoride substrate where the host hydrocarbon molecule is maintained in a crystalline state. This has several advantages which enhance the fluorination reaction. The reaction of elemental fluorine and substrate is highly exothermic which usually leads to fragmentation of the carbon skeleton. However, because the host molecule is adsorbed on the surface of the sodium fluoride particulate, the sodium fluoride can act as a heat sink; this allows the release of energy to occur in the lattice of the NaF rather than totally in the carbon skeleton. Once a hydrocarbon radical is formed, its position is maintained on the sodium fluoride substrate; this retardation of mobility prevents dimerization of two hydrocarbon radicals. The sodium fluoride particulate also serves as a shield which can protect one hemisphere of the molecule from collision with gaseous fluorine molecules. The inorganic solid also serves as a Lewis base which can react with the by-product, hydrogen fluoride, and thus (from a chemical equilibrium viewpoint) aid in driving the reaction to completion. Other possible advantages in the use of sodium fluoride include a catalytic effect involving the fluoride ion and the ability of the fluoride ion to react with carbocations to produce uncharged products.

The aerosol direct fluorination permits all the host substrate molecules to be evenly exposed to gaseous fluorine. Prior methods either utilized a solution in which the substrate is dissolved or a finely ground solid powder of the substrate; thus the procedure relied on the fluorine diffusing to all substrate molecules.

Also in this method all substrate molecules are equally exposed to gaseous fluorine at all stages during the reaction process. Initially as a molecule is exposed to gaseous fluorine, the reaction conditions maintained keep the concentration of fluorine low; at this stage the temperature is also kept low in order to retard fragmentation. However, as the reaction proceeds and the degree of fluorination increases, the activation energy required for further fluorination also increases. Hence the molecules that did not sufficiently undergo collisions to achieve only partial fluorination in the reaction-limiting stage will not likely withstand more vigorous conditions in the final stages of the reaction. Therefore, it is important to expose all substrate molecules equally to gaseous fluorine at all stages in the reaction process.

As the organic molecule is introduced into the reaction chamber, the initial concentration of fluorine is kept at a minimum. This has several benefits: (a) less heat per unit time is generated because there is a reduction in the overall rate of reaction; (b) the probability of multiple simultaneous reactions on a lone molecule is substantially reduced; and (c) the probability of forming adjacent radicals, which then might combine, is also drastically reduced.

Additionally at the onset of the reaction, low temperatures are maintained. Low temperature lowers the overall kinetic energy of a molecule which in turn reduces the number of effective reaction collisions. The low temperature at this time also helps in

dissipating heat that is generated from the exothermic fluorine reactions.

The conditions described above are not sufficient to permit perfluorination of the molecule. As the number of hydrogens that are replaced with fluorine increase, the probability of an effective collision between a fluorine molecule and the remaining hydrogens decrease. Also as fluorine atoms are substituted onto the molecule, the new fluorine-carbon bond is longer than the previous carbon-hydrogen bond. This, in conjunction with fluorine's electronegativity, renders the residual hydrogen more sterically hindered and electron deficient, thus reducing its susceptibility to further fluorine attack. Additionally unless the quantity of fluorine is renewed, there is less fluorine available for collisions with the hydrocarbon molecule. Therefore, after the reaction-limiting conditions, the molecule must encounter a region where reaction-forcing conditions are prevalent.

A high concentration of fluorine is required in the reaction-forcing stage of the reaction because the number of molecular collisions required to overcome the reaction rate problems stated above must increase. Higher temperatures in this region are also necessary for the same reasons. Therefore, as the reaction progresses, the reactant molecules are allowed to traverse a temperature gradient.

Once a fluorinated molecule exits the reactor volume, experience has shown that it is generally no more than 60 percent fluorinated.[51] When neopentane was used as a representative

hydrocarbon, increasing the fluorine concentration in the final stages of the reactor volume by 40 times the stoichiometric value, resulted in a distribution of fluorinated products. The average degree of fluorination was 80 percent, but only 9 percent perfluorination was achieved. Therefore, a photochemical finishing stage is used to enhance perfluorination. The use of the photochemical stage has resulted in the reduction of the quantity of fluorine necessary for perfluorination to a minimum value of 1.2 times the stoichiometric amount. In reactions run without the use of the photochemical finishing cell, a Gaussian distribution of partially fluorinated products results. However, when the same conditions were utilized in a subsequent reaction, except that the photochemical finishing cell was also used, the Gaussian distribution did not simply shift to higher degrees of fluorination but the overall Gaussian curve decreased in size while the degree of perfluorination simultaneously increased. It appears that the exposure of the partially fluorinated compound and fluorine to ultraviolet light increases the molecule's vibrational temperature, making the molecule more likely to achieve perfluorination. The aerosol direct fluorination apparatus is discussed in detail in the experimental section.

Several types of fluorination reactions, many yielding perfluorinated products in high yields, have been carried out in the aerosol reactor. The aerosol direct fluorination technique has been shown, for example, to produce perfluorinated species from alkanes,[51] ethers,[51-54] ketals,[53] orthoesters,[55] acid chlorides and fluorides,[56]

ketones,[53,57,58] and alkyl chlorides.[56,59,60] The potential utility of aerosol direct fluorination is vast but thus far only minimal results have been obtained compared to the reactor's potential.

C. Syntheses of Perfluoroethers

Previous literature methods for the synthesis of perfluorinated ethers are numerous and unique. Most include reagents that are already highly fluorinated and the reactions are multi-step and occur in low yields. Perfluorinated ethers have received considerable attention because of their potential use as polymerizable monomers and their high degree of thermal and chemical stability.[61] For instance, perfluorinated polyethers have been found to be suitable replacements for pump oil used in electron beam instruments.[62] Previously polymer films would deposit on instrument components, and cause problems. Also perfluorinated polyether fluids with molecular weights of about 6500 have suitable lubricating properties for use in rotary pumps. More volatile perfluoropolyethers ($\sim$3000 Daltons) are suitable for use in vapor-stream pumps.[63] Factors that give perfluorinated polyethers their unusual physical properties include strong covalent bonds (C-O,C-F,C-C), the absence of hydrogen, and a neutral Lewis acid/base character. Typical properties of this class of compounds are: (1) good viscostatic lubricity, (2) low internal cohesion energy, (3) excellent dielectric properties, (4) high thermal stability, (5) low pour point temperature, (6) chemical inertness, (7) high compatibility with metals in the presence of air and at high

temperatures, (8) high compatibility with resins, plastomers, and rubbers, and (9) high resistance to radiations and accelerated particles (electrons, neutrons, protons).[64] Also these compounds exhibit exceptionally good chemical stability and are fuel resistant and therefore are attractive for use in the presence of fuels.[65] The literature contains a number of schemes to synthesize partially fluorinated ethers. However, since the purpose of this research is to produce completely fluorinated ethers, the history of the synthesis of partially fluorinated ethers will be omitted.

One of the most useful techniques for perfluoroether synthesis is the electrochemical process developed by Simons.[66] This is a commercial method for the preparation of perfluorinated compounds directly from organic compounds and hydrogen fluoride. The fluorination cell, which is constructed from a metal that is resistant to hydrogen fluoride, contains two packs of electrodes. After the cell is charged with hydrogen fluoride and the organic reactant, a low potential of five to six volts is allowed to pass through the cell. Degradation of the carbon skeleton can be a problem with this procedure; therefore, the exact reaction conditions in any one run determine the products. A number of perfluorinated organic materials can be synthesized by this method including perfluoroethers.

Henne and Richter,[67] in 1952, synthesized perfluorinated cyclic ethers by reducing perfluorinated dibasic esters to diols which were then cyclized to ethers. However, this left a dihydryl compound which was chlorinated to remove the hydrogen and then the chlorine removed

with fluoride to give the perfluorinated cyclic ether. During the halogen exchange, any ring larger than six-membered was found to open. Thompson,[68] in 1967, obtained perfluorinated methyl ethyl ether while attempting to synthesize some perfluorinated trioxides by direct fluorination of salts of trifluoroacetic acid. In 1966, Prager[69] obtained a perfluorinated epoxide by the direct fluorination of 1-hydroxy-3-trichloroacetoxypropane. However, this product had previously been reported in a patent issued to Kauck and Simons in 1952.[70] One very interesting and unique way of obtaining perfluorinated ethers was the process utilizing the previously described LTG technique.[71-74] Direct fluorination of polyethers yielded a large variety of compounds formed in low relative yields. The polyether precursor was first finely ground (<120 mesh), and then direct fluorination was carried out. As the reaction progressed, the reaction mixture volume was allowed to reach a temperature of 110 °C, which promoted fragmentation. In none of these experiments was a product obtained that was the perfluorinated analog of the starting material. When an ethylene oxide polymer was used as the organic sample, the crude product contained mostly perfluoromono-, di-, tri-, tetra- and pentaglyme (ethylene glycol dimethyl ether) and perfluoromono-, di-, tri-, tetra- and pentaethylene glycol methyl ether. A backbone of three or more carbons linked together in a perfluorinated product can be obtained if the same analogous repeating unit known as Tabata's polymer[75] is used as a starting material. Also polypropylene oxide gave several perfluorinated fragments but when

polymethylene oxide was used, the reaction failed. A number of perfluoroethers and a variety of synthetic schemes are given in Table 1.

A method for preparing perfluorinated cyclic diethers was devised by Bagnall and co-workers,[76] in 1977. 2,2-Bis(trifluoromethyl)-1,3-dioxolane was fluorinated to the perfluorinated analog. In 1967, Varetti and Aymonino,[77] in an attempt to find new photochemical routes to perfluorinated species, irradiated perfluoromethyl peroxide in the presence of carbon monoxide in hopes of obtaining perfluoromethyl carbonate. Even though some of this product was obtained, perfluoromethyl ether was the main product. Toy and Stringham[78] found that the fluoroxy addition of perfluoro-tert-butyl hypofluorite to hexafluoropropene gives high yields of perfluoro-n-propyl-perfluoro-tert-butyl ether. Also these researchers found that the same reaction occurred with cyclic olefins in the presence of ultraviolet light.[79]

Since a goal of this research project is to synthesize perfluorinated polymers from their hydrocarbon analogs, other known synthetic methods for perfluorinated polyethers will be mentioned briefly. Perfluoropolyethers with the difluoromethylene oxide (CF_2O) repeating unit have been reported in two patents by Sianesi and co-workers.[80,81] The reaction involves an ozone sensitized reaction of oxygen with difluorocarbene to give a perfluorinated acid fluoride polymer containing the perfluorinated methylene oxide group ($CF_3O(CF_2O)_nCF_2COF$). Also the same researchers synthesized a

TABLE 1

SYNTHESES OF PERFLUOROETHERS

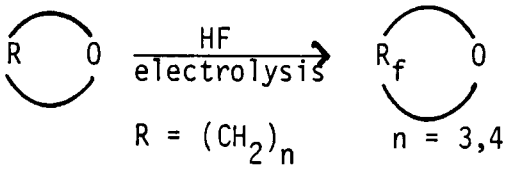
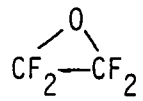
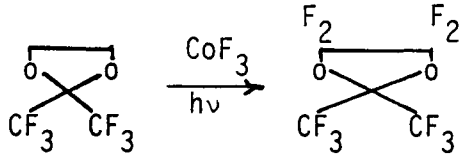
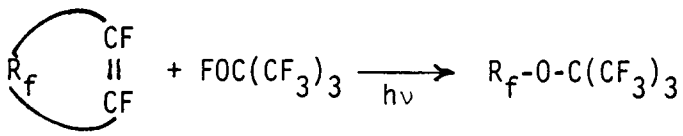
Synthesis	Ref.
$R\text{-}O\text{-}R' \xrightarrow[\text{electrolysis}]{HF} R_f\text{-}O\text{-}R'_f$ R or R' = C_3H_7, C_6H_{13}, $CH_3\text{-}O\text{-}C_2H_4$, C_2H_5, $C_2H_5\text{-}O\text{-}C_2H_4\text{-}O\text{-}C_2H_5$	66
 R = $(CH_2)_n$ n = 3,4	66
$R_fO_2\,CCF_2\,(CF_2)_nCF_2\,CO_2\,R_f \xrightarrow[Cl_2,\ SbF_3Cl_2]{\text{reduction}} (\overline{CF_2)_3\text{-}O\text{-}(CF_2}})_2$	67
$CF_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \xrightarrow{F_2} CF_3\text{-}O\text{-}CF_2\text{-}CF_3$	68
$HO(CH_2)_3\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CCl_3 \xrightarrow{F_2}$ 	69
$(\text{-}CH_2\text{-}CH_2\text{-}O)_n \xrightarrow{\text{La Mar}} (\text{-}CF_2\text{-}CF_2\text{-}O)_{1\text{-}5}$	71,74
$(\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CF_3)_2\text{-})_n \xrightarrow{\text{La Mar}}$ $(CF_3)_2\,CFO\,CF_2\,CF_2\,CF\,(CF_3)_2$, $(CF_3)_2\,CFO\,CF_2\,CF_2\,CF_2CF\,(CF_3)_2$, $(CF_3)_2\,CFO\,CF_2\,CF_2\,C(CF_3)_2O\,CF_2\,CF_3$, $(CF_3)_2\,CFO\,CF_2\,CF_2C(CF_3)_2O\,CF_2\,CF_2CF(CF_3)_2$ $(CF_3)_2\,CO\,CF_2\,CF_2\,C(CF_3)_2O\,CF_2CF_2\,CF(CF_3)_2$	72

TABLE 1 (Continued)

Syntheses	Ref.
$(-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-O)_n \xrightarrow{LTG}$ $CF_3\text{-}CF_2\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_3$ $CF_3\text{-}O\text{-}CF(CF_3)\text{-}CF_2O\text{-}CF_2CF_3$ $CF_3\text{-}CF_2\text{-}CF_2O\text{-}CF(CF_3)\text{-}CF_2O\text{-}CF_2\text{-}CF_3$ $CF_3\ CF_2\ CF_2O\ [CF\ (CF_3)\ CF_2O]_2\ CF_2CF_3$	73
	76
$CF_3\text{-}O\text{-}O\text{-}CF_3 \xrightarrow{CO} CF_3\text{-}CF_2\text{-}O\text{-}CF_3$	77
$CF_3\ CF = CF_2 + FOC(CF_3)_3 \longrightarrow CF_3\text{-}CF_2\text{-}CF_2\text{-}O\text{-}C(CF_3)_3$	78
 $R_f = C_5F_9,\ C_6F_{10}$	79
$C_7F_{15}\ COCl + (CF_3)_3\ COH \xrightarrow{DMF} C_7F_{15}\ CO_2C(CF_3)_3$	80

perfluoropolyether fluid ($CF_3(C_3F_6O)_m$-$(CF_2)_n$-CF_3), which was a product of the photooxidation reaction of hexafluoropropene.[82,83]

D. Syntheses of Perfluoroesters

The development of synthetic techniques for perfluorinated esters has lagged behind that of perfluoroethers. Perfluorinated esters are useful for the preparation of high temperature solvent resistant elastomers and they also show promise as specialty rubbers which exhibit good thermal stability and oil resistance.[84] DePasquale[85] reported that the reaction between a perfluorinated acid chloride and perfluorinated alcohol in the presence of dimethylforamide yielded the respective perfluorinated ester. In an attempt to synthesize perfluorinated amides from the $HNF_2 \cdot KF$ adduct and perfluoroacyl fluorides, Couch and co-workers[86] found that, at lower reaction temperatures (-105°C), the major products were perfluorinated esters. DeMarco and co-workers[87] reported that perfluorinated acid fluorides, in the presence of alkali metal fluorides, will dimerize to give the respective perfluorinated ester. However, yields are very low unless KF-HNF_2 is present. The dissociation pressure of HNF_2-KF at the reaction temperature is negligible.[88] Therefore, the addition of HNF_2 cannot be assumed only to be forming "activated" KF by complexation and dissociation. To ascertain the validity of this, KF was "activated" by the formation and decomposition of the hexafluoroacetone adduct, but no ester resulted in the subsequent reaction. Also $(CF_3)_2NOH$, which undergoes complexation and

substitution in an analogous manner to HNF_2, was used; but again no ester was formed. Furthermore, vacuum dried KF-HF, which was present after HNF_2 reacted with the acid fluoride, was used also without success. One interesting aspect of this work was that, even though perfluorinated esters are generally stable, they rapidly decompose in the presence of alkali metal fluorides at -78°C and above.

Johnson and Tittle[89] prepared perfluorinated esters by two different methods. In the first method, an acid chloride was treated with the potassium salt of perfluoro-tert-butyl alcohol to yield potassium chloride and the perfluorinated ester. The second method involved the reaction of phosgene or thionyl chloride with a perfluoro acid salt and a tertiary alcohol salt in a polar solvent. These reactions were carried out at low temperature and in the absence of water. When heating perfluoro-3-ethyl-3-pentylpropanoate ($(C_2F_5)_3COCOC_2F_5$) at 250°C for 12 hours, no decomposition was seen. However, in the presence of a fluoride ion in catalytic amounts, considerable decomposition occurred yielding perfluorinated 3-pentanone and an acid fluoride (C_2F_5COF). Chang and co-workers[90] found that pentafluorophenyllithium, when treated with trifluoroacetyl chloride, yielded a perfluorinated ester. Walker and Desmarteau[91] developed a method for synthesizing perfluorotert-butyl esters from acid fluorides and potassium perfluorotert-butoxide. These reactions produced high yields of products and were run without the use of solvents. Majid and Shreeve[92] were able to react a perfluorinated tertiary alcohol in the presence of a metal fluoride with

perfluorinated acetyl fluoride to give the corresponding perfluorinated ester. All of these reactions described above are summarized in Table 2.

TABLE 2

SYNTHESES OF PERFLUOROESTERS

Synthesis	Ref.
$CF_3\ C(O)F + MF \longrightarrow CF_3CF_2O_2CC(CF_2)_3$ M = K or Cs	86
$(CF_3)_2\ CO + R_fC(O)F \xrightarrow{MF} R_f\ CO_2\ CF(CF_3)_2$ M = K or Cs, R_f = F, CF_2, C_2F_5, C_3F_7	86
$R_fCOCl + KOC(C_2F_5)_3 \longrightarrow R_fCO\text{-}O\text{-}C(C_2F_5)_3$	89
$R_F\text{-}CO\text{-}OK + KOC(C_2F_5)_3 + SOCl_2 \longrightarrow R_f\text{-}CO\text{-}O\text{-}C(C_2F_5)_3$	
$C_6F_5Li + CF_3CO\ Cl \longrightarrow (C_6F_5)_2\ C(CF_3)\ O\ CO\ CF_3$	90
$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}F + KOC(CF_3)_3 \longrightarrow RC(O)O(CF_3)_3$ R = F, CF_3, CH_3, CF_3O, $(CF_3)_3CO$	91
$R_f - \overset{R'_f}{\underset{R''_f}{\overset{\|}{C}}} - OH \xrightarrow[CsF]{\overset{O}{\overset{\|}{CF_3CF}}} R_f - \overset{R'_f}{\underset{R''_f}{\overset{\|}{C}}} - O - \overset{O}{\overset{\|}{C}} - CF_3$	92

CHAPTER II

EXPERIMENTAL PROCEDURES

A. Brief Description of the Aerosol Fluorinator

A brief description of the aerosol fluorinator will be given here and a detailed discussion of the various components will be given in the discussion section. The compounds reported herein were synthesized using two different reactors. The basic aerosol fluorination systems are schematically shown in Figures 1 and 2, and are called the horizontal and vertical reactors.

A nickel boat filled with anhydrous sodium fluoride is placed in an oven with a main carrier helium flow channeled over the boat. The sodium fluoride is sublimed and carried by the helium stream from the oven to a heat exchanger that is maintained at -196°C. This creates a cold condensation site for the organic substrate once the chilled sodium fluoride particles enter the reactor. Simultaneously the substrate is delivered from a pump to a flash evaporator which is usually maintained ten to twenty degrees above the boiling point of the organic substrate. Therefore the material is vaporized immediately once it enters the flash evaporator. A small secondary helium stream ($\sim$50 cc/min) enters from the bottom of the flash evaporator and carries the vaporized sample out of the flash evaporator volume where it meets a primary helium stream ($\sim$450 cc/min) which in turn carries the sample into the reactor. The main carrier sodium fluoride/helium stream and

Figure 1. Horizontal Aerosol Fluorination System.

A heated bed of sodium fluoride (A) sublimes NaF particles into the helium carrier gas; the NaF particles are then chilled by passing through the liquid nitrogen cooled heat exchanger (B). The chilled NaF particles are mixed within the aerosol generator (C) with a hydrocarbon stream from the flash evaporator (D) and the aerosol passed through the reactor modules (E,F,G) where it is mixed with elemental fluorine. Following the last module is an endcap (H) and a water-cooled photochemical stage (I). Hydrogen fluoride is removed in the scrubber (J) and the products collected in the liquid nitrogen cooled product trap (K). Excess fluorine is removed by passing the gas stream through an alumina trap.

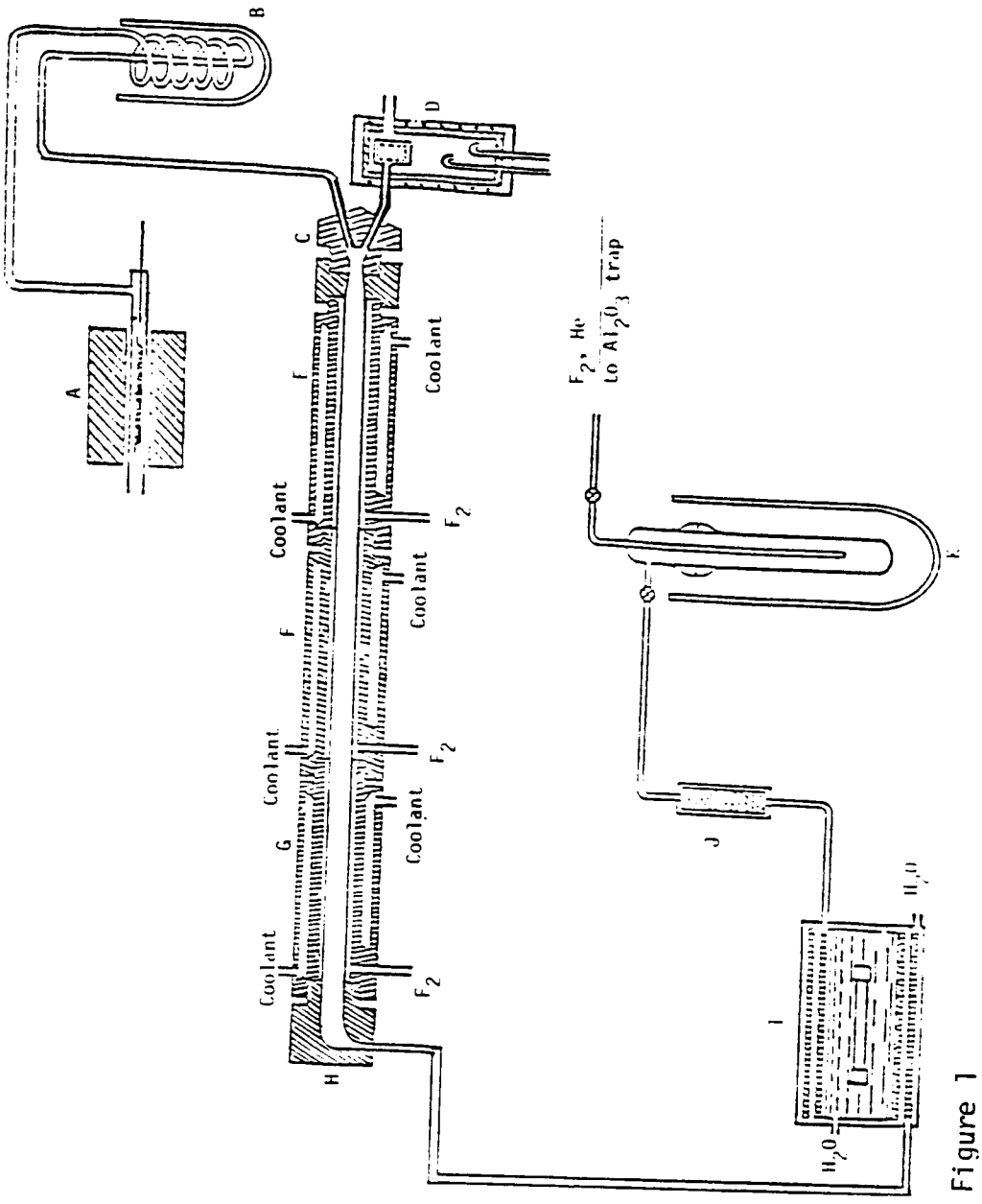


Figure 1

Figure 2. Vertical Aerosol Fluorination System.

A heated bed of sodium fluoride (A) sublimes NaF particles into the helium carrier gas; the NaF particles are then chilled by passing through liquid nitrogen cooled heat exchanger (B). The chilled NaF particles are mixed within the aerosol generator (C) with a hydrocarbon stream from the flash evaporator (D) and the aerosol passed through the reactor modules (E,F) where it is mixed with elemental fluorine. Following the last module is an endcap (G) and a water-cooled photochemical stage (H). Hydrogen fluoride is removed in the scrubber (I) and the products collected in the liquid nitrogen cooled product trap (J). Excess fluorine is removed by passing the gas stream through an alumina trap.

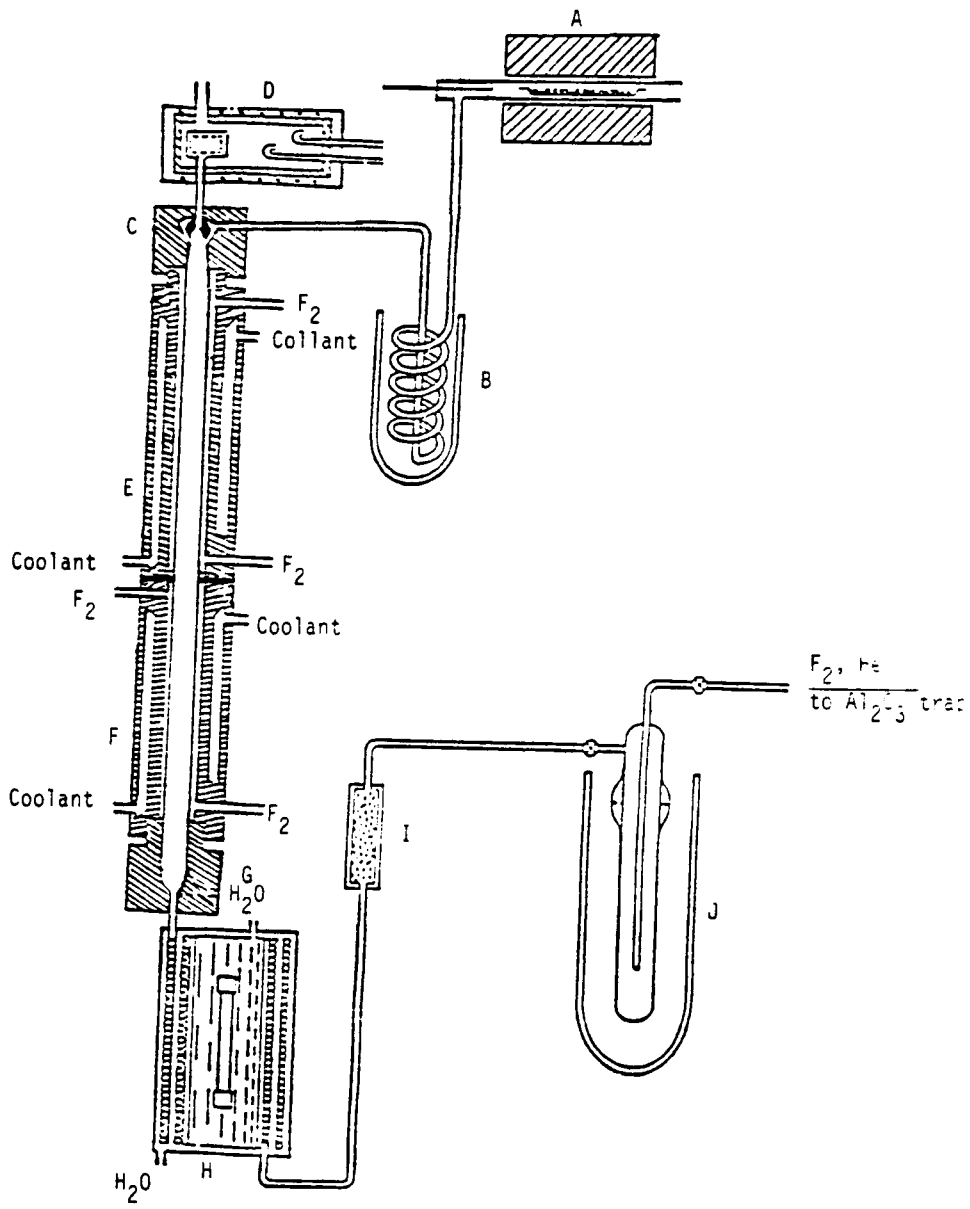

A
D
C
F_2
Coolant
B
E
Coolant
F_2
F_2
Coolant
F
Coolant
F_2
G
H_2O
I
J
F_2, He
to Al_2O_3 trap
H_2O
H

Figure 2

the substrate/helium stream enter the aerosol generator where they intersect at a focal point that is centered in the reactor's cross-section. The gaseous substrate condenses onto the chilled sodium fluoride particles which is then carried through the reactor volume. As the aerosol is carried through the reactor, it passes through three modular zones. Each module has the ability to control independently and simultaneously the fluorine concentration, helium flow and temperature. A premixed volume of fluorine and helium is injected into each module where it diffuses slowly through a porous monel filter element and into the reaction stream where fluorination takes place.

After the partially fluorinated species exit the reactor, they enter a photochemical finishing stage where perfluorination takes place. The product stream then passes through a chamber containing sodium fluoride pellets where the hydrogen fluoride by-product is scrubbed out, and then through a glass product trap, cooled to -196°C, where the products are collected. The unreacted fluorine and helium then pass through an alumina trap where the fluorine is scrubbed out. A complete description of the aerosol fluorinator and discussion of problems and modifications/improvements of the device are discussed in detail later.

B. Materials

All materials were used as received unless otherwise noted.

Alumina - Alcoa Products.

Benzene - Fisher Scientific.

Bis-2-methoxyethyl ether - Aldrich Chemical.

Bornyl methyl ether - supplied by Department of Chemistry, University of North Carolina.

Cyclohexene oxide - Aldrich Chemical.

Deuterochloroform - Aldrich Chemical (99.8 atom.%).

Diethyl ether (anhydrous) - Fisher Scientific.

1,1-Dimethylethanol - Fisher Scientific.

2,4-Dimethylpentane - Wiley Organics.

Ethyl Propanoate - Eastman Kodak.

Ethylene glycol dimethyl ether - Aldrich Chemical.

Fluorine (gas) - Air Products.

Freon 11 - Allied Chemical (Genetron 11).

Helium (gas) - Air Products.

Hydrochloric acid - Fisher Scientific.

Isobutyl chloride - Fisher Scientific.

Magnesium sulfate - Fisher Scientific.

Methanol - Fisher Scientific.

Methyl 2-methoxypropanoate - Minnesota Mining and Manufacturing.

Methyl Propanoate - Eastman Kodak.

Molecular sieves - Fisher Scientific.

Nitrogen (gas) - Burdett Oxygen Company.

2-Propanol - Fisher Scientific.

Propionyl chloride - Aldrich Chemical.

Pyridine - Fisher Scientific.

Sodium bicarbonate - Fisher Scientific.

Sodium fluoride - Fisher Scientific.

Sodium fluoride pellets - Harshaw Chemical.

Tetraethylene glycol dimethyl ether - Aldrich Chemical.

Tetramethylsilane - Mallinckrodt.

Triethylene glycol dimethyl ether - Aldrich Chemical.

Trimethylacetyl chloride - Aldrich Chemical.

C. Characteristics of Compounds

The crude product is transferred from the glass trap to an all glass vacuum line where it is fractionated with various slush baths. Vapor phase infrared spectra are taken of the various fractions to determine the possible location of desired product. Mixtures are then further separated by gas chromatography. Characterization of compounds is done by chemical ionization and electron impact mass spectrometry, vapor phase infrared spectroscopy, and ^{1}H and ^{19}F nuclear magnetic resonance (nmr) spectroscopy. Effluent efficiency and percent yields were determined by gas chromatography assay (cut and weigh method) and by nmr integration.

Vacuum Line. An all glass vacuum line was utilized for transfers, fractionations, and storage. Different areas within the vacuum line were separated by Teflon stopcocks (Kontes Scientific Glassware). A Welch Duo-seal vacuum pump (model 1402B) gave pressures down to 3 microns of mercury (Hastings vacuum gauge, model VT-5B).

Gas Chromatography. A Bendix model 2300 gas chromatograph (subambient, multicontroller) was utilized for gas chromatographic separations. Columns used were a 7 meter x 3/8 inch 13 percent Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh acid-washed Chromosorb P conditioned at 225°C (12 hours) and a 4 meter x 3/8 inch 10 percent SE-52 phenylmethyl silicone rubber stationary phase on acid-washed Chromosorb P conditioned at 250°C (12 hours). The carrier gas was helium at a flow rate of 50 cc/min. Injections were made using Precision Sampling Corporation "Pressure-Lok" syringes. Retention times were measured relative to time of injection.

Infrared Spectra. Infrared spectra were taken on gaseous samples in a 10 centimeter gas cell with potassium chloride windows. Spectra were taken on a Perkin Elmer model 1330 infrared spectrometer.

Mass Spectra. Mass spectra were recorded on a Hewlett-Packard GC/MS (5710A GC, 5980 MS, 5934A computer). Both electron impact (70 eV) and chemical ionization (CH_4 plasma) were recorded.

Nuclear Magnetic Resonance Spectra. A JEOL FX90Q (omniprobe) nmr spectrometer was used to take both ^{1}H and ^{19}F nmr spectra. Internal standards were tetramethylsilane (TMS) for proton spectra, and 0.2 percent $CHCl_3$ in $CDCl_3$ with 1 percent $CFCl_3$ for ^{19}F spectra.

D. Preparation of Starting Materials

Methyl 2,2-dimethylpropanoate was synthesized by the following method. Approximately 0.42 moles of methanol (∿2 equivalents) were placed in 1.1 moles of pyridine (∿5 equivalents), which serves both

as solvent and as a means of removing the hydrochloric acid by-product. To this solution was added drop-wise 0.21 moles of trimethylacetyl chloride (∿1 equivalent) at 0°C. After the reaction was complete, aqueous hydrochloric acid was added to neutralize the excess pyridine. The resulting solution was washed with diethyl ether and dried with anhydrous magnesium sulfate. After filtration, the diethyl ether was removed by distillation. The ^1H nmr spectrum of the residue confirmed that it contained the desired product in almost 100 percent purity.

$$(CH_3)_3\text{-}C\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + HO\text{-}CH_3 \xrightarrow{\text{pyridine}} (CH_3)_3\text{-}C\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_3 + HCl$$

Methyl 2-methylpropanoate was prepared in a similar manner to that of methyl 2,2-dimethylpropanoate. The quantities of methanol, pyridine, and isobutyryl chloride that were used were 0.42 moles (∿2 equivalents), 1.1 moles (∿5 equivalents) and 0.21 moles (∿1 equivalent), respectively. The product was almost 100 percent pure by ^1H nmr spectroscopy.

Isopropyl propanoate was also synthesized in a fashion similar to that of methyl 2,2-dimethylpropanoate. Propionyl chloride (0.46 mole, ∿1 equivalent) was reacted with 2-propanol (0.91 mole, ∿2 equivalents) in pyridine (1.5 mole, ∿3.3 equivalents). ^1H nmr spectroscopy again showed the product to be approximately 100 percent pure.

$$(CH_3)_2\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + HO\text{-}CH_3 \xrightarrow{\text{pyridine}} (CH_3)_2\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_3 + HCl$$

tert-Butyl propanoate was synthesized in a manner similar to that of methyl 2,2-dimethylpropanoate. However, because the propionyl chloride tended to react slowly, the reaction solution was refluxed for several hours to drive the reaction to completion. Additionally, after the excess pyridine was neutralized with aqueous hydrochloric acid, the solution was washed with ether and then sodium bicarbonate was added to remove any propanoic acid that might have formed from propionyl chloride hydrolysis. Quantities of reagents used in the reaction were 0.46 moles (∿1 equivalent) of propionyl chloride, 0.92 moles (∿2 equivalents) of 1,1-dimethyl ethanol, and 2.3 moles (∿5 equivalents) of pyridine. As before, ^{1}H nmr analysis of the product revealed it to be the desired product in approximately 100 percent purity.

$$CH_3\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + HO\text{-}C(CH_3)_3 \xrightarrow{\text{pyridine}} (CH_3\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}C(CH_3)_3 + HCl$$

E. Aerosol Fluorination of Ethylene Glycol Dimethyl Ether

The aerosol fluorination of ethylene glycol dimethyl ether (glyme) was carried out on the horizontal reactor. An injection of 1.73 grams of starting material (19.3 mmole) gave 2.29 grams of crude product. Details of the fluorination parameters are given in Table A1, Appendix A. Approximately 45 minutes after the termination of the reaction, the crude product was transferred to the vacuum line and fractionated into -45°C, -78°C, -131°C and -196°C cold traps. The -196°C trap collected 0.40 grams of fragmented material, while

the -45°C trap contained nothing. An infrared analysis was run on the -78°C and -131°C fractions and gave very similar results. Therefore these two fractions, weighing a total of 1.89 grams, were combined. This combined fraction was then subjected to gas chromatography on the SE-52 column. The inlet and detector temperatures were 90°C and 180°C, respectively. The column temperature was set at 25°C and kept there for five seconds after injection and then increased by 2°C per minute until no more peaks were seen on the recorder. The first peak, with retention time of 2.7 minutes, comprised 98 percent of the injected sample. The second peak, with a retention time of 3.3 minutes, comprised 1.1 percent of the sample, while the final peak, with a retention time of 3.9 minutes, comprised only 0.5 percent of the sample. The small second and third peaks may be mono- and dihydryl analogues, respectively, of the perfluorinated product. Because F-ethylene glycol dimethyl ether had previously been synthesized,[32] only an infrared analysis of the first peak was carried out for characterization purposes. The infrared spectrum matched exactly to that of F-ethylene glycol dimethyl ether reported in the literature. Details are given in Table B1, Appendix B. Based on overall throughput the yield of the desired product was 36 percent.

F. Aerosol Fluorination of Bis-2-Methoxyethyl Ether

The direct aerosol fluorination of 1.87 grams of (14.0 mmole) of bis-2-methoxyethyl ether (diglyme) was carried out on the horizontal reactor, giving 1.60 grams of crude product after a four hour run.

Details of the fluorination parameters are given in Table A2, Appendix A. After the run was stopped, a very small amount of helium was allowed to flow through the system overnight while the crude product trap was maintained at liquid nitrogen temperature. The next morning the contents of the crude product trap were transferred to the vacuum line and fractionated through the -45°C, -78°C, -131°C and -196°C cold traps. Only 0.24 grams of fragmented material was collected in the -196°C trap and no material was collected in the -131°C trap. Most of the product collected in the -78°C trap and only a small amount in the -45°C trap. An infrared assay of the -45°C and -78°C fractions gave similar results. Therefore the two fractions were combined and gave a total weight of 1.36 grams. The combined fractions were gas chromatographed on the SE-52 column with an injection temperature of 90°C and a detector temperature of 180°C. The initial column temperature was 25°C and was maintained there only five seconds after which it was increased at 2°C per minute until all peaks had exited the column. Six peaks were detected. The first four peaks with retention times between 2.5 and 3.4 minutes were combined and accounted for only 5.9 percent of injected material; these were thought to be perfluorinated fragmented material. The sixth peak, having a retention time of 4.2 minutes, accounted for only 5.3 percent of the total injection area. The fifth and major peak, which comprised 89 percent of the product mixture, had a retention time of 3.5 minutes. This sample, whose infrared spectrum matched exactly to the previously reported literature spectrum[32] of F-bis-2-methoxyethyl

ether, was formed in 22 percent yield. Characterization details are given in Table B2, Appendix B.

G. Aerosol Fluorination of Triethylene Glycol Dimethyl Ether

The aerosol fluorination of triethylene glycol dimethyl ether (triglyme) was carried out many times with the horizontal reactor. Typical examples of fluorination parameters are given in Table A3, Appendix A. The first four hour reaction, beginning with 1.97 grams of this material, gave 1.29 grams of crude material. After a small helium flow had passed through the reactor volume overnight while maintaining the crude product trap at liquid nitrogen temperature, the material was transferred to the vacuum line and fractionated through -78°C, -131°C and -196°C traps. The -196°C trap contained 0.13 grams of fragmented perfluorinated material while the -78°C trap held 1.16 grams of material; nothing collected in the -131°C trap. The -78°C fraction was separated by gas chromatography on the SE-52 column; the gc had an inlet temperature of 90°C and a detector temperature of 180°C. To achieve good separation only a three microliter injection size was used. The initial column temperature was maintained at 25°C for five seconds and then increased at 2°C per minute until no further peaks were observed. Six compounds came off the column. The first three very small peak areas overlapped; their retention times occurred between 2.5 and 3.5 minutes and they had combined peak area of 4.0 percent. The fifth and sixth peaks, which had retention times of 5.7 and 7.0 minutes, were also small and overlapped, and accounted

for 4.7 percent of the total peak area. The fourth and major peak had a retention time of 4.2 minutes and comprised 91 percent of the total product peak area. Infrared spectroscopy, ^{19}F nmr spectroscopy and both chemical ionization and electron impact mass spectrometry were carried out on this compound which proved to be F-triethylene glycol dimethyl ether. The infrared spectrum agreed with previous literature spectra.[33,34] Details of the characterization of this product are given in Table B3, Appendix B. There were, however, some discrepancies in the ^{19}F nmr spectrum of this compound and literature values. These discrepancies are discussed in a subsequent section. This experiment gave an overall throughput yield of 20 percent. However, in a subsequent run increasing the reaction temperature increased the overall throughput yield to 30 percent but its peak area relative to the other products dropped to 81 percent.

H. Aerosol Fluorination of Tetraethylene Glycol Dimethyl Ether

The aerosol fluorination of tetraethylene glycol dimethyl ether (tetraglyme) was carried out with the horizontal reactor. Even though the vertical reactor should improve yields, modifications to the photochemical cell, which is discussed later, are necessary before the problem with substrates containing ten or more carbons is likely to be solved. A 2.02 gram (9.10 mmole) sample of tetraethylene glycol dimethyl ether produced 1.02 grams of crude product after a four hour run. The aerosol fluorination parameters are given in Table A4, Appendix A. Forty-five minutes after the reaction was terminated,

the crude product was transferred to the vacuum line and fractionated into -45°C, -78°C, -131°C and -196°C traps. Only 0.13 grams of perfluorinated fragments collected in the -196°C trap; the remaining material was found in the -45°C trap. After an infrared spectrum was taken, the -45°C fraction was chromatographed on the SE-52 column; the gc had an inlet temperature of 120°C and a detector temperature of 180°C. To enhance separation of peaks an injection size of four microliters was used. The column temperature was kept at 25°C for five seconds and then increased at 2°C per minute until no further peaks were observed. Eight peaks appeared in the chromatograph. The first five peaks accounted for 5.5 percent of the crude product and had retention times between 2.5 and 4.3 minutes. The seventh and eighth peaks together comprised only 1.1 percent of the total peak area and had retention times of 6.6 to 7.3 minutes. The sixth peak, which made up 93.4 percent of the peak area, had a retention time of 5.5 minutes. This was the only compound formed in sufficient amounts for characterization, whose details are given in Table B4, Appendix B. The infrared spectrum agreed with literature values[33,34] for perfluorinated tetraethylene glycol dimethyl ether. A discrepancy in our and the literature's ^{19}F nmr values is discussed later. Both electron impact and chemical ionization mass spectrometry gave similar results to the other synthesized perfluorinated glyme ethers. The yield of product, based on ether input, was only 15 percent because losses in the reactor increase with the less volatile,

higher molecular weight compounds. However, the effluent concentration was 94 percent.

I. Aerosol Fluorination of Bornyl Methyl Ether

Parameters are given in Table A5, Appendix A, for the aerosol fluorination of bornyl methyl ether whose preparation has been previously outlined.[93] This fluorination was also carried out with the horizontal reactor. Although this is not the highest molecular weight compound perfluorinated to date, it does contain more carbons (11) than any other compound run to date. A 2.6 gram (3.9 mmole) sample yielded 0.94 grams of crude product after a four hour run. The perfluorinated product had extremely low vapor pressure and was difficult to transfer on the vacuum line. One hour after completion of the reaction, the crude product was transferred to the vacuum line and fractionated through the -45°C, -78°C, -131°C and -196°C cold traps. Just a trace of material collected in the -196°C trap and the remaining material was found in the -45°C trap. An infrared spectrum of the major fraction showed no C-H stretch, but did show the strong C-F stretch in the usual 1000 to 1400 cm^{-1} region. The fraction was then chromatographed on the QF-1 column; the gc had an inlet temperature of 130°C. The initial temperature of the column was maintained at 70°C for eight minutes and then was increased by 2°C per minute until the chromatography was complete. Seven peaks were seen in the chromatogram. The first five peaks were small and had retention times from 11.4 to 18.1 minutes and had a total combined

area of 9 percent. The sixth and seventh peaks were formed in a five to one ratio which is the same as for the endo- and exo- isomers in the starting material. The retention times for these latter peaks were 18.9 and 20.9 minutes, respectively. Total peak area comprised 91 percent for peaks six and seven. The throughput yield of the perfluorinated ether was 11 percent. Details of the chemical characterization of this compound are given in Table B5, Appendix B.

J. Aerosol Fluorination of Cyclohexene Oxide

The aerosol fluorination of cyclohexene oxide was carried out with the vertical reactor. An eight hour run with 3.9 grams (40 mmoles) of starting material yielded 4.6 grams of crude product. Parameter details are given in Table A6, Appendix A.

The crude product was transferred to the vacuum line forty-five minutes after the reaction was terminated and fractionated through the -45°C, -78°C, -131°C and -196°C cold traps. A trace amount of material was found in the -45°C trap and the remainder of the product in the -78°C trap. These fractions were combined and analyzed by gas chromatography on a QF-1 column; the gc had an injection temperature of 90°C and a detector temperature of 180°C. The column temperature was kept at 30°C for one minute and then increased by 2°C per minute until 60°C was reached and maintained at this value until no further peaks were observed. Several peaks with retention times ranging from ten to twenty-three minutes were observed. However, only three of the peaks were major. The first of these, with a retention time of

fifteen minutes, made up 21 percent of the total peak area. The perfluorinated product corresponded to the second of the three major peaks; it had a retention time of 19.5 minutes and accounted for 65 percent of the total peak area. The last of the three major peaks, with a retention time of 21.5 minutes, made up 6 percent of the total peak area. The remaining peaks accounted for 8 percent of the total peak area. The major product gave a chemical ionization mass spectrum with a peak at m/e of 279 (C_6HOF_{10}) at 40 percent intensity. Details of the characterization of this compound are given in Table B6, Appendix B. Based on epoxide input, the yield of F-cyclohexene oxide was 27 percent.

K. Aerosol Fluorination of Methyl 2,2-Dimethylpropanoate

The aerosol fluorination of 2.23 grams of methyl 2,2-dimethylpropanoate was carried out on the vertical reactor and yielded 5.5 grams of product after a five hour reaction. Details of the fluorination parameters are given in Table A7, Appendix A. After allowing helium to pass through the system for approximately 45 minutes after termination of the reaction, the crude product was transferred to the vacuum line and fractionated into the -45°C, -78°C, -131°C, and -196°C cold traps. Just a trace of material collected in the -45°C and the -196°C traps, and none in the -131°C trap. The remainder (5.2 grams) collected in the -78°C cold trap. An infrared spectrum of the -78°C fraction revealed a strong carbonyl stretch

at 1830 cm^{-1} which is typical of perfluorinated esters. The carbonyl stretch for acid fluorides at 1875 cm^{-1} was not seen.

Since perfluorinated esters have the propensity to decompose on gc columns, the distribution of the perfluorinated ester and other minor products was determined by nmr spectroscopy on the combined fractions. Results from this as well as other characterization details are given in Table B7, Appendix B. The yield of the perfluorinated ester based on ester input was 86 percent; its effluent concentration was 100 percent.

L. Aerosol Fluorination of Methyl 2-Methylpropanoate

The aerosol fluorination of 2.67 grams (26.2 mmole) of methyl 2-methylpropanoate was carried out on the vertical reactor and gave 5.5 grams of crude product after a six hour run. Details of the fluorination are given in Table A8, Appendix A.

Forty-five minutes after the reaction was over, the crude product was transferred to the vacuum line and fractionated into the -45°C, -78°C, -131°C and -196°C cold traps. The combined weight of the material in the -131°C and the -196°C traps was 0.75 grams. Infrared analysis of these two fractions showed the material to be mostly silicon fluoride (1020 cm^{-1}). The remaining product appeared to be evenly distributed between the -45°C and the -78°C traps. An infrared analysis of these fractions showed a strong carbonyl stretch (1830 cm^{-1}) indicating that they contained perfluorinated ester. Again, to ascertain the distribution of products the -45°C and the

-78°C fractions were combined (4.75 grams) and analyzed by ^{19}F nmr. The product was F-methyl 2-methylpropanoate. Details of this as well as other characterization details are given in Table B8, Appendix B. The yield of F-methyl 2-methylpropanoate was 48 percent based on ester input.

M. Aerosol Fluorination of Methyl Propanoate

The aerosol fluorination of 2.75 grams of methyl propanoate (Eastman, used as received) was carried out on the vertical reactor and produced 5.7 grams of product after a six hour run. Parameters for this aerosol fluorination are given in Table A9, Appendix A. Forty-five minutes after the reaction was completed, the crude product was transferred to the vacuum line and fractionated into the -45°C, -78°C, -131°C and -196°C cold traps. Just a trace of material was found in the -196°C trap and the remainder evenly divided between the other three traps. Infrared spectra showed that the -45°C fraction contained mostly perfluorinated ester (carbonyl stretch at 1830 cm^{-1}) and a trace of perfluorinated acid fluoride (carbonyl stretch at 1875 cm^{-1}). The infrared analysis showed the -78°C fraction to contain more perfluorinated acid fluoride than did the -45°C fraction, but the majority of the fraction was still perfluorinated ester. Infrared analysis revealed the -131°C fraction to contain some perfluorinated ester, but mostly perfluorinated acid fluoride. These three fractions were combined (5.5 grams) and analyzed by ^{19}F nmr. Characterization details are given in

Table B9, Appendix B. The yield of the perfluorinated ester was 43 percent based on hydrocarbon input; the effluent purity was 55 percent.

N. Aerosol Fluorination of Ethyl Propanoate

The aerosol fluorination of 2.68 grams of ethyl propanoate (Eastman, used as received) was carried out on the vertical reactor and, after a six hour run, produced 4.6 grams of crude product. Details of the aerosol fluorination are given in Table A10, Appendix A. Forty-five minutes after the reaction was completed, the crude product was transferred to the vacuum line and then fractionated through the -45°C, -78°C, -131°C and -196°C cold traps. A trace of SiF_4 (IR, 1020 cm^{-1}) collected in the -196°C trap. Most of the remaining product collected in the -78°C trap. A trace of product was also found in the -131°C trap and no material was found in the -45°C trap. Infrared analysis of the material in the -78°C and the -131°C traps showed the presence of perfluorinated ester (1830 cm^{-1}) in the -78°C trap and perfluorinated ester and a trace of perfluorinated acid fluoride (1875 cm^{-1}) in the -131°C trap. These two fractions were combined (3.5 grams) and analyzed by ^{19}F nmr. Characterization details are given in Table B10, Appendix B. Perfluorinated ester was formed in a 23 percent yield. The effluent concentration of the perfluorinated ester was 75 percent.

O. Aerosol Fluorination of Isopropyl Propanoate

The aerosol fluorination of 2.60 grams of isopropyl propanoate was carried out on the vertical reactor and produced 5.3 grams of crude product after a six hour run. Details of this aerosol fluorination are given in Table A11, Appendix A.

Forty-five minutes after reaction termination, the crude product was transferred to the vacuum line and fractionated into the -45°C, -78°C, -131°C and -196°C cold traps. A trace of material collected in the -196°C trap, and the remainder stopped in the -78°C trap. An infrared spectrum of the -78°C fraction showed the contents to be mostly perfluorinated ester (1830 cm^{-1}), with some perfluorinated acid fluoride (1875 cm^{-1}). The distribution of ester and acid fluoride was determined by ^{19}F nmr. The yield of the perfluorinated ester, based on ester input, was 65 percent and the effluent concentration was 92 percent. Details of the characterization are given in Table B11, Appendix B.

Another experiment on this compound was run using the same parameters as in the previous case except that lithium fluoride was used in place of sodium fluoride. Details of this fluorination are discussed in a subsequent chapter.

P. Aerosol Fluorination of tert-Butyl Propanoate

The aerosol fluorination of tert-butyl propanoate was carried out on the vertical reactor and gave 2.7 grams of crude product after

a six hour reaction. Details of the fluorination parameters are given in Table A12, Appendix A.

The crude product was transferred to the vacuum line approximately forty-five minutes after reaction termination and fractionated into the -45°C, -78°C, -131°C and -196°C cold traps. A trace of material was seen visually in the -196°C trap and none in the -131°C trap. The remainder of the product collected in the first two traps, with about twice as much material in the -78°C trap as in the -45°C trap. Infrared spectra of these fractions revealed perfluorinated ester (1830 cm^{-1}) in the -45°C fraction and perfluorinated ester and a trace of perfluorinated acid fluoride (1875 cm^{-1}) in the -78°C fraction. These two fractions were combined and analyzed by ^{19}F nmr to ascertain the relative yields of the two products. Based on ester input, the yield of perfluorinated ester was 33 percent; the effluent concentration was 94 percent. The ^{19}F nmr data and other characterization details are given in Table B12, Appendix B.

Q. Aerosol Fluorination of Methyl 2-Methoxypropanoate

The parameters for the aerosol fluorination of methyl 2-methoxypropanoate are given in Table A13, Appendix A. A seven hour run on 3.5 grams (30 mmoles) of starting material with the vertical reactor produced 4.8 grams of crude product. About one hour after reaction termination, the crude product, which was slightly yellow, was transferred to the vacuum line and fractionated through the -45°C, -78°C, -131°C and -196°C cold traps. The -45°C and -196°C traps

collected nothing. Infrared analysis of the material in the other two traps showed the characteristic absorption of an acid fluoride at 1875 cm^{-1}. In addition, analysis of the -131°C fraction revealed the characteristic carbonyl absorption of the fluorinated ester (1830 cm^{-1}). Both of the available gc columns enhance decomposition of acid fluorides. Therefore additional purification of products was accomplished by a series of re-fractionations on the vacuum line; a -95°C cold trap was introduced to help separate constituents. After every re-fractionation, infrared spectra were taken to determine the degree of purity of each fraction. Infrared spectroscopy, ^{19}F nmr, and mass spectrometry confirmed the identities of the perfluorinated ester and the perfluorinated acid fluoride in the traps. Throughput yield of F-methyl 2-methoxypropanoate was estimated at 55 percent. Characterization details are given in Tables B13 and B14, Appendix B.

R. Aerosol Fluorination of 2,4-Dimethylpentane

The aerosol fluorination parameters of 2,4-dimethylpentane on the horizontal reactor are given in Table A14, Appendix A. The fluorination of 1.34 grams (13.4 mmole) of hydrocarbon produced 3.0 grams of crude product after a four hour run. After allowing a small flow of helium to pass through the system overnight, the contents of the crude product trap were transferred to the vacuum line and fractionated into the -45°C, -78°C, -131°C and -196°C cold traps. The -196°C trap contained 0.1 grams of perfluorinated fragments and the -131°C trap contained nothing. The remaining material was found

primarily in the -78°C trap, with a small amount collecting in the -45°C trap. Infrared spectra of these two fractions were similar. Therefore they were combined to give 2.9 grams of material. This sample was further separated by gas chromatography utilizing the QF-1 column; the gc had an inlet temperature of 70°C and a detector temperature of 180°C. Because many peaks were found in the chromatograph, an injection size of no more than five microliters was used in order to maximize separation of peaks. The initial column temperature was 30°C and was kept at this value for five minutes and then increased by 1°C per minute until 75°C was reached and then maintained at that value. There were 14 peaks in the chromatogram, with five of them considered to be major peaks. ^{1}H nmr showed all major products to contain hydrogen. Obviously perfluorination of 2,4-dimethylpentane was not achieved. Characterization of the various products are given in Tables B15, B16, B17 and B18, Appendix B, and is discussed later in a subsequent chapter.

S. Aerosol Monofluorination of Benzene

The reason for fluorinating benzene was to see if monofluorination could be achieved. The fluorination of benzene was attempted on the horizontal reactor and fluorination parameters are given in Table A15, Appendix A. Because we desired to limit the degree of fluorination, the photochemical cell was removed from the reaction stream and the hydrogen fluoride scrubber was connected to the end of the reactor via a short piece of copper tubing.

Fluorination of 1.32 grams (16.9 mmole) of hydrocarbon produced 0.51 grams of crude product after a four hour run. The crude product was fractionated into the -45°C, -84°C, -131°C and -196°C cold traps. No visible products were seen in either the -45°C or the -196°C cold traps. About 90 percent of the product collected in the -84°C fraction and the remainder in the -131°C cold trap. These two fractions were combined and separated further by gas chromatography (twenty-five microliter injections) on the QF-1 column; the gc had an inlet temperature of 75°C and a detector temperature of 180°C. The initial temperature of the column was kept at 75°C for five minutes and then increased by a 2°C per minute throughout the duration of the chromatography. The first observed peak, with a retention time of 14.5 minutes, accounted for 96 percent of the total peak area, while the second peak, with a retention time of 17.2 minutes, accounted for the remaining 4 percent. Comparison of infrared and mass spectra with literature values[94,95] confirmed that the first peak was unreacted benzene and the second peak was monofluorobenzene. Throughput yield of monofluorobenzene was 7.2 percent. Details of the characterization of monofluorobenzene are given in Table B19, Appendix B.

CHAPTER III

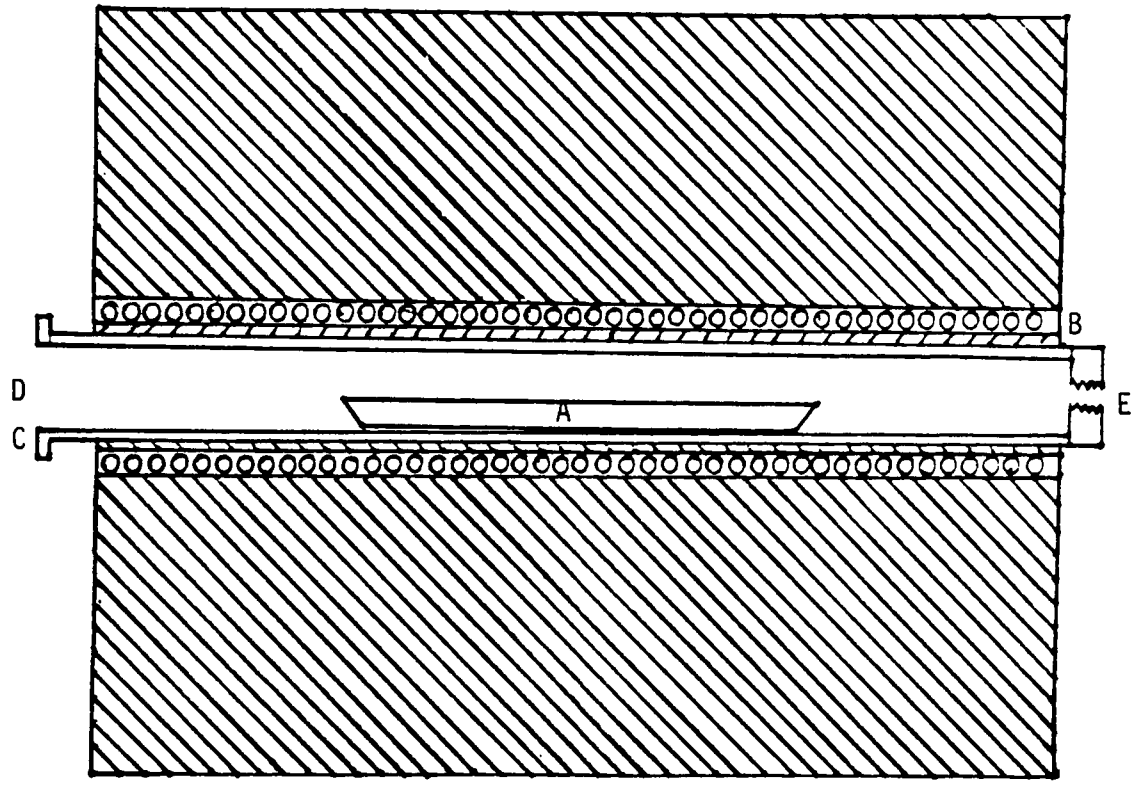
RESULTS AND DISCUSSION

A. The Basic Aerosol System

In the past the aerosol direct fluorination technique has generally produced high effluent concentrations of desired product. However, yields based on total input of reactant have often been low. A major concern of this research project has been to ascertain where losses in the reactor are occurring so that a more efficient system could be engineered. All of the compounds were synthesized on one of two different reactors, both of which will be described in detail.

Horizontal Reactor

The basic aerosol fluorination system is schematically shown in Figure 1 (p. 22). Gaseous helium is injected into a furnace (Figure 3) which contains a nickel boat filled with anhydrous sodium fluoride. The temperature of the furnace typically reaches a value of 700-850°C during the reaction time. This causes the sodium fluoride to disperse into fine particulates approximating 17.5 Å in size.[96] The main carrier helium stream flows through the oven chamber carrying the sodium fluoride particles into a long length of 1/4 inch copper tubing formed in the shape of a coil that is submerged in liquid nitrogen. The coil allows a long residual time of the sodium fluoride/helium stream with the coolant. The liquid nitrogen cools



Legend:
A. Nickel boat
B. Electrical heating element
C. Stainless steel tube
D. Helium inlet
E. Helium outlet

Figure 3. Sodium Fluoride Furnace.

the hot sodium fluoride so that it may serve as a condensation site for the host reactant. The coil is wrapped with insulation and placed physically close to the aerosol generator to retard particle warming before entering the reactor.

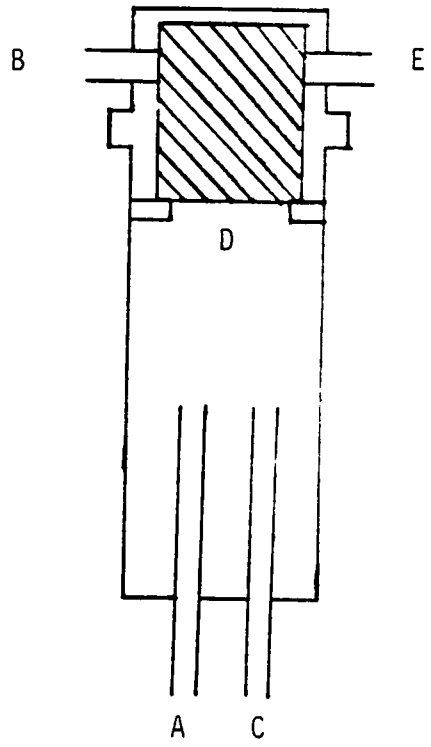
The sodium fluoride particles serve several functions. The reactants during fluorination must be in the crystalline phase while their gas-like mobility is simultaneously maintained. Therefore, the reactant requires a condensation site which can be carried through the reactor in a gaseous medium. As reactants undergo initial fluorination, the heat of reaction is very high. This has caused explosions and fires using other fluorination methods. The sodium fluoride behaves as a heat sink for the heat of reaction and deters fragmentation of the reactant. As the particles are carried through the reaction volume, adsorption of the reactant onto the sodium fluoride particles is maintained which reduces the probability of reactant radical recombination.

A type K thermocouple is placed in a thermocouple well deep inside the furnace volume. The electrical analog signal from the thermocouple is digitized and monitored by an Omega Series CN300 temperature controller. All temperature controls are calibrated by an Altek Series 22 thermocouple source. The main carrier helium flow is controlled and monitored by a Matheson Series 7400 rotameter.

The reactant is placed in a 5 ml Precision Sampling Corporation "Pressure-Lok" syringe which is driven by a (Sage Model 341a) syringe pump. As the reactant is delivered from the syringe, it is introduced

into a flash evaporator (Figure 4) which is fitted onto the aerosol generator. The flash evaporator has a small cylindrical volume, heated by a 5.0 foot length (13.2 ohm) of nichrome wire which is wrapped over an asbestos paper covering. Another layer of asbestos paper is wrapped over the wire and then covered by a thick layer of synthetic porcelain which serves as a thermal insulator. A thermocouple wire is wrapped around the stainless steel body to monitor the temperature. The flash evaporator is constructed from stainless steel, and contains a two micron, inline filter element (Nupro SS-4TF2-2BP4-2). Inlet C functions as the reactant inlet and is fitted to a stainless steel 1/16 inch tube coming from the syringe. Inlet A, which is monitored and controlled by a Matheson Series 7400 rotameter, is the secondary helium flow which carries the reactant vapor into the primary helium stream. Inlet B serves as a primary helium flow and is also controlled by a Matheson Series 7400 rotameter. As the reactant is injected into the flash evaporator, it is immediately vaporized. Normally the flash evaporator volume is maintained at a temperature from ten to twenty degrees above the boiling point of the reactant. A small helium flow (typically 50 cc/min) from the secondary port carries the vapor through the filter where it merges with the primary helium stream (typically 500 cc/min) and is carried into the aerosol generator.

This flash evaporator design caused problems which resulted in low yields of fluorinated products. The flash evaporator was attached to the aerosol generator in a vertical position. When using



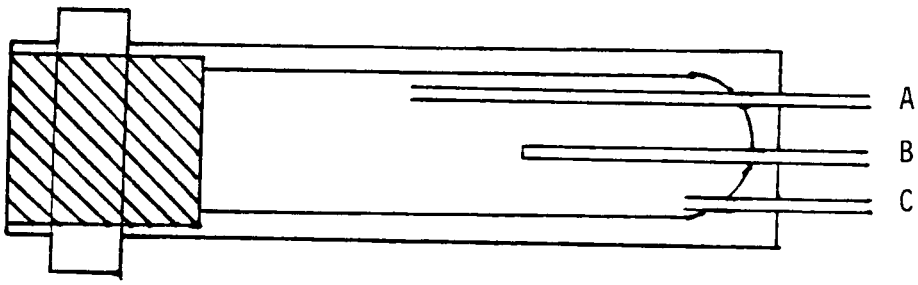
Legend:
A. Secondary helium
B. Primary helium
C. Reactant inlet
D. Inline filter
E. Reactant vapor inlet

Figure 4. Flash Evaporator.

triglyme as a model ether, the flash evaporator gained as much as 0.6 grams of weight during a reaction in which only 2.0 grams of sample was injected. Some reactant did not vaporize and was trapped as a liquid in the bottom of the flash evaporator, deflating yields by as much as 30 percent.

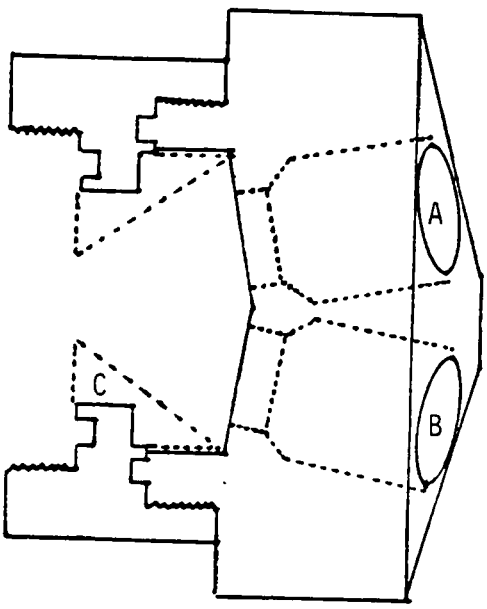
The modified flash evaporator is shown in Figure 5. It was constructed from copper rather than stainless steel to enhance thermal conductivity. An Omega Series CN300 temperature controller with a type J thermocouple was used to monitor and control the temperature. A thermocouple well was integrated into the bottom of the unit to measure temperature more accurately. The entire flash evaporator was configured in a horizontal fashion with a two to five degree tilt toward the bottom. A longer reactant inlet is inserted into the evaporator volume, which allows for any liquid reactant to drip onto the inside wall. The reactant would spread over the wall giving a large surface area for the helium to flow over. Hopefully all of the reactant would eventually be carried into the aerosol generator as a vapor.

The aerosol generator is schematically shown in Figure 6. Its function is to focus the two incoming streams in the center of the reactor's cross-section. The generator is constructed from a solid piece of brass and machined to fit onto the reactor. Two drilled holes that angle toward the focal point contain teflon inserts with another small hole in it to aid focusing. Two types of adaptors were used between the aerosol generator and the reactor. These were



Legend: A. Reactant inlet
B. Thermocouple well
C. Secondary helium

Figure 5. Modified Flash Evaporator.



Legend: A. Reactant vapor inlet
B. Sodium fluoride inlet
C. Teflon insert

Figure 6. Aerosol Generator.

constructed from stainless steel to enhance a temperature gradient. The first adaptor simply fit between the reactor and the generator with the aid of machined threads and O-rings. Often after an experiment, reactant residue could be seen on the inside of the adaptor wall. Apparently due to eddy currents or improper focusing, some reactant was allowed to come in contact with the cold wall and would condense, deflating yields.

A modified aerosol generator adaptor was designed to overcome these problems. The basic design was the same except that a teflon, funnel-shaped insert was fitted inside the generator. This kept the reactant from coming in contact with the generator wall and channeled the streams into the reactor chamber.

Figure 7 shows a reactor module. The horizontal reactor comprised three modules which were configured in series. The construction and functions of each are identical. The module's outside jacket was constructed from monel. At each end, a 3/8 inch, welded monel tube protruded outward two inches. This served as entry and exit ports for chilled freon. The reactor was heavily wrapped with insulation for better temperature control. Another port on the end of each module extends to an inner jacket where pre-diluted fluorine in a helium stream is introduced. The jacket contains a porous monel filter element (3/4 inch O. D. and 1/2 inch I. D.) with pores two microns in average diameter. The diluted fluorine is allowed to diffuse through the holes into the reaction chamber. This allows a partial pressure gradient from the reactor wall to the center of the

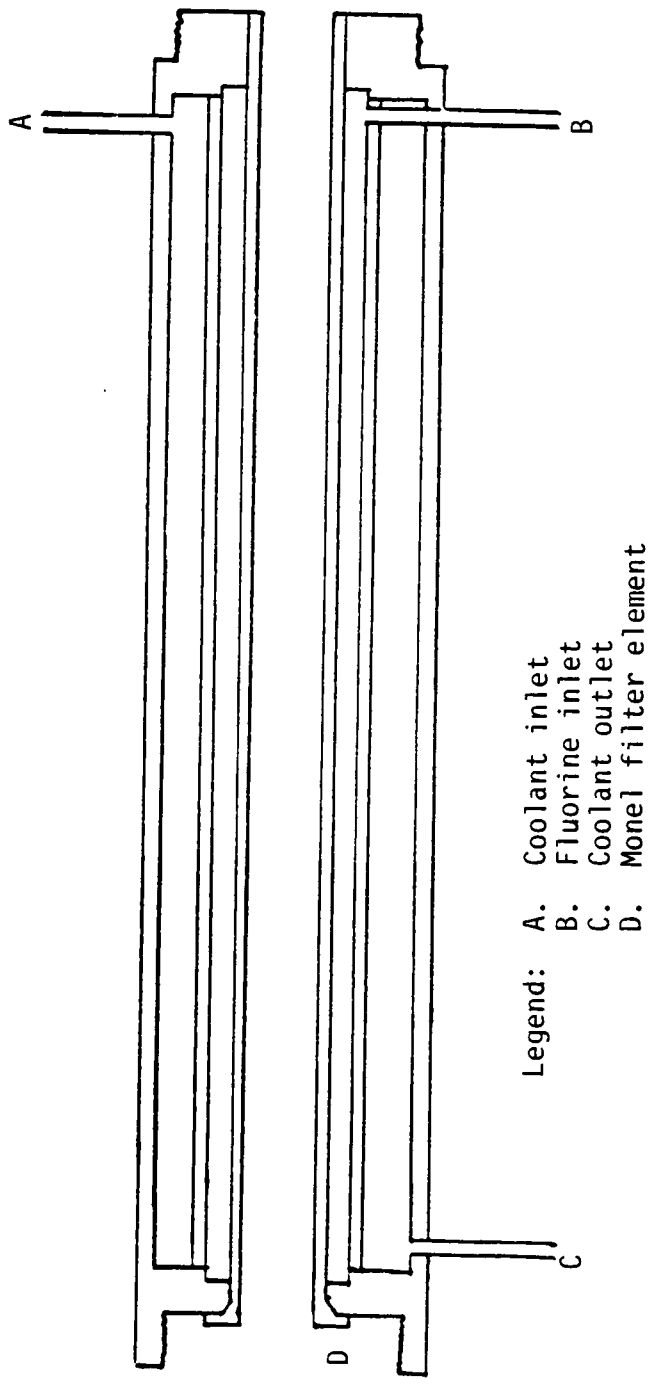


Figure 7. Reactor Module.

reactor volume, which aids in keeping reactants from coming in contact with the reactor's walls. The helium flows were controlled by Matheson rotameters (types 600 or 603), and Whitey valves (model SS1KS4). The fluorine was controlled by Whitey valves (M1KS4 and M21RS4) and monitored by a Hastings mass flowmeter (model LF-20X) and Hastings mass flow transducers (model LF-20X), types F-100M and F-20M). Even though the initial introduction of fluorine is not homogeneous in nature, a steady-state is achieved quickly in each module because the fluorine and helium mixture is allowed to run thirty minutes prior to hydrocarbon injection. Temperature, fluorine concentration, and helium flow can be independently controlled for each module. A fluorine concentration gradient is maintained to minimize fragmentation and maximize fluorination. Likewise the lowest temperature is maintained in module one, while the highest temperature is maintained in module three. Fragmentation of the reactant skeleton is likely to occur if fluorine concentration or temperature is too high at the onset of the reaction.

Stoichiometrically one molecule of fluorine is needed for each hydrogen to be replaced.

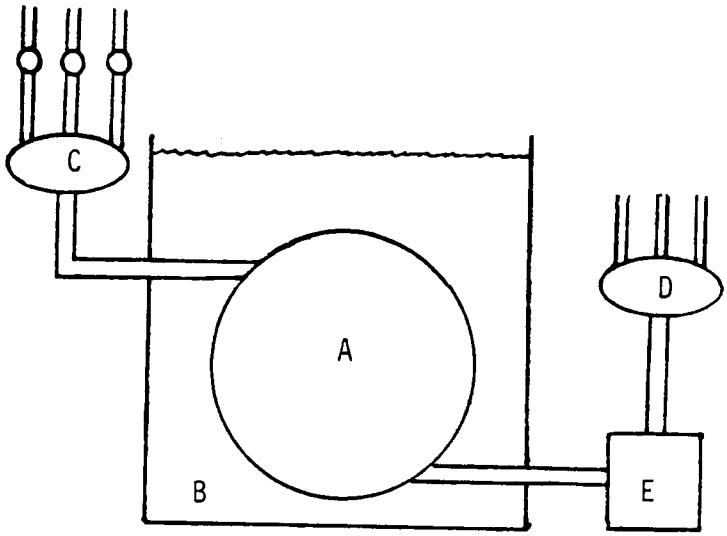
$$C_xH_y + YF_2 \rightarrow C_xF_y + YHF$$

However, to achieve optimum yields, approximately two to four fluorine equivalents are required per hydrogen equivalent on the reactant. If less fluorine is used, perfluorination will not be achieved, while more fluorine leads to reactant fragmentation.

Temperature control of the reactor modules is achieved by pumping freon through the outer jacket. Figure 8 schematically shows the design of this system. Freon is kept in a storage tank that is submerged in a methanol/dry ice bath. The freon is pumped by an Eastman/Iwaki mag-drive pump, model MD-15T, and channeled separately to each module. On the exit port of each module is placed a Type J thermocouple connected to an Omega Series CN300 temperature controller which drives a solenoid valve (Asco).

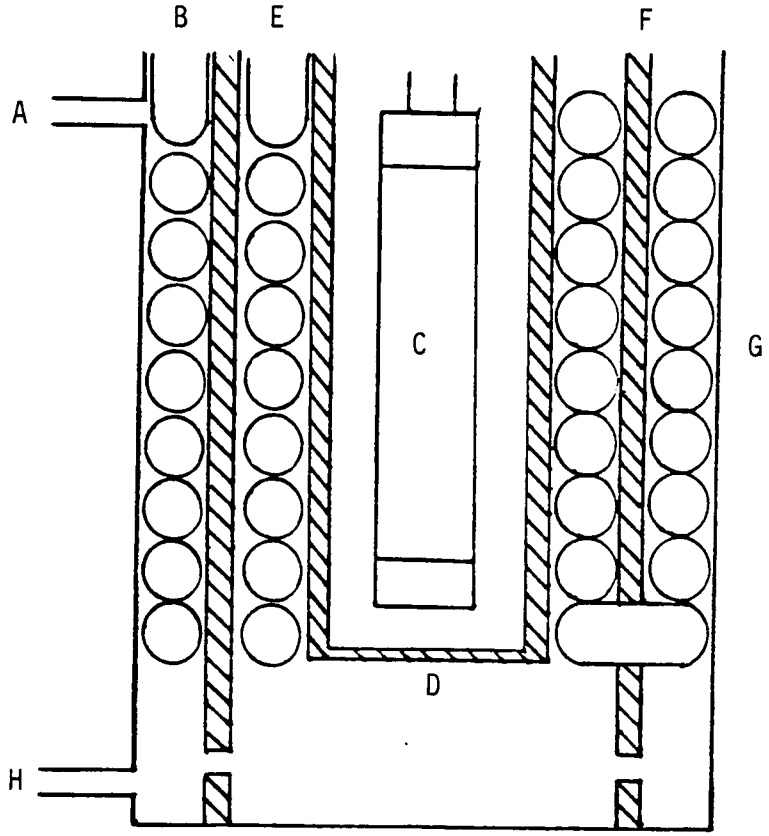
The degree of fluorination of reactants exiting the reactor is only about 50 to 60 percent,[51] therefore the products are introduced to a photochemical finishing cell. If the ratio of fluorine to hydrogens is 40:1, only about 10 percent of perfluorinated product is achieved in the absence of the photochemical finishing cell. However, ultraviolet light tends to fragment reactants that have not been sufficiently fluorinated. Fluorinated species entering the photochemical cell are more capable of resisting fragmentation.

The photochemical cell is shown in Figure 9. The cell is composed of a stainless steel well in which water is circulated to act as a heat exchanger. The reactants in the helium stream pass through the cell via a 10 meter length of 0.015 inch wall, 3/8 inch FEP Teflon tubing. One layer of the tubing is wrapped around a 50 mm x 390 mm quartz immersion well (Ace Glass) containing a 550 watt medium pressure mercury arc lamp (Hanovia), and a second layer is concentrically wrapped around an overlying 75 mm Pyrex tube. This configuration allows the reactants to pass through the volume with



Legend:
A. Freon reservoir
B. Methanol and dry ice
C. Coolant return from modules
D. Coolant to modules
E. Pump

Figure 8. Module Cooling System.



Legend:
A. Cooling water outlet
B. Inlet
C. Ultraviolet lamp
D. Quartz immersion well
E. Outlet
F. Pyrex tube
G. Stainless steel container
H. Cooling water inlet

Figure 9. Photochemical Stage.

Pyrex-filtered wavelengths first (>300 nm) and then through the more energetic area with wavelengths down to 225 nm. The FEP cutoff wavelength is approximately 225 nm.[51]

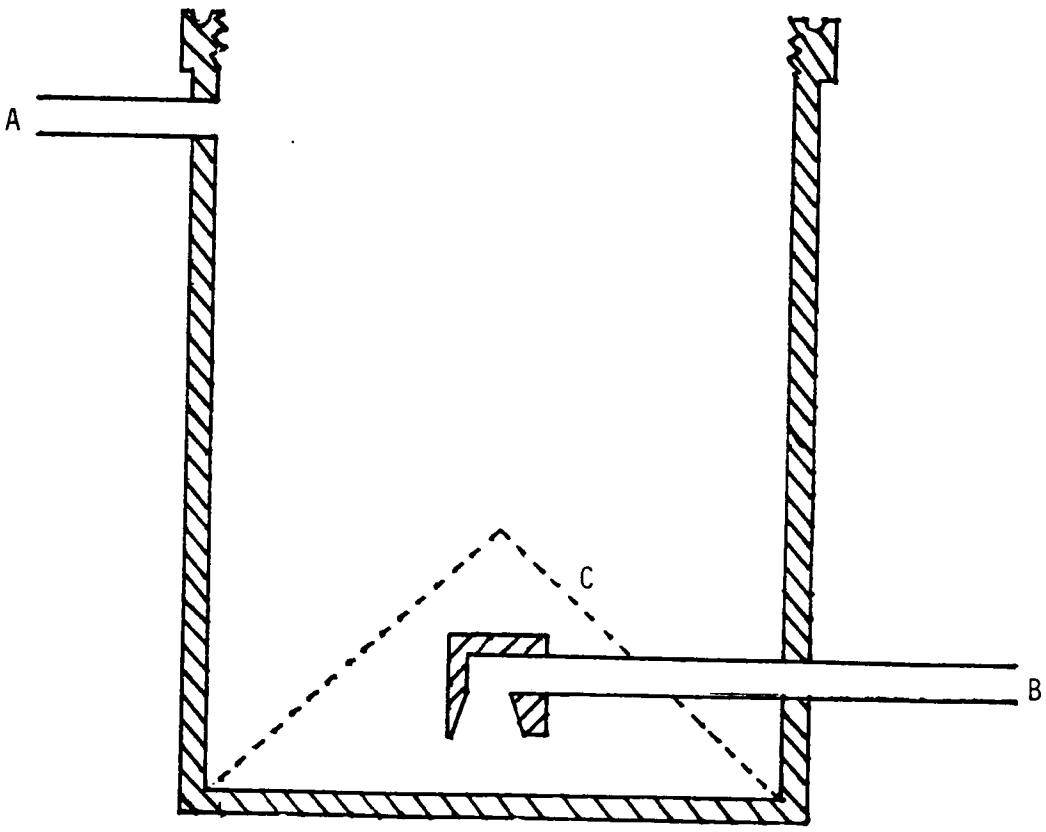
Hydrogen fluoride, a by-product of the fluorination reaction which is produced in large amounts, must be removed from the reaction stream prior to coming into contact with the borosilicate crude product trap. This is accomplished with the hydrogen fluoride scrubber shown in Figure 10. A brass cylinder, 35 ml in volume, is placed between the photochemical cell and the crude product trap. Sodium fluoride pellets are placed inside the cylinder and over a copper gauze screen that is cone shaped to keep the pellets from clogging the scrubber. Hydrogen fluoride forms an adduct, $NaHF_2$, with sodium fluoride.

$$NaF + HF \rightarrow NaHF_2$$

The crude product trap, which can be fitted via ultra-torr fittings to an all-glass vacuum line, is constructed from borosilicate glass (Ace) and two teflon stopcocks (Kontes Scientific Glassware). The trap is placed inside a dewar filled with liquid nitrogen. The remaining helium and unreacted fluorine stream passes through an alumina trap to scrub out fluorine and then the remaining helium is vented into a hood.

Vertical Reactor

Even though effluent concentration of products from the horizontal reactor are often good, overall yields have been less than



Legend: A. Outlet
B. Inlet
C. Copper gauze screen

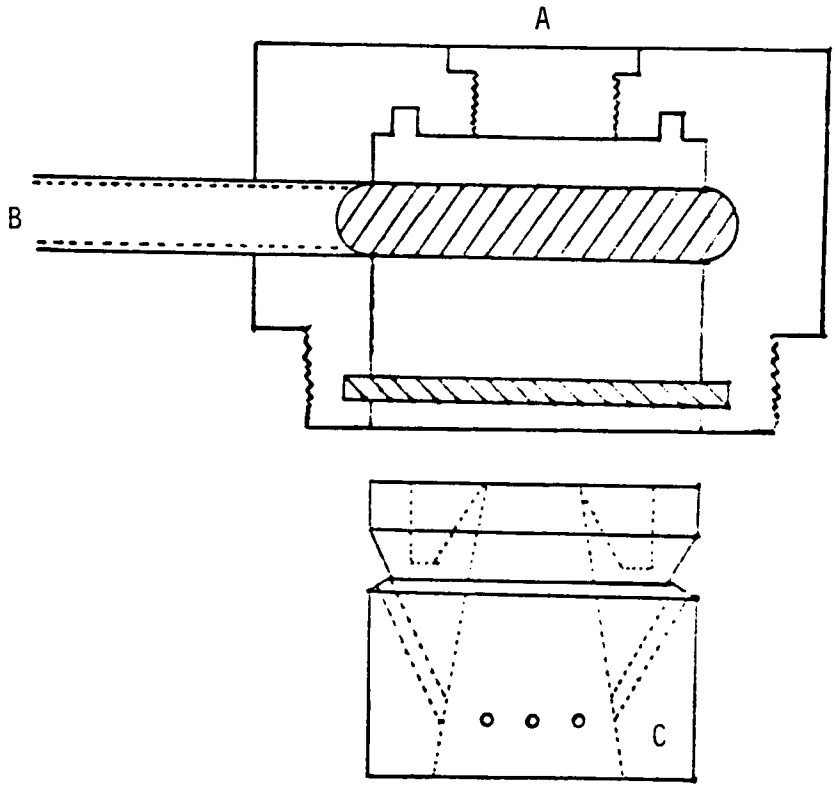
Figure 10. Hydrogen Fluoride Scrubber.

desirable. One purpose of this research has been to determine where losses occur. For example, when tetraglyme was perfluorinated, the effluent purity of desired product was 94 percent, but the yield was only 15 percent. Generally the yields increase as the reaction time increases. This indicates that fixed volume losses must be overcome initially before the system operates more efficiently. Generally as the molecular weight of the reactant is increased, the throughput yield is decreased.

Triethylene glycol dimethyl ether (triglyme) was used as a standard in which parameters were altered to determine where losses occurred. Several areas of loss were determined by net weight loss or gain of reactor components. The majority of loss in the system was found in three specific areas. (1) The flash evaporator was found to gain 30 percent reactant weight during a reaction run; hence only 70 percent of injected reactant was actually delivered into the reactor. (2) Other losses were due to polymer formation occurring in the photochemical cell. This was possibly due to inefficient cooling coupled with wall interaction. After a few runs with the glyme ethers, the FEP Teflon tubing was removed from the photochemical cell and washed with acetone. While some oil still remained, weight loss of the tubing was 13.5 grams. Normally only 2.0 ml of reactant was injected in one run, with up to 30 percent of this lost in the flash evaporator ahead of the photochemical cell. (3) The other area of major loss was due to improper stream focusing in the aerosol generator. Very often tars and oils were found inside

the aerosol generator after a run. The porous monel filter inserts would often become clogged and block the helium/fluorine mixture. When they were removed and baked at 900°C to burn off carbon materials, weight loss of the three modules would be as high as 7.3 gm.

The vertical reactor is shown in Figure 2 (p. 24). The modifications to this reactor were designed to overcome losses that occurred previously. The inside diameter of the horizontal reactor was 0.5 inches while the vertical reactor's diameter was 1.0 inches. This gives approximately a four-fold increase in cross-sectional area. The vertical reactor includes three major modifications/ improvements over the horizontal reactor. (1) In the horizontal reactor improper focusing would cause material to fall out of the reaction stream. The new reactor was configured in a vertical position which allows a precipitate to fall with the stream through the reactor. (2) A modified aerosol generator is shown in Figure 11. The vaporized reactant is injected directly into the system through a short piece of FEP Teflon tubing surrounded by a cylindrical piece of Teflon. This configuration gives better thermal isolation to inhibit premature reactant vapor condensation. The sodium fluoride/ helium stream is injected into the aerosol generator at a thirty degree angle around the circumference of the reactant inlet stream. The sodium fluoride/helium stream comes in contact with the reactant by passing through eight 1/16 inch holes that angle toward the focal point of the reactor's cross-section. (3) The previously described



Legend: A. Reactant vapor inlet
B. Sodium fluoride inlet
C. Teflon insert

Figure 11. Modified Aerosol Generator.

horizontal flash evaporator was also integrated into the vertical reactor. Even before parameter optimization, initial testing of the vertical reactor with dioxane as the substrate, gave increased yields over the horizontal reactor by a factor of two.

Two other modifications in the reactor system have been made to the photochemical finishing cell and the crude product trap. The vertical reactor with these modifications is shown schematically in Figure 12.

The modified photochemical finishing cell extends from the bottom of the last module. It is constructed from a straight one inch diameter quartz tube with an inside coating of FEP Teflon. Two 550 watt medium pressure mercury arc lamps (Hanovia) are stacked in a vertical fashion adjacent to the length of quartz tube. Each lamp is contained in a glass immersion well that uses a stream of water in its jacket as a heat exchanger. A squirrel cage fan forces air over the cell to aid in cooling. As reactants exit the last module, they are allowed to fall with the stream through the photochemical cell without having to make critical turns that were present in the old system. Any particle falling with the stream will pass through this region into the product trap. Initial testing of this design has shown no evidence of product loss in this area. The higher flux of ultraviolet light has also enhanced the degree of perfluoration.

The modified crude product trap is shown in Figure 13. During a fluorination reaction the hydrogen fluoride scrubber would often gain more weight than expected. The modified product trap

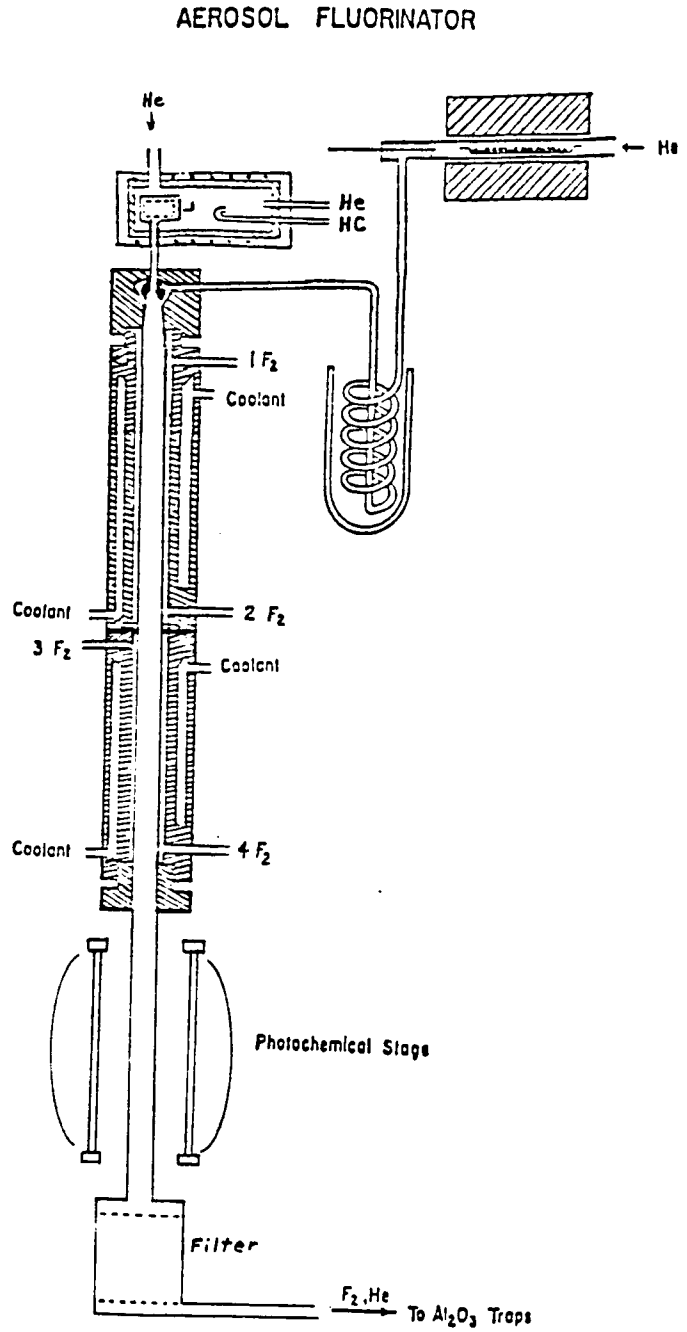
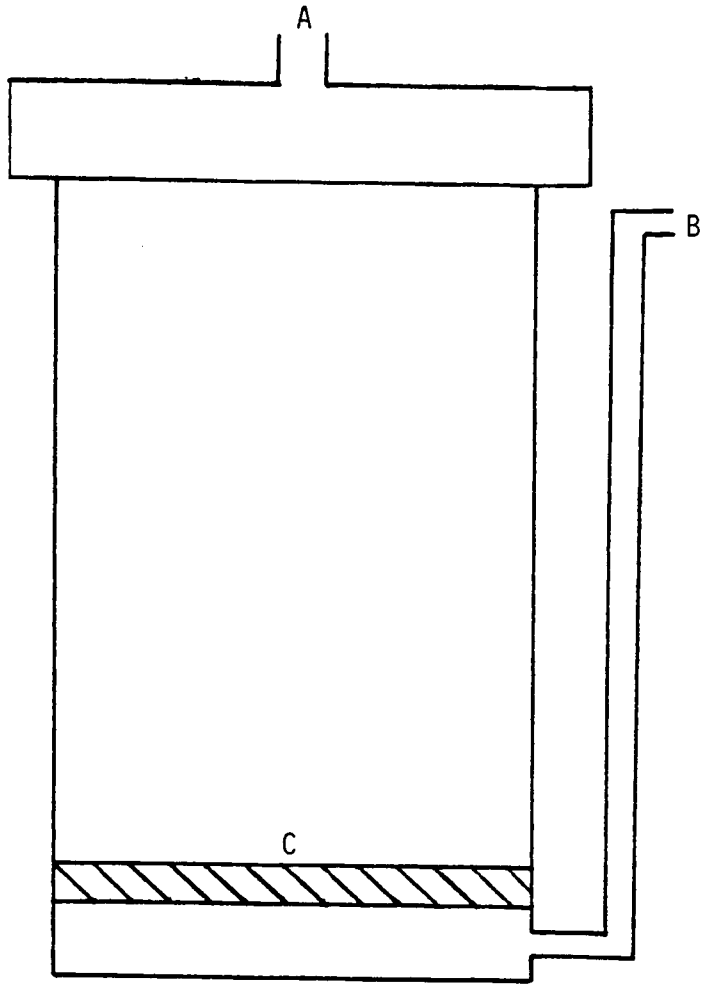


Figure 12. Modified Vertical Fluorination System.



Legend: A. Inlet
B. Outlet
C. Filter Element

Figure 13. Modified Crude Product Trap.

incorporates the scrubber and trap into one unit. As the reactant stream passes through the trap both the product and hydrogen fluoride are trapped. Two Whitey ball valves are fitted onto the trap to allow it to be detached from the reactor and integrated onto the vacuum line. As the contents are allowed to warm slowly, the crude product transfers onto the vacuum line while the hydrogen fluoride forms an adduct with the sodium fluoride pellets and is left behind. There has been speculation that some product did not trap out in the old glass trap. Therefore a porous monel filter element with two - micron holes is integrated in the bottom of the trap to aid in stopping the desired product and allowing the helium/fluorine mixture to pass through to the alumina traps. Initial testing has given increased yields over the old system.

In the vertical design gravity is utilized to allow reactants to pass through the system. A substrate that is introduced into the top of the system falls with the stream from the beginning of the reaction until its completion. However, a temperature gradient is maintained with module one being the coldest zone and the photochemical finishing cell being the warmest zone. Because warmer, less-dense gases always rise, this causes a partial turbulence in the reactor and enhances mixing.

B. Chemical Reactions

Synthesis of F-Ethylene Glycol Dimethyl Ether

The aerosol fluorination of ethylene glycol dimethyl ether (glyme) produced F-ethylene glycol dimethyl ether as the major product. Based on throughput the yield of perfluoroether was 36 percent, while its effluent concentration was 98 percent. Only two other peaks were seen in the gas chromatograph and they comprised the remaining 2 percent. Even though there was not enough material in these two peaks for characterization, they are likely to be mono- and dihydryl analogues of the perfluorinated ether. Because F-ethylene glycol dimethyl ether had been synthesized and characterized previously, only an infrared analysis was carried out on our product to verify its identification.[32] Infrared analysis of F-ethylene glycol dimethyl ether gave absorption at 1410(w), 1295(s), 1200(w), 1170(sh), 1155(s), 1105(w), 923(w), 887(m), 865(w), 819(w), 730(w), and 690(w) cm^{-1}. Details of the characterization of this compound are given in Table B1, Appendix B.

Synthesis of F-Bis-2-methoxyethyl Ether

The aerosol fluorination of bis-2-methoxyethyl ether produced F-bis-2-methoxyethyl ether in 22 percent yield, while its effluent concentration was 89 percent. In aerosol direct fluorination the yields of perfluorinated ethers generally decrease as their molecular weights increase. This occurs not only because of losses in the system due to the volatility of the substrates but also because there

are more hydrogens to replace, thus resulting in a higher probability of residual hydrogens remaining on the ethers. In the gas chromatograph four closely spaced peaks, which comprised 6 percent of the total peak area, came off the column before the perfluorinated ether; these compounds were thought to be perfluorinated fragment products. Another peak, which came off the column after the perfluorinated ether, comprised 5 percent of the total peak area and is likely to be the monohydryl perfluorinated ether.

Again, because F-bis-2-methoxyethyl ether has been synthesized and characterized previously, only an infrared analysis was carried out.[32] The fingerprint region in the infrared spectrum of this compound agreed with previous literature values.[32] Absorptions in the infrared spectrum occurred at 1385(w), 1295(s), 1250(s), 1220(sh), 1200(w), 1165(s), 1145(s), 920(w), 900(w), 770(m) and 730(m) cm^{-1}. Details of the characterization of this compound are given in Table B2, Appendix B.

Synthesis of F-Triethylene Glycol Dimethyl Ether

The direct aerosol fluorination of triethylene glycol dimethyl ether produced F-triethylene glycol dimethyl ether as the major product. This reaction was run numerous times to evaluate modifications and improvements to the reactor system. In a typical experiment where all parameters had their normal values, the yield of product was 20 percent with an effluent concentration of 91 percent. When the temperature was increased from -30°C, -20°C and 0°C for modules one, two and three, respectively, to -20°C, -10°C and 0°C,

the effluent concentration of the desired product decreased to 81 percent, but the yield increased to 30 percent.

The perfluorinated ether was characterized by infrared analysis, chemical ionization and electron impact mass spectrometry, and ^{19}F nmr spectroscopy. Details of the characterization are given in Table B3, Appendix B. Absorptions in the infrared occurred at 1290(s), 1245(vs), 1230(s), 1200(m), 1160(vs), 1140(s), 900(w), 790(w), 738(w) and 685(w) cm^{-1}. Previous values were only reported for the fingerprint region for this compound and they agreed with our results.[33,34]

The chemical ionization mass spectrum exhibited peaks at m/e = 185 corresponding to $C_3F_7O^+$, and m/e = 135 corresponding to $C_2F_5O^+$. The electron impact mass spectrum exhibited peaks at m/e = 185 corresponding to $C_3F_7O^+$ and m/e = 135 corresponding to $C_2F_5O^+$.

The ^{19}F nmr spectrum of this compound was slightly different than previous literature spectra.[33,34] Lagow reported that the perfluorinated methyl and methylene groups differed in chemical shifts by 32.6 ppm. Our spectra yielded a chemical shift difference of 33.34 ppm, a 2.2 percent discrepancy. The ^{19}F nmr spectrum of F-triethylene glycol dimethyl ether consisted of a triplet, a singlet and a quartet with chemical shifts of -55.93, -89.27 and -91.31 ppm, respectively.

Synthesis of F-Tetraethylene Glycol Dimethyl Ether

Fluorination of tetraethylene glycol dimethyl ether (tetraglyme) produced F-tetraethylene glycol dimethyl ether as the major product. Tetraethylene glycol dimethyl ether has the highest molecular weight (222 g/mol) of any compound fluorinated by the aerosol direct

fluorination technique. This resulted in a lower yield of the desired perfluorinated product than found in any other synthesis to date. As the molecular weight of the host ether increases, its volatility decreases, which causes it to collect in the flash evaporator and be trapped in the photochemical cell. Even though yields are low for non-volatile compounds, the aerosol fluorination process should be adaptable to low volatility oils. A total of eight peaks were observed in the gas chromatogram of the crude product. The major peak, which corresponded to the desired product, comprised 93 percent of the total peak area, and was formed in a 15 percent yield. Five peaks that came off the column before the perfluorinated ether comprised a total of 6 percent of the total peak area. Even though there was not enough material for characterization of these compounds, they are likely perfluorinated fragment products. Two additional peaks came off the column after the perfluorinated ether and accounted for 1 percent of the total peak area; these compounds are probably mono- and dihydryl perfluorinated ethers.

The fingerprint region of the infrared spectrum of the desired compound has been previously reported[33,34] and agreed with our results. The infrared spectrum of F-tetraethylene glycol dimethyl ether gave absorption at 1280(s), 1235(vs), 1215(s), 1190(s), 1150(s), 1125(s), 1020(m), 895(w), 835(w), 750(w) and 720(w) cm^{-1}.

The chemical ionization mass spectrum for the perfluorinated ether exhibited peaks at m/e = 185 corresponding to $C_3F_7O^+$, m/e = 135 corresponding to $C_2F_5O^+$, m/e = 119 corresponding to $C_2F_6^+$, and m/e = 103 corresponding to $C_2F_4OH^+$. In the electron impact mass spectrum

only four peaks were observed corresponding to $C_2F_5^+$, CF_3^+ and CF_2^+. Complete characterization details are given in Table B4, Appendix B.

The ^{19}F nmr gave three peaks: a triplet at -55.97 ppm, a singlet at -89.34 ppm and a quartet at -91.35 ppm. These corresponded to the perfluorinated methyl, the internal CF_2 groups and the CF_2 groups alpha to the methyl groups, respectively. The ^{19}F nmr spectrum of this compound was slightly different than previous literature spectra.[33,34] Lagow reported relative chemical shift differences of 32.5 ppm and 2.1 ppm when referenced to trifluoracetic acid. Our relative chemical shift differences ($CFCl_3$ internal standard) were 33.37 and 2.01 ppm, values differing from Lagow's work by 3 and 4 percent, respectively.

Synthesis of F-Bornyl Methyl Ether

The aerosol direct fluorination of bornyl methyl ether produced F-bornyl methyl ether in 11 percent yield, while its effluent concentration was 91 percent. Bornyl methyl ether contains 11 carbons in its skeleton, the largest number of carbons in a compound subjected to aerosol fluorination to date. The perfluorinated product had a low vapor pressure and was difficult to transfer on the vacuum line.

The gas chromatogram of the product mixture resulted in seven peaks. The first five peaks comprised 8 percent of the total peak area and are thought to be perfluorinated fragment products. The sixth and seventh peaks, which were isomers of F-bornyl methyl ether, were in a 5:1 ratio which is the same as the ratio of the endo- and exo- isomers of the starting material.

The infrared spectrum of the perfluorinated product gave absorptions at 1320(m), 1275(s), 1240(s), 1190(s), 1175(m), 1135(m), 1115(m), 1060(m), 1020(m), 990(m), 950(w) and 720(m) cm^{-1}. The ^{19}F nmr spectrum of these compounds are very complex due to the large number of spin systems. Complete characterization details are given in Table B5, Appendix B.

Aerosol Fluorination of Cyclohexene Oxide

Perfluorocyclohexene oxide is a likely starting material for perfluorinated polyether polymers which might have interesting physical properties. Since a major problem in direct fluorination is fragmentation of the carbon skeleton, ring opening of the three-membered epoxide ring in this system is a potentially serious problem. Coe et al.[97], in a scheme to produce a perfluorinated amine, treated cyclohexene oxide with potassium fluoride in dry sulfolane and found it to rearrange to a ketone.

The aerosol fluorination of cyclohexene oxide produced a compound in 65 percent effluent concentration and it has been tentatively identified as F-cyclohexene oxide. Tentative identification of this compound was supported by the chemical ionization mass spectrum which exhibited a peak corresponding to the molecular ion of F-cyclohexene oxide and the ^{19}F nmr spectrum. The nmr spectrum was not in accord with F-cyclohexanone. Perfluorocyclohexene oxide will exhibit eight peaks for the eight inequivalent fluorines on the four CF_2 groups and two CF peaks (attached to the epoxide ring) due to the chair and boat isomers. While the ^{19}F nmr spectrum is

complicated, the correct number of CF_2 and CF peaks were exhibited. The synthesis resulted in a 27 percent yield of F-cyclohexene oxide. Complete characterization details of this compound are given in Table B6, Appendix B.

Ether Discussion

Previous syntheses of perfluoroglyme ethers by a variety of methods have produced perfluoro -glyme, -diglyme, and -tetraglyme. The synthesis of perfluoroglyme was first reported by Simons[98] in 1950 who electrolyzed 1,4-dioxane in liquid hydrogen fluoride. F-1,2-dimethoxyethane and bis-2-methoxyethyl ether have been made previously employing the LTG techniques.[32] However, LTG is a batch process and gave yields of 21 and 16 percent, respectively. Later perfluorodimethoxyethane was synthesized in an unspecified yield by degradation of perfluoro-1,4-dioxane which had been produced by electrochemical fluorination in liquid HF[99]. The first synthesis of perfluoro -triglyme, -tetraglyme and -pentaglyme was carried out by Gerhardt and Lagow.[33,34] The ethers were contained in a complex mixture of products isolated from the direct fluorination of polyethylene oxide and formed in 0.66, 0.66, and 0.68 percent yields, respectively. Table 3 compares the yields of the perfluorinated glyme ethers from the LTG and aerosol method.

Prior syntheses of perfluorinated glymes from their respective ether analogs have been successful only for perfluorinated glyme and diglyme. The higher molecular weight perfluorinated glyme ethers have been synthesized by subjecting elemental fluorine to glyme polyethers

TABLE 3

SYNTHESES OF PERFLUOROGLYME ETHERS

Compound	Effluent Concentration	Yield vs. Input
CF_3-O-CF_2-CF_2-O-CF_3	98% (<50%)*	36% (21%)*
CF_3-(O-CF_2-CF_2)$_2$-O-CF_3	89% (<50%)	22% (16%)
CF_3-(O-CF_2-CF_2)$_3$-O-CF_3	92% (<1%)	20% (1%)
	81%	30%
CF_3-(O-CF_2-CF_2)$_4$-O-CF_3	94% (<1%)	15% (1%)

*Percentages in parentheses are yields from the "LTG" method.

under conditions that promote fragmentation of the carbon skeleton. Thus, the crude product of these reactions contained numerous perfluorinated fragment products. The aerosol fluorination synthesis, compared to previous techniques, gives higher yields of the desired perfluorinated glyme ether and uses the ether precursors as starting material in all cases. The lowest yield we observed was 15 percent for F-tetraethylene glycol dimethyl ether. However, the low yield is somewhat misleading since effluent purity in this case was 94 percent. Table 3 also summarizes effluent purities of these ethers by the LTG and aerosol methods. Once improvements to overcome loses in the aerosol system are made, yields of these glyme ethers should increase even more. Several runs were made on triglyme to determine what caused the low yields. When more ether was injected into the system (longer run), this resulted in an increased yield. Therefore, a fixed volume loss is partly responsible for low yields and must be overcome before the system operates efficiently. The flash evaporator retained 30 percent of the weight of injected ether during a reaction; hence only 70 percent of the ether was actually delivered. This deflates yields significantly. Other losses due to oil formation occurred in the photochemical cell, possibly because of inefficient cooling of the cell. In most runs material tended to condense in the early stages of the reactor, probably because of improper focusing of the aerosol streams. Therefore, the immediate problem is to improve the engineering of the apparatus rather than chemistry.

Synthesis of F-Methyl 2,2-Dimethylpropanoate

The aerosol fluorination of methyl 2,2-dimethylpropanoate produced F-methyl 2,2-dimethylpropanoate in an 86 percent yield and 100 percent effluent concentration.

The infrared spectrum of this compound gave absorptions at 1820(m), 1265(s), 1220(m), 1170(m), 1125(s), 1020(s), 990(m) and 835(w) cm^{-1}. The ^{19}F spectrum nmr consisted of two singlets of relative intensity of 1:3 at ϕ = -58.57 ppm and ϕ = -63.64 ppm, respectively, and corresponded to the methoxy group and the tertiary butyl methyl groups.

The chemical ionization mass spectrum exhibited peaks at m/e = 185, 160, 136 and 70 corresponding to the $C_3F_7O^+$, $C_4F_5OH^+$, $C_2F_5OH^+$ and CF_3H^+ fragments, respectively. The electron impact mass spectrum gave peaks at m/e = 159, 135 and 69 corresponding to $C_4F_5O^+$, $C_2F_5O^+$ and CF_3, respectively. Complete characterization details are given in Table B7, Appendix B.

Synthesis of F-Methyl 2-Methylpropanoate

The aerosol fluorination of methyl 2-methylpropanoate gave a 48 percent yield of F-methyl 2-methylpropanoate with 64 percent effluent concentration.

Absorptions in the infrared spectrum of this compound occurred at 1820(m), 1350(m), 1305(s), 1250(s), 1165(s), 1140(s), 1090(s), 1040(m), 1020(s), 990(m) and 835(m) cm^{-1}. The chemical ionization mass spectrum exhibited peaks at m/e = 179 corresponding to $C_4F_6OH^+$, m/e = 161 corresponding to $C_4F_5OH_2^+$, m/e = 157

corresponding to $C_4F_4O_2H^+$, and m/e = 69 corresponding to CF_3^+. The electron impact mass spectrum exhibited peaks for m/e = 197 which represents the molecular ion minus a methoxy group, m/e = 179 corresponding to $C_4F_6O^+$ and m/e = 85 corresponding to CF_3O^+. The ^{19}F nmr spectrum exhibited a singlet (ϕ = -58.46 ppm relative to $CFCl_3$) corresponding to the methoxy group, a doublet (ϕ = -74.57 ppm) corresponding to the methyl groups and a multiplet (ϕ = -182.2) corresponding to the methyne group. Characterization details are given in Table B8, Appendix B.

Two other products resulting from this reaction were F-methyl 2-hydryl-F-2-methylpropanoate and F-hydrylmethyl F-2-methylpropanoate. Evidence for these compounds could be seen in the electron impact mass spectrum which showed a peak (m/e = 51), corresponding to CF_2H^+, and in the ^{19}F nmr which had a doublet (ϕ = -63.68 ppm) corresponding to the methyl group attached to a CH, and ϕ = -90.8 ppm corresponding to the $-OCF_2H$ group.

Synthesis of F-Methyl Propanoate

The aerosol fluorination of methyl propanoate produced F-methyl propanoate in a yield of 43 percent and an effluent concentration of 55 percent.

The absorptions in the infrared spectrum for this compound were at 1810(m), 1335(m), 1270(s), 1245(s), 1220(s), 1160(s), 1120(s), 1020(s) and 835(w) cm^{-1}. The chemical ionization mass spectrum exhibited a peak at m/e = 214, $C_4F_7O_2H^+$, which corresponds to the molecular ion minus fluorine. Additional peaks occurred at m/e = 197,

147 and 115, corresponding to $C_4F_7O^+$, $C_3F_5O^+$ and $C_2F_3O_2H_2^+$, respectively. The electron impact mass spectrum displayed peaks at m/e = 147, 119, 85 and 69 corresponding to $C_3F_5O^+$, $C_2F_5^+$, CF_3O^+ and CF_3^+. The ^{19}F nmr spectrum exhibited a singlet (ϕ = -59.22 ppm with respect to $CFCl_3$) corresponding to the methoxy group, a singlet (ϕ = -83.73 ppm) corresponding to the methyl group and a singlet (ϕ = -91.69 ppm) corresponding to the CF_2 group. Complete details of the characterization of this compound are given in Table B9, Appendix B.

Another major product of this reaction was F-methyl 1-hydryl-F-propanoate. Evidence for this compound was obtained from the electron impact mass spectrum which had a peak at m/e = 51 corresponding to CF_2H^+, and the ^{19}F nmr which displayed a singlet (ϕ = -92.52 ppm) corresponding to the CF_2 group and a doublet (ϕ = -122.86 ppm) corresponding to the CF_2H methyl group. This compound had an effluent concentration of 40 percent although 5 percent of this effluent concentration was due to perfluorinated acid fluoride resulting from ester scission.

Synthesis of F-Ethyl Propanoate

The aerosol fluorination of ethyl propanoate produced F-ethyl propanoate in 23 percent yield and its effluent concentration was 75 percent.

The infrared spectrum of this compound exhibited absorptions of 1830(m), 1270(m), 1230(s), 1160(s), 1120(s), 1095(s) and 1015(s) cm^{-1}. The chemical ionization mass spectrum gave m/e = 283

($C_5F_{10}O_2H^+$) which corresponds to the molecular ion. Additional peaks occurred with m/e = 233, 183, 147 and 119 corresponding to $C_4F_8O_2^+$, $C_3F_6O_2^+$, $C_3F_5O^+$ and $C_2F_5^+$, respectively. The electron impact mass spectrum exhibited peaks at m/e = 147, 119, 69 and 50 corresponding to $C_3F_5O^+$, $C_2F_5^+$, CF_3^+ and CF_2^+, respectively. The ^{19}F nmr spectrum exhibited a singlet at ϕ = -83.76 ppm (relative to $CFCl_3$) corresponding to the methyl which is beta to the ester oxygen, a singlet at ϕ = -87.42 ppm corresponding to the other methyl, a singlet at ϕ = -92.45 ppm corresponding to the CF_2 group which is alpha to the ester oxygen, and a singlet at ϕ = -122.61 ppm corresponding to the other CF_2 group. Complete characterization details are given in Table B10, Appendix B.

Two other minor products of this reaction were F-ethyl 2-hydryl-F-propanoate with an effluent concentration of 16 percent and F-methyl propanoate with an effluent concentration of 5 percent. These compounds were identified by ^{19}F nmr and mass spectra.

Synthesis of F-Isopropyl Propanoate

The aerosol fluorination of isopropyl propanoate was very clean and gave F-isopropyl propanoate in a yield of 65 percent yield; its effluent concentration was 92 percent.

Absorptions in the infrared spectrum for this compound occurred at 1835(m), 1335(m), 1300(s), 1240(s), 1220(s), 1170(s), 1130(s), 1105(s) and 940(w) cm^{-1}. The chemical ionization mass spectrum exhibited a peak at m/e = 313 which corresponds to the molecular ion less fluorine. Additional peaks occurred at m/e = 235,

233, 167, 147, 119, 117, 97 and 69 corresponding to $C_4F_9O^+$, $C_4F_8O_2H^+$, $C_3F_6OH^+$, $C_3F_5^+$, $C_2F_5^+$, $C_2F_4OH^+$, $C_2F_3O^+$ and CF_3^+, respectively. The electron impact mass spectrum exhibited peaks at m/e = 169, 147, 119 and 69 corresponding to $C_3F_7^+$, $C_3F_7^+$, $C_3F_5O^+$, $C_2F_5^+$ and CF_3^+, respectively. The ^{19}F nmr spectrum gave four singlets, ϕ = -79.46, -83.55, -122.03 and -142.95 ppm relative to $CFCl_3$, corresponding to $C\underline{F}_3$-CF, CF_3, CF_2 and CF, respectively. Complete characterization details are given in Table B11, Appendix B.

An additional reaction on the starting material was attempted. The experimental conditions were identical to the ones used before except that lithium fluoride was used instead of sodium fluoride. Surprisingly, the results were not as good as with sodium fluoride: F-isopropyl propanoate was produced in 19 percent yield and its effluent concentration was 40 percent. Lithium fluoride has a melting point of 842°C while sodium fluoride has a melting point of 988°C. Lithium fluoride and sodium fluoride have similar densities, being 2.635 and 2.558 g/cc, respectively. Because their densities are similar and the melting point of lithium fluoride is less than sodium fluoride, lithium fluoride might be expected to function as a condensation site as well as sodium fluoride as a nucleating agent.

Other products from this reaction were identified as F-isopropyl F-2-hydrylpropanoate, F-2-hydrylisopropyl propanoate, and F-2-hydrylisopropyl 2-hydrylpropanoate; they had 39, 13 and 8 percent effluent concentrations, respectively. Because the reaction parameters of these two reactions were the same, clearly the

fluorination efficiency was better with sodium fluoride. In the past there has been speculation that the aerosol fluorination reaction utilizes sodium fluoride as a catalyst. The above results, while not conclusive, lend support to this hypothesis. Clearly more research is needed to determine the effects of using different aerosols.

Synthesis of F-tert-Butyl Propanoate

The aerosol fluorination of tert-butyl propanoate produced F-tert-butyl propanoate in a 33 percent yield and 94 percent effluent purity.

Absorptions of this compound in the infrared occurred at 1830(m), 1330(w), 1270(s), 1230(s), 1160(m), 1130(s), 1090(m), 1005(s), 980(s) and 805(w) cm^{-1}. The chemical ionization spectrum gave peaks at m/e = 198 ($C_4F_7OH^+$), 182 ($C_4F_7H^+$), 170 ($C_3F_7H^+$), 166 ($C_3F_6O^+$), 164 ($C_3F_5O_2H^+$), 148 ($C_3F_5OH^+$), 146 ($C_3F_4O_2H_2^+$), 132 ($C_3F_5H^+$), 120 ($C_2F_5H^+$), 101 ($C_2F_4H^+$), 97 ($C_2F_3O^+$), 94 ($C_2F_2O_2^+$) and 69 (CF_3). The electron impact mass spectrum gave peaks at m/e = 147 ($C_3F_5O^+$), 131 ($C_3F_5^+$), 119 ($C_2F_5^+$) and 69 (CF_3^+). The ^{19}F nmr spectrum exhibited a singlet at ϕ = -70.48 ppm which is due to the three equivalent tert-butyl methyl groups. This peak represents the three methyls that are alpha to the ester oxygen. Two other singlets occurred at ϕ = -83.58 ppm and ϕ = -121.52 ppm which corresponded to the other methyl group and the CF_2 group, respectively. Complete characterization details are given in Table B12, Appendix B.

Synthesis of F-Methyl 2-Methoxypropanoate and F-2-Methoxypropanoyl Fluoride

The aerosol direct fluorination of methyl 2-methoxypropanoate, which was supplied by 3M, produced a mixture of F-methyl-2-methoxypropanoate and F-2-methoxypropanoyl fluoride with a combined yield of 55 percent. Difficulty was encountered in separating these two compounds. When the mixture was analyzed by gas chromatography, the relative intensities of the pertinent peaks changed from one analysis to another, suggesting that decomposition of one or both compounds was taking place on the column. To purify these two compounds, a series of fractionations on the vacuum line were made until each compound appeared 95 percent pure by infrared analysis. Even though it was not possible to determine the effluent purity of the two compounds, it is certain that these were the only compounds in the mixture, with the perfluorinated acid fluoride predominating.

The infrared absorptions of F-2-methoxypropanoyl fluoride occurred at 1875(s), 1330(m), 1280(s), 1220(vs), 1150(s), 1120(s), 1090(m), 1000(s), 895(w) and 835(m) cm^{-1}. The infrared absorptions for F-methyl 2-methoxypropanoate occurred at 1830(m), 1285(s), 1250(s), 1230(s), 1175(m), 1145(m), 1125(m) and 1025(m) cm^{-1}.

The ^{19}F nmr spectrum of F-methyl 2-methoxypropanoate gave a doublet at ϕ = -55.44 ppm (relative to $CFCl_3$ internal standard) corresponding to CF_3-O-CF, a singlet at ϕ = -58.53 ppm corresponding to the ester methyl, a doublet at ϕ = -81.63 ppm corresponding to the methyl group and a multiplet at ϕ = -133.50 ppm corresponding to the CF group. The ^{19}F nmr spectrum of F-2-methoxypropanoyl fluoride gave

a triplet at ϕ = -56.17 ppm (relative to $CFCl_3$ internal standard) corresponding to the methoxy group, a doublet of doublets at ϕ = -82.12 ppm corresponding to the methyl group, a multiplet at ϕ = -132.42 corresponding to the CF group and a multiplet at ϕ = +26.96 corresponding to the acid fluoride. Complete details of the characterization of these two compounds are given in Tables B13 and B14, Appendix B.

General Discussion of F-esters

Very few perfluorinated esters have been synthesized in the past. Most previous synthetic procedures involved reacting species that are already highly fluorinated. Careful handling of the perfluorinated esters is required because of their hydrolytic instability which results in the formation of perfluorinated acids. The only previously reported direct method for synthesizing perfluorinated esters is by the "LTG" method.[36] Direct fluorination of an ester often leads to the cleavage of the ester linkage, to give an acid fluoride. In the LTG method, Lagow has been able to preserve up to 80 percent of the ester linkages in selected polyesters. For instance, the LTG method has produced perfluorinated methyl methacrylate from its hydrogen analog.[100] Due to the lack of research in this area, a study pertaining to the ability and limitations of the direct fluorination of esters was desirable.

Because fragmentation of ester linkages can occur upon fluorination, it is important to ascertain what factors influence the fragmentation of the carbon skeleton. While Lagow

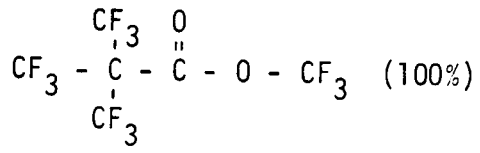
maintained up to 80 percent ester linkages in his compound, the two groups on either side of the carbonyl group were bulky, thus protecting the carbonyl group from fluorine attack. To see how this contributes to the degree of skeletal integrity, a series of esters was perfluorinated by the aerosol method in which the hydrocarbon groups on either side of the ester linkage were changed. These esters along with yields of the various products from the fluorination reactions are listed in Table 4.

A series of methyl esters included tert-butyl, isopropyl and ethyl groups attached to the carbonyl group. Methyl 2-methylpropanoate, which has an isopropyl group attached to the carbonyl group, gave F-methyl 2-methylpropanoate in 64 percent effluent purity. However, 33 percent of this mixture consisted of monohydryl isomers of the ester analog. This means that only 3 percent or less effluent concentration is due to compounds that resulted from ester cleavage. Ester cleavage proceeds by a fluoride attacking the positive carbonyl group. If there is a residual hydrogen on the carbon which is alpha to the carbonyl group, the small positive charge on the carbonyl group is reduced which reduces the propensity for fluoride attack. Therefore, ester cleavage should be enhanced for a perfluorinated ester compared to a partially fluorinated one. To examine the degree of ester cleavage in this series of compounds, comparison of relative yields between the acid fluoride and the perfluorinated ester must be made, rather than effluent purity of the crude product. In the fluorination of methyl 2-methylpropanoate there was 5 percent ester

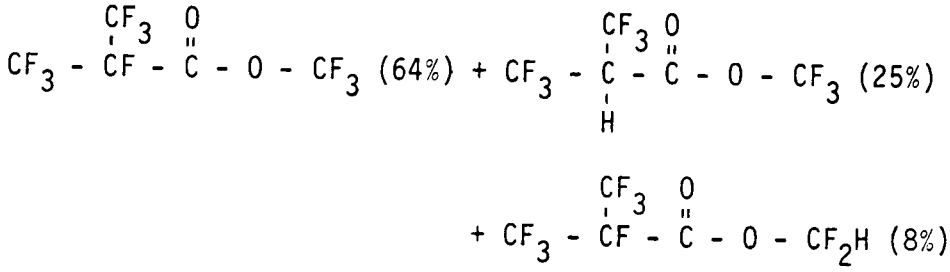
TABLE 4

EFFLUENT PURITIES OF FLUORINATED ESTERS

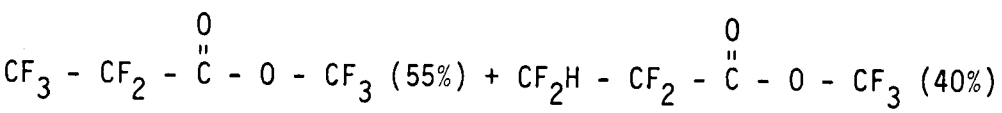
F-Methyl 2,2-dimethylpropanoate



F-Methyl 2,2-dimethylpropanoate



F-Methylpropanoate



F-Ethylpropanoate

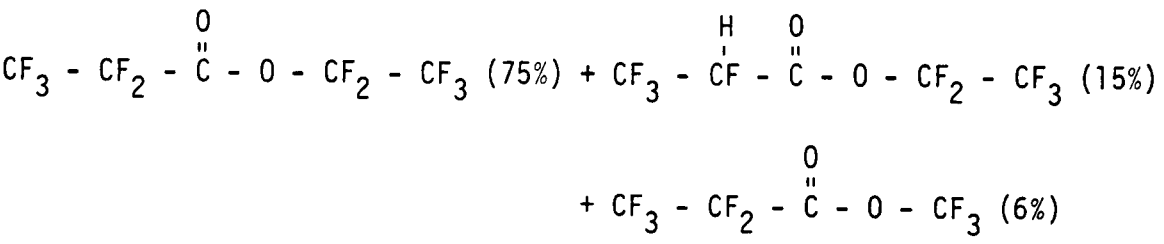
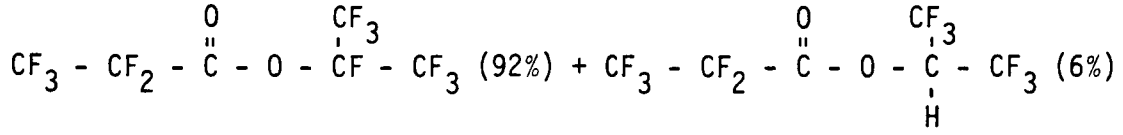
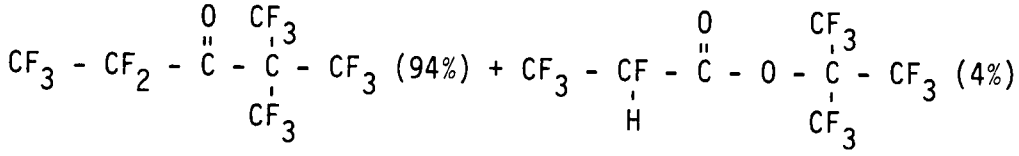


TABLE 4 (continued)

F-Isopropylpropanoate



F-tert-Butylpropanoate



cleavage of the perfluorinated analog. Methyl 2,2-dimethylpropanoate which has a tert-butyl group attached to the carbonyl group gave F-methyl 2,2-dimethylpropanoate with 100 percent effluent purity; thus no ester cleavage resulted. The fluorination of methyl propanoate, on the other hand, produced F-methyl propanoate in 55 percent effluent concentration while 40 percent of the product mixture was due to a monohydryl isomer. The remaining 5 percent (9 percent of perfluorinated analog) in this case was due to perfluorinated acid fluoride resulting from ester cleavage. The above results indicate that ester scission was not a major problem in these reactions, but as the alkyl group that is attached to the carbonyl group becomes less bulky, ester cleavage increases.

The fluorination of methyl 2-methoxypropanoate is anomalous, since the major product was F-2-methoxypropanoyl fluoride. The methoxy group which is attached to the carbon alpha to the carbonyl group should be more electron withdrawing than in the case of methyl 2-methylpropanoate and less electron withdrawing than in the case of methyl propanoate. Since this is intermediate between the two, the expected degree of ester cleavage should be between 5 and 9 percent. Obviously other unknown factors are involved which indicate that the presence of the methoxy group greatly influences the degree of ester cleavage. However, the position of the methoxy group relative to the carbonyl group is more important than just its presence. Presently in our laboratory a co-worker, Marie Brennan, is investigating the aerosol fluorination of methyl 4-methoxybutanoate.

Preliminary results indicate that greater than 80 percent effluent purity of F-methyl 4-methoxybutanoate results from this reaction, with less than 15 percent ester cleavage. In this case the methoxy group is three carbons away from the carbonyl group which substantially reduces its influence on ester cleavage. While the degree of ester cleavage is much less in this case, it is still greater than in any of the cases where alkyl groups were attached to the carbonyl group. Clearly, additional esters with different substituents need to be investigated to determine why this anomaly exists.

In a second series of reactions, ethyl, isopropyl and tert-butyl propanoate were fluorinated. Ethyl propanoate which had the least bulky ester substituent resulted in the largest amount of ester scission but still produced 75 percent of F-ethyl propanoate and 21 percent monohydryl isomers of the ester analog. Only 4 percent (5 percent of the perfluorinated analog) of the products resulted from ester cleavage. Isopropyl propanoate, which has an isopropyl group attached to the ester oxygen, gave 92 percent effluent concentration of F-isopropyl propanoate and 6 percent monohydryl isomers of the ester analog, leaving 2 percent ester cleavage. tert-Butyl propanoate, which has a bulky tertiary butyl group attached to the ester oxygen, gave 94 percent effluent concentration of F-tert-butyl propanoate, 2 percent acid fluoride and 4 percent monohydryl isomers of the ester analog.

Three conclusions can be made from this series of experiments: (1) As the alkyl group that is attached to the carbonyl group becomes more bulky, the carbonyl becomes more protected from attack by fluoride, thus enhancing skeletal integrity. (2) A bulky group attached directly to the carbonyl group influences skeletal integrity more than the same alkyl group attached to the ester oxygen. (3) Methyne/ester linkages are more difficult to fluorinate since they are sterically hindered. Once a methyl group attached to the CH group is perfluorinated, the CH hydrogen is even more sterically hindered than before. The same analogy can be seen from the results of the fluorination of 2,4-dimethylpentane which is discussed later.

While three of the six esters gave effluent concentrations of 92 percent or better for the perfluorinated esters, the lower effluent concentrations for the lower molecular weight esters are due both to the lack of complete perfluorination and fragmentation. Better optimization of the reaction parameters should enhance perfluorination and reduce the monohydryl isomer yield. Cleavage of the ester linkage may not be a major problem in the perfluorination of these esters by the aerosol direct fluorination method. However, better optimization of parameters needs to be achieved to be conclusive.

Aerosol Fluorination of 2,4-Dimethylpentane

The fluorination of 2,4-dimethylpentane gave many products, only five of which were major products. Sufficient material from four of these was available for structure identification and all

identified products contained residual hydrogens. If any of the remaining unidentified minor products were F-2,4-dimethylpentane, its effluent concentration would be 2 percent or less.

As expected, the four identified major products contained residual hydrogens on either carbon two or three or both since these hydrogens are the most highly hindered. The compound that had the highest effluent concentration (23 percent) was identified as F-2-hydryl-2,4-dimethylpentane. Other products were F-2,4-dihydryl-2,4-methylpentane (20 percent effluent concentration), F-2,3-dihydryl-2,4-dimethylpentane (17 percent effluent concentration) and F-3-hydryl-2,4-dimethylpentane (9 percent effluent concentration). Complete characterization of these four compounds are given in Tables B15, B16, B17 and B18, Appendix B.

Synthesis of Monofluorobenzene

The aerosol direct fluorination of benzene yielded fluorobenzene in 1.3 percent yield and 4.0 percent effluent concentration. Because monofluorobenzene has previously been synthesized and characterized, only an infrared spectrum and a mass spectrum were used for identification. The chemical ionization mass spectrum exhibited peaks at m/e = 97 corresponding to the molecular ion plus hydrogen, m/e = 79 corresponding to $C_6H_7^+$, m/e = 78 corresponding to $C_6H_6^+$ and m/e = 77 corresponding to $C_6H_5^+$. The electron impact mass spectrum exhibited peaks at m/e = 96 corresponding to the molecular ion, m/e = 78 corresponding to $C_6H_6^+$, m/e = 70 corresponding to $C_4H_3F^+$ and m/e = 50 corresponding to $C_4H_2^+$. Absorptions in the

infrared spectrum were at 3020(s), 1585(s), 1480(s), 1215(vs) and 730(s) cm^{-1}. Complete characterization details are given in Table B19, Appendix B.

Discussion of Hydrocarbon Fluorinations

Previous studies have shown that a hydrogen on a tertiary carbon is fluorinated easier than one on a secondary carbon and a hydrogen on a secondary carbon is more easily fluorinated than one on a primary carbon.[101] However, these studies were carried out in liquid phase at a low temperature (-80°C) and dealt only with monofluorination.

The purpose in choosing 2,4-dimethylpentane as a model was to determine if aerosol fluorination gave fluorination of all sites. Because the molecule has only three hydrogen environments, the number of isomers upon the synthesis of the mono- and dihydryl fluorinated analog is limited. The highly symmetrical hydrocarbon has twelve identical primary hydrogens, two identical secondary hydrogens and two identical tertiary hydrogens giving a 1°:2°:3° hydrogen ratio of 6:1:1.

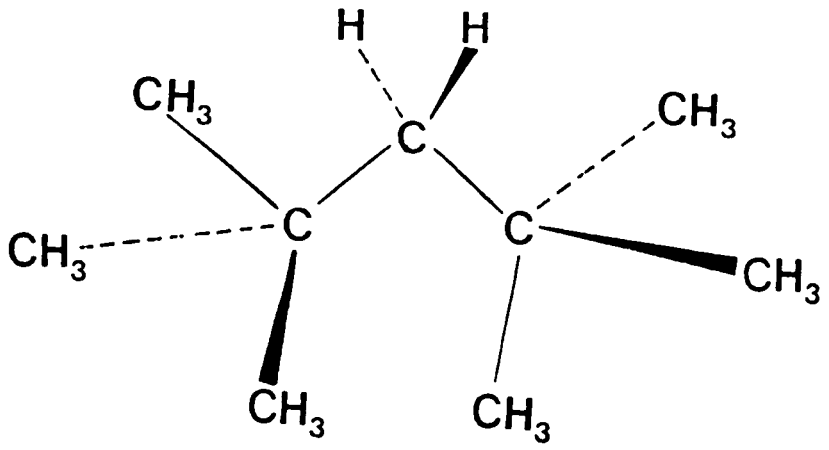
If fluorine attack on various carbon centers in the hydrocarbon is statistical, monohydryl isomers should occur in this compound with a 6:1:1 ratio for the hydrylmethyl-, hydrylmethylene- and hydrylmethyne isomers. No previous studies have been undertaken on the aerosol fluorination system pertaining to preferential fluorine reactivity of a methyne or a methylene. However, Adcock and

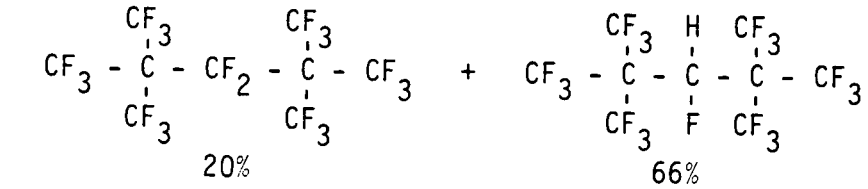
co-workers found[51] that, in the fluorination of neopentane, statistical substitution of hydrogens holds true until pentafluoroneopentane (42 percent fluorination) is obtained. At this point these researchers showed that a hydrogen on a CH_3 group is more reactive than a hydrogen on a CH_2F or CHF_2 group. As the degree of fluorination increases, reactivity of the hydrogen on a CH_2F group is greater than the hydrogen on a CHF_2 group. The apparent order of hydrogen reactivity is $CH_3 > CH_2F > CHF_2$. The yields of various isomers of fluorinated neopentane indicate that fluorine prefers to react with the more electron-rich hydrogens.

A similar compound, 2,2,4,4-tetramethylpentane has been fluorinated by the LTG technique.[47] The structure of this compound and the structures and the yields of the various products are given in Table 5. The reaction gave three isomers: F-2,2,4,4-tetramethylpentane (20 percent), F-3,3-dihydryl-2,2,4,4-tetramethylpentane (66 percent) and F-3,3-dihydryl-2,2,4,4-tetramethylpentane (14 percent). Even though the degree of fluorination of this compound is much higher than for 2,4-dimethylpentane, 2,2,4,4-tetramethylpentane does not contain the sterically hindered CH group that 2,4-dimethylpentane has. All hydrogens in 2,2,4,4-tetramethylpentane are accessible to fluorine attack, except those on the methylene carbon. Lagow reported that the isomers containing residual hydrogens were inert to further fluorination.[47] Lagow concluded that, before any reasonable degree of fluorination of this compound is achieved, the CH_2 group must first be fluorinated if the perfluorinated analog is to be produced.

TABLE 5

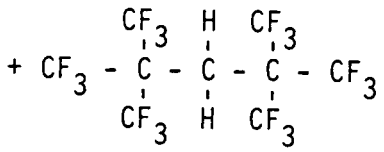
2,2,4,4-TETRAMETHYLPENTANE





20%

66%



14%

Once the methyl groups are fluorinated the CH_2 groups become sterically hindered and thus protected from fluorine attack.

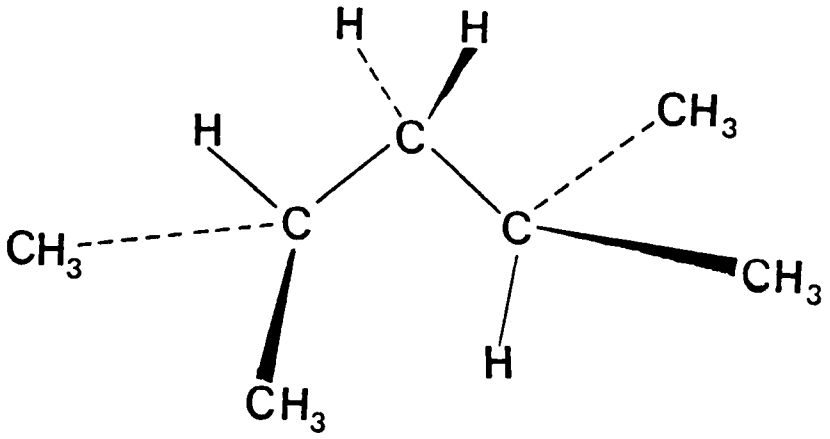
The structure of 2,4-dimethylpentane and the structures and yields of the identified products are given in Table 6. The results clearly indicate that fluorination does not proceed statistically because there were no products that contained methyl hydrogens. Since the two products that had the highest effluent concentration contained a methyne hydrogen, one can conclude that steric effects play a substantial role in preferential fluorine attack.

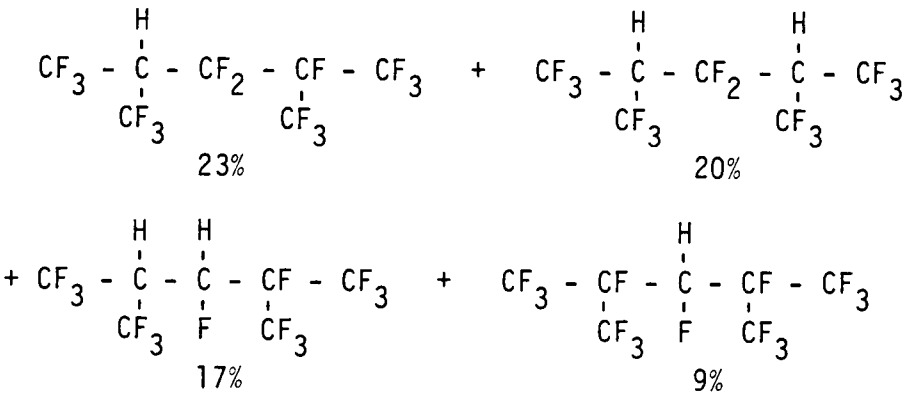
The synthesis of monofluorobenzene can be carried out by several routes. For instance, electrochemical oxidation of benzene in the presence of a fluoride ion is reported to provide monofluorination.[102] Reaction of benzene with XeF_2 gave fluorobenzene in a 68 percent yield.[103,104] Likewise, benzene reacts with silver difluoride to give monofluorobenzene.[105] Grakauskas developed a direct fluorination method in the liquid phase.[106] Benzene reacts with a complex diazonium fluoride to give fluorobenzene.[107] Monofluorobenzene has also been synthesized by introduction of fluorine by diazotization in anhydrous hydrogen fluoride.[108,109]

Past experience has shown that attempts to perfluorinate benzene by the direct aerosol technique gave instead perfluorinated cyclohexane. In order to limit the degree of fluorination so that monofluorination occurs, a system highly diluted with helium is required and a very fine control of the fluorine flow. Although the aerosol fluorination reactor was not designed for monofluorination,

TABLE 6

2,4-DIMETHYLPENTANE





it did work well in the present case and with some minor modifications, the yields of fluorobenzene could be greatly enhanced. A major problem that developed during the course of these experiments was benzene condensation on the cold reactor walls. The vertical reactor should help overcome this problem and enhance yields.

CHAPTER IV

SUMMARY

A series of perfluoroesters and perfluoroethers were synthesized by the aerosol direct fluorination technique. In all cases the hydrogen analog was used as the starting material. The study of the synthesis of the perfluoroesters showed that in the aerosol fluorination system the cleavage of the ester linkage is generally not a major problem. A series of perfluorinated glyme ethers were synthesized with the largest of these compounds being perfluorinated tetraethylene glycol dimethyl ether which has the highest molecular weight of any compound synthesized by the aerosol fluorination process to date. A compound containing sterically hindered hydrogens, 2,4-dimethylpentane, was fluorinated to ascertain the limitations of the aerosol fluorination system. An epoxide, perfluorocyclohexene oxide, was synthesized making available a monomer which can possibly be made into a useful polymer. Monofluorobenzene was synthesized by this one-step process utilizing fine control of the reactor system. The perfluorinated products, several of which have been synthesized by other methods, were characterized by electron impact and chemical ionization mass spectrometry, infrared analysis and both ^{19}F and ^{1}H nmr spectroscopy.

While throughput yields based on reactant input into the reactor system have often been less than desirable, effluent

concentrations of the desired perfluorinated product are usually high. A series of experiments were conducted to determine where losses in the reactor system occur. Modifications and improvements were made to the fluorinator to overcome these losses and to show that this synthetic technique for many classes of perfluorinated compounds is clearly the method of choice.

LIST OF REFERENCES

LIST OF REFERENCES

1. H. Moissan, Comp. Read., 110, 951 (1890).
2. P. Lebeau and A. Damiens, Comp. Read., 182, 1340 (1926).
3. P. Lebeau and A. Damiens, Comp. Read., 191, 939 (1930).
4. F. S. Swarts, Bull. Sci. Acad. Roy. Gelg., 17 27 (1931).
5. O. Ruff and O. Bretschneider, Z. Org. Chem., 210, 173 (1933).
6. O. Ruff, O. Bretschneider and R. Ebert, Z. Org. Chem., 217, 1 (1934).
7. O. Croft, Quart. Rev., 14, 1 (1960).
8. E. G. locke, W. R. Brode and A. L. Henne, J. Am. Chem. Soc., 55, 273 (1933).
9. J. H. Simons and L. P. Block, J. Am. Chem. Soc., 59, 1407 (1937).
10. J. H. Simons and L. P. Block, J. Am. Chem. Soc., 61, 2962 (1937).
11. W. Bockemuller, Annalen, 506, 20 (1933).
12. L. A. Bigelow, in "Fluorine Chemistry," Vol. 1, J. H. Simons, Ed., Academic Press, New York, 1970, p. 373.
13. W. K. R. Musgrave and F. Smith, J. Chem. Soc., 3201 (1949).
14. W. K. R. Musgrave and F. Smith, J. Chem. Soc., 3026 (1949).
15. R. N. Haszeldine and F. Smith, J. Chem. Soc., 2689 (1950).
16. R. HN. Haszeldine and F. Smith, J. Chem. Soc., 2787 (1950).
17. E. A. Tyczkowski and L. A. Bigelow, J. Am. Chem. Soc., 77, 3007 (1955).
18. A. F. Maxwell, F. E. Detoro and L. A. Bigelow, J. Am. Chem. Soc., 82, 5827 (1960).

19. B. C. Bishop, J. B. Hynes and L. A. Bigelow, J. Am. Chem. Soc., 86, 1827 (1964).

20. R. D. Fowler, W. B. Burford, J. M. Hamilton, R. G. Sweet, C. E. Weber, J. S. Kasper and I. Litant, Ind. Eng. Chem., 39, 292 (1947).

21. M. Stacey and J. C. Tatlow in "Advances in Fluorine Chemistry," Vol. 1, M. Stacey, J. C. Tatlow and A. G. Sharpe, Eds., Butterworths, London, 1960, p. 166.

22. J. S. Simons, T. J. Brice, R. J. Dresdner, C. E. Francis, H. R. Hurland, J. D. Hogg, W. H. Pearlson and R. D. Wilson, J. Electrochem. Soc., 95, 47 (1949).

23. J. H. Simons in "Fluorine Chemistry," Vol. 1, J. H. Simons, Ed., Academic Press, New York, 1950, p. 414.

24. J. H. Simons and T. J. Brice in "Fluorine Chemistry," Vol. 2, J. H. Simons, Ed., Academic Press, New York, 1954, p. 333.

25. S. Nagase in "Fluorine Chemistry Reviews," Vol. 1, R. Tarrant, Ed., Dekker, New York, 1967, p. 77.

26. J. Burden and J. C. Tatlow in "Advances in Fluorine Chemistry," Vol. 1, M. Stacey, J. C. Tatlow and A. G. Sharpe, Eds., Butterworths, London, 1960, p. 129.

27. R. J. Lagow and J. L. Margrave in "Progress in Inorganic Chemistry," Vol. 26, S. J. Lippard, Ed., John Wiley and Sons, New York, 1979, p. 161.

28. R. J. Lagow and J. L. Margrave, Proc. Natl. Acad. Sci. U.S., 67, 4, 8A (1970).

29. D. Glasgow, Chem. Eng. News, 40 (1974).

30. N. J. Maraschin and R. J. Lagow, J. Am. Chem. Soc., 94, 8601 (1972).

31. N. J. Maraschin and R. J. Lagow, Inorg. Chem., 12, 1459 (1973).

32. J. L. Adcock and R. J. Lagow, J. Org. Chem., 38, 3717 (1973).

33. G. E. Gerhardt and R. J. Lagow, Chem. Commun., 8, 259 (1977).

34. G. E. Gerhardt and R. J. Lagow, J. Org. Chem., 43, 4505 (1978).

35. R. J. Lagow and S. Inoue, U.S. Patent 4,113,772 (1978).

36. R. J. Lagow, U.S. Patent 4,076,916 (1978).

37. R. J. Lagow and J. L. Margrave, Inorg. Nucl. Chem., 35, 2084 (1973).

38. N. J. Maraschin and R. J. Lagow, Inorg. Chem., 14, 1855 (1975).

39. E. K. S. Liu and R. J. Lagow, J. Am. Chem. Soc., 98, 8270 (1976).

40. E. K. S. Liu and R. J. Lagow, J. Orgnometal. Chem., 145, 161 (1978).

41. E. K. S. Liu and R. J. Lagow, Chem. Commun., 8, 450 (1977).

42. R. J. Lagow, R. B. Baddachhape, J. L. Wood and J. L. Margrave, J. Chem. Soc., 1268 (1974).

43. R. J. Lagow, R. B. Baddachhape, J. L. Wood and J. L. Margrave, J. Am. Chem. Soc., 96, 2381 (1974).

44. N. J. Maraschin and R. J. Lagow, Inorg. Chem., 12, 1459 (1973).

45. N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen and R. J. Lagow, J. Am. Chem. Soc., 97, 513 (1975).

46. G. Robertson and E. K. S. Liu, J. Org. Chem., 43, 4981 (1978).

47. L. A. Shimp and R. J. Lagow, J. Org. Chem., 42, 3437 (1976).

48. J. L. Adcock and R. J. Lagor, J. Org. Chem., 38, 2617 (1973).

49. J. L. Adcock and R. J. Lagow, J. Am. Chem, Soc., 96, 7588 (1974).

50. J. L. Adcock, R. A. Beh and R. J. Lagow, J. Org. Chem., 40, 3271 (1975).

51. J. L. Adcock, K. Horita and E. B. Renk, J. Am. Chem. Soc., 103, 6937 (1981).

52. J. L. Adcock and E. B. Renk, U.S. Patent 4,330,475 (1982).

53. J. L. Adcock and M. L. Robin, J. Org. Chem., 49, 191 (1984).

54. J. L. Adcock and M. L. Cherry, J. Fluoring Chem., submitted.

55. J. L. Adcock and M. L. Cherry, J. Org. Chem., submitted.

56. W. D. Evans, "The Utility of Aerosol Direct Fluorinatino for the Preparation of Functional Fluorocarbons," Dissertation, The University of Tennessee, Knoxville, 1963, p. 65.

57. J. L. Adcock and M. L. Robin, J. Org. Chem., 49, 1442 (1984).

58. J. L. Adcock and M. L. Robin, J. Org. Chem., 48. 2437 (1983).

59. J. L. Adcock, W. D. Evans and L. Heller-Grossman, J. Org. Chem., 48, 4953 (1983).

60. J. L. Adcock and W. D. Evans, J. Org. Chem., 49, 2719 (1984).

61. R. E. Banks in "Fluorocarbons and Their Derivatives," McDonald and Co. Ltd., London, 1970, p. 161.

62. L. Holland, L. Laurenson, P. N. Baker and H. J. Davis, Nature, 238, 36 (1972).

63. M. A. Baker, L. Holland and L. Laurenson, Vacuum, 21, 479 (1971).

64. G. Caporiccio, C. Corti, S. Soldini and A. Rolando, Ind. Eng. Chem. Prod. Res. Dev., 21, 520 (1982).

65. K. J. L. Paciorek, J. Kaufman, J. H. Nakajara, T. I. Ito, R. H. Kratzer, R. W. Rosser and J. A. Parker, J. Fluorine Chem., 10, 277 (1977).

66. J. H. Simons, J. Electrochem. Soc., 95, 47 (1949).

67. A. L. Henne and S. B. Richter, J. Am. Chem. Soc., 74, 5421 (1952).

68. P. G. Thompson, J. Am. Chem. Soc., 89, 4316 (1967).

69. J. H. Prager, J. Org. Chem., 31, 392 (1966).

70. E. A. Kauck and J. H. Simons (to Minnesota Mining and Manufacturing Co.) British Patent 672,720 (1952).

71. G. E. Gerhardt and R. J. Iagow, J. Chem. Soc. Chem. Commun., 8, 259 (1977).

72. G. E. Gerhardt, E. T. Dumitri and R. J. Lagow, J. Polym. Sci., Polym. Chem. Ed., 18, 157 (1981).

73. G. E. Gerhardt and R. J. Lagow, J. Chem. Soc. Perkin Trans. 1, 5, 1321 (1981).

74. G. E. Gerhardt and R. J. Lagow, J. Org. Chem., 43, 4505 (1978).

75. Y. Tabata, W. Ito, K. Oshima and Y. Yamamota, Adv. Chem. Ser., 129 (1973).

76. R. D. Bagnall, W. Bell and K. Pearson, J. Fluorine Chem., 9, 359 (1977).

77. E. L. Varetti and P. J. Aymonio, Chem. Commun., 680 (1967).

78. M. S. Toy and R. S. Stringham, J. Fluorine Chem., 5, 25 (1975).

79. M. S. Toy and R. S. Stringham, J. Fluorine Chem., 5, 481 (1975).

80. D. Sianesi, G. Bernardi and G. Moggi, French Patent 1,531,902 (1968).

81. D. Sianesi, G. Bernardi and G. Moggi, French Patent 1,545,639 (1968).

82. D. Sianesi, A. Pasetti and C. Corti, British Patent 1,104,482 (1968).

83. D. Sianesi, A. Pasetti, R. Fontanelli, G. C. Bernardi and G. Caporiccio, Chem. Inc., 55, 208 (1973).

84. A. M. Lovebee, D. A. Rausch and W. Postelnek in "Aliphatic Fluorine Compounds," Reinhold Publishing Co., New York, 1958, p. 230.

85. R. J. DePasquale, J. Org. Chem., 38, 3025 (1973).

86. D. A. Couch, R. A. De Marco and J. M. Shreeve, J. Chem. Soc. D, 2, 91 (1971).

87. R. A. De Marco, D. A. Couch and J. M. Shreeve, J. Org. Chem., 37, 3332 (1972).

88. E. A. Lawton, D. Pilipovich and R. D. Wilson, Inorg. Chem., 4, 118 (1965).

89. P. G. Johnson and B. Tittle, J. Fluorine Chem., 3, 1 (1973).

90. I. S. Chang, J. T. Price, A. J. Tomlinson and C. J. Willis, Canad. J. Chem., 5-, 512 (1972).

91. N. S. Walker and D. D. Desmarteau, J. Fluorine Chem., 5, 135 (1975).

92. A. Majid and J. M. Shreeve, J. Org. Chem., 38, 4028 (1973).

93. R. Vivilecchia and B. L. Karger, J. Am. Chem. Soc., 93, 6593 (1971).

94. Sadtler Research Laboratories, 24014K (1972).

95. Sadtler Research Laboratories, 136K (1972).

96. W. Espenscheid, E. Matijevic and M. Kerber, J. Phy. Chem., 68, 2831 (1964).

97. P. L. Coe, J. H. Sleigh and J. C. Tatlow, J. Fluorine Chem., 15, 339 (1980).

98. J. H. Simons, U.S. Patent 2,500,388 (1950).

99. V. V. Berenblit, Y. P. Dolnakov, V. P. Sass, L. N. Senyushov and S. V. Soklov, Zhur. Org. Khim., 10, 2031 (1974).

100. R. J. Lagow and J. L. Margrave in "Progress in Inorganic Chemistry," Vol. 26, S. J. Lippard, Ed., John Wiley and Sons, New York, 1979, p. 169.

101. J. M. Tedder in "Advances in Fluorine Chemistry," Vol. 2, M. Stacey, J. C. Tatlow and A. G. Sharpe, Eds., Butterworths, London, 1961, p. 105.

102. A. N. Rozhkov, A. V. Bukjtiarov and I. L. Knunjants, Isv. Akad. Nauk. SSSR, Ser. Khim., 5, 1130 (1972).

103. D. H. R. Burton, J. Chem. Soc., Chem. Commun., 806 (1968).

104. D. H. R. Burton, J. Chem. Soc., Perkin Trans. 1, 2889 (1972).

105. A. Zqeig, R. G. Fischer and J. E. Lancaster, J. Org. Chem., 45, 3597 (1980).

106. V. Grakauskas, J. Org. Chem., 35, 723 (1970).

107. P. H. Cheek, R. H. Wiley and A. Roe, J. Am. Chem. Soc., 71, 1863 (1949).

108. R. L. Ferm, C. A. Van der Werf, J. Am. Chem. Soc., 72, 4809 (1950).

109. W. J. Shenk and G. R. Pellon, U.S. Patent 2,563,796 (1952).

APPENDICES

APPENDIX A

TABLE A1

AEROSOL FLUORINATION OF ETHYLENE GLYCOL DIMETHYL ETHER

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	14
Helium diluent (cc/min)	
Module 1	140
Module 2	130
Module 3	150
Reactor temperature (°C)	
Module 1	-40
Module 2	-30
Module 3	0
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	120
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Tertiary	-
Hydrocarbon throughput (mmol/hr)	4.83
Reaction time (hr)	4.0
Overall F_2:hydrocarbon ratio	30:1
Product[a] distribution, % collected	98
Product yield (grams)	2.29
Product yield, % theoretical	36

[a] F-Ethylene glycol dimethyl ether

TABLE A2

AEROSOL FLUORINATION OF BIS-2-METHOXYETHYL ETHER

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	18
Helium diluent (cc/min)	
Module 1	140
Module 2	130
Module 3	150
Reactor temperature (°C)	
Module 1	-40
Module 2	-30
Module 3	0
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	200
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Tertiary	-
Hydrocarbon throughput (mmol/hr)	3.50
Reaction time (hr)	4.0
Overall F_2:hydrocarbon ratio	44:1
Product[a] distribution, % collected	89
Product yield (grams)	1.60
Product yield, % theoretical	22

[a] F-Bis-2-methoxyethyl ether

TABLE A3

AEROSOL FLUORINATION OF TRIETHYLENE GLYCOL DIMETHYL ETHER

Parameters	Reaction 1	2	3
Fluorine flows (cc/min)			
Module 1	20	20	20
Module 2	20	20	20
Module 3	35	35	35
Helium diluent (cc/min)			
Module 1	140	140	140
Module 2	130	130	130
Module 3	150	150	150
Reactor temperature (°C)			
Module 1	-40	-20	-20
Module 2	-30	-10	-10
Module 3	0	0	0
Main carrier helium (cc/min)	500	500	500
Evaporator/sublimator temp (°C)	240	240	250
Evaporator/sublimator flows (cc/min)			
Primary	450	450	450
Secondary	50	50	50
Tertiary	-	-	-
Hydrocarbon throughput (mmol/hr)	2.77	2.77	2.77
Reaction time (hr)	4.0	4.0	4.0
Overall F_2:hydrocarbon ratio	72:1	72:1	72:1
Product[a] distribution, % collected	91	81	91
Product yield (grams)	1.16	2.06	1.01
Product yield, % theoretical	20	30	17

[a] F-Triethylene glycol dimethyl ether

TABLE A4

AEROSOL FLUORINATION OF TETRAETHYLENE GLYCOL DIMETHYL ETHER

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	35
Helium diluent (cc/min)	
Module 1	140
Module 2	130
Module 3	150
Reactor temperature (°C)	
Module 1	-40
Module 2	-30
Module 3	0
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	300
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Tertiary	-
Hydrocarbon throughput (mmol/hr)	2.28
Reaction time (hr)	4.0
Overall F_2:hydrocarbon ratio	88:1
Product[a] distribution, % collected	94
Product yield (grams)	1.02
Product yield, % theoretical	15

[a] F-Tetraethylene glycol dimethyl ether

TABLE A5

AEROSOL FLUORINATION OF BORNYL METHYL ETHER

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	70
Helium diluent (cc/min)	
Module 1	150
Module 2	130
Module 3	150
Reactor temperature (°C)	
Module 1	-40
Module 2	-30
Module 3	0
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	200
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Tertiary	-
Hydrocarbon throughput (mmol/hr)	3.9
Reaction time (hr)	4.0
Overall F_2:hydrocarbon ratio	76:1
Product[a] distribution, % collected	91
Product yield (grams)	0.94
Product yield, % theoretical	11

[a] F-Bornyl methyl ether

TABLE A6

AEROSOL FLUORINATION OF CYCLOHEXENE OXIDE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1 - Top	5
Module 1 - Bottom	12
Module 2 - Top	20
Module 2 - Bottom	-
Helium diluent (cc/min)	
Module 1 - Top	150
Module 1 - Bottom	150
Module 2 - Top	150
Module 2 - Bottom	-
Reactor temperature (°C)	
Module 1	-20
Module 2	-10
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	129
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Hydrocarbon throughput (mmol/hr)	5.0
Reaction time (hr)	5.0
Overall F_2:hydrocarbon ratio	20:1
Product[a] distribution, % collected	65
Product yield (grams)	3.0
Product yield, % theoretical	27

[a] F-cyclohexene oxide

TABLE A7

AEROSOL FLUORINATION OF METHYL 2,2-DIMETHYLPROPANOATE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1 - Top	5
Module 1 - Bottom	8
Module 2 - Top	20
Module 2 - Bottom	-
Helium diluent (cc/min)	
Module 1 - Top	150
Module 1 - Bottom	150
Module 2 - Top	150
Module 2 - Bottom	-
Reactor temperature (°C)	
Module 1	-20
Module 2	-10
Main carrier helium (cc/min)	500
Evaporator/Sublimator temp (°C)	110
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Hydrocarbon throughput (mmol/hr)	3.84
Reaction time (hr)	5.0
Overall F_2:hydrocarbon ratio	30:1
Product[a] distribution, % collected	100
Product yield (grams)	5.5
Product yield, % theoretical	86

[a] F-methyl 2,2-dimethylpropanoate

TABLE A8

AEROSOL FLUORINATION OF METHYL 2-METHYLPROPANOATE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1 - Top	5
Module 1 - Bottom	16
Module 2 - Top	20
Module 2 - Bottom	-
Helium diluent (cc/min)	
Module 1 - Top	150
Module 1 - Bottom	150
Module 2 - Top	150
Module 2 - Bottom	-
Reactor temperature (°C)	
Module 1	-20
Module 2	-10
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	110
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Hydrocarbon throughput (mmol/hr)	4.4
Reaction time (hr)	6.0
Overall F_2:hydrocarbon ratio	25:1
Product[a] distribution, % collected	64
Product yield (grams)	3.5
Product yield, % theoretical	48

[a] F-methyl 2-methylpropanoate

TABLE A9

AEROSOL FLUORINATION OF METHYL PROPANOATE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1 - Top	5
Module 1 - Bottom	13
Module 2 - Top	20
Module 2 - Bottom	-
Helium diluent (cc/min)	
Module 1 - Top	150
Module 1 - Bottom	150
Module 2 - Top	150
Module 2 - Bottom	-
Reactor temperature (°C)	
Module 1	-20
Module 2	-10
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	95
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Hydrocarbon throughput (mmol/hr)	5.2
Reaction time (hr)	6.0
Overall F_2:hydrocarbon ratio	25:1
Product[a] distribution, % collected	55
Product yield (grams)	3.1
Product yield, % theoretical	43

[a] F-methyl propanoate

TABLE A10

AEROSOL FLUORINATION OF ETHYL PROPANOATE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1 - Top	5
Module 1 - Bottom	16
Module 2 - Top	20
Module 2 - Bottom	-
Helium diluent (cc/min)	
Module 1 - Top	150
Module 1 - Bottom	150
Module 2 - Top	150
Module 2 - Bottom	-
Reactor temperature (°C)	
Module 1	-20
Module 2	-10
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	115
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Hydrocarbon throughput (mmol/hr)	4.1
Reaction time (hr)	6.0
Overall F_2:hydrocarbon ratio	27:1
Product[a] distribution, % collected	75
Product yield (grams)	3.5
Product yield, % theoretical	23

[a] F-ethyl propanoate

TABLE A11

AEROSOL FLUORINATION OF ISOPROPYL PROPANOATE

Parameters	Reaction 1	Reaction 2[b]
Fluorine flows (cc/min)		
Module 1 - Top	5	5
Module 1 - Bottom	17	17
Module 2 - Top	20	20
Module 2 - Bottom	-	-
Helium diluent (cc/min)		
Module 1 - Top	150	150
Module 1 - Bottom	150	150
Module 2 - Top	150	150
Module 2 - Bottom	-	-
Reactor temperature (°C)		
Module 1	-20	-20
Module 2	-10	-10
Main carrier helium (cc/min)	500	500
Evaporator/sublimator temp (°C)	125	125
Evaporator/sublimator flows (cc/min)		
Primary	450	450
Secondary	50	50
Hydrocarbon throughput (mmol/hr)	3.7	3.7
Reaction time (hr)	6.0	6.0
Overall F_2:hydrocarbon ratio	30:1	30:1
Product[a] distribution, % collected	92	40
Product yield (grams)	4.9	1.4
Product yield, % theoretical	65	19

[a] F-isopropyl propanoate

[b] Condensing particulate was LiF

TABLE A12

AEROSOL FLUORINATION OF TERT-BUTYL PROPANOATE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1 - Top	5
Module 1 - Bottom	18
Module 2 - Top	20
Module 2 - Bottom	-
Helium diluent (cc/min)	
Module 1 - Top	150
Module 1 - Bottom	150
Module 2 - Top	150
Module 2 - Bottom	-
Reactor temperature (°C)	
Module 1	-20
Module 2	-10
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	130
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Hydrocarbon throughput (mmol/hr)	3.3
Reaction time (hr)	6.0
Overall F_2:hydrocarbon ratio	36:1
Product[a] distribution, % collected	94
Product yield (grams)	2.5
Product yield, % theoretical	33

[a] F-tertiarybutyl propanoate

TABLE A13

AEROSOL FLUORINATION OF METHYL 2-METHOXYPROPANOATE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	5
Module 2	22
Module 3	20
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperature (°C)	
Module 1	0
Module 2	0
Module 3	0
Main carrier helium (cc/min)	500
Evaporator/sublimator temp (°C)	125
Evaporator/sublimator flows (cc/min)	
Primary	450
Secondary	50
Tertiary	-
Hydrocarbon throughput (mmol/hr)	4.2
Reaction time (hr)	7
Overall F_2:hydrocarbon ratio	30:1
Product yield[a] (grams)	2.6
Product yield,[a] % theoretical	55

[a] F-methyl 2-methoxypropanoate plus F-2-methoxypropanoyl fluoride

TABLE A14

AEROSOL FLUORINATION OF 2,4-DIMETHYLPENTANE

Parameters	Reaction 1	2	3	4
Fluorine flows (cc/min)				
Module 1	20	0	0	5
Module 2	20	10	5	10
Module 3	40	35	15	45
Helium diluent (cc/min)				
Module 1	140	140	140	150
Module 2	140	140	140	130
Module 3	140	140	140	140
Reactor temperature (°C)				
Module 1	5	-10	-10	-10
Module 2	5	-5	-5	-5
Module 3	5	0	0	0
Main carrier helium (cc/min)	500	500	500	500
Evaporator/sublimator temp (°C)	150	150	150	110
Evaporator/sublimator flows (cc/min)				
Primary	450	450	450	450
Secondary	50	50	50	50
Tertiary	-	-	-	-
Hydrocarbon throughput (mmol/hr)	3.35	1.65	1.67	3.35
Reaction time (hr)	4.0	5.0	5.0	4.0
Overall F_2:hydrocarbon ratio	64:1	73:1	32:1	48:1

TABLE A15

AEROSOL FLUORINATION OF BENZENE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	1.2
Module 2	-
Module 3	-
Helium diluent (cc/min)	
Module 1	135
Module 2	150
Module 3	145
Reactor temperature (°C)	
Module 1	-40
Module 2	-40
Module 3	-25
Main carrier helium (cc/min)	800
Evaporator/sublimator temp (°C)	100
Evaporator/sublimator flows (cc/min)	
Primary	400
Secondary	10
Tertiary	-
Hydrocarbon throughput (mmol/hr)	4.22
Reaction time (hr)	4.0
Overall F_2:hydrocarbon ratio	0.60:1
Product[a] distribution, % collected	4
Product yield (grams)	0.505
Product yield, % theoretical	7.2

[a]Fluorobenzene

APPENDIX B

TABLE B1

CHARACTERIZATION OF F-ETHYLENE GLYCOL DIMETHYL ETHER

Infrared (cm^{-1}):
1410(w), 1295(s), 1250(s), 1200(w), 1170(sh), 1155(s), 1105(w),
923(w), 887(m), 865(w), 819(w), 730(w), 690(w).

TABLE B2

CHARACTERIZATION OF F-BIS-2-METHOXYETHYL ETHER

Infrared (cm^{-1}):
1385(w), 1295(s), 1250(s), 1220(sh), 1200(w), 1165(s), 1145(s), 920(w), 900(w), 770(m), 730(m).

TABLE B3

CHARACTERIZATION OF F-TRIETHYLENE GLYCOL DIMETHYL ETHER

Infrared (cm^{-1}):

1290(s), 1245(vs), 1230(s), 1200(m), 1169(vs), 1140(s), 900(w), 790(w), 738(w), 685(w)

Mass Spectra [m/e (int.) formula]:

CI (CH_4):

266(39)$C_5F_{10}O$; 200(63)C_4F_8; 185(22)C_3F_7O; 163(6)$C_3F_5O_2$; 135(13)C_2F_5O; 121(8)CF_4O_2H; 119(55)C_2F_6; 117(43)C_5F_3; 113(28)$C_2F_3O_2$; 103(21)C_4F_2OH; 101(37)CF_4O_2; 99(42)$C_4F_2O_2$; 97(39)C_2F_3O; 95(100) C_5FO; 87(14)C_3F_2O; 85(20)CF_3O; 83(17)CO_2F_2H; 81(30)C_2F_3; 79(64)C_2OF_2H; 77(81)$X_2O_2FH_2$; 75(34)C_2O_2F; 69(93)XF_3; 67(27)CF_2OH;

EI (70eV):

185(6)C_3F_7O; 135(12)C_2F_5O; 119(100)C_2F_5; 100(6)C_2F_4; 85(6)CF_3O; 81(14)C_2F_3; 69(94)CF_3

---

^{19}F NMR [ϕ_{CFCl_3} = 0.0 ppm; ø (mult.); integral]:

CF_3-O-CF_2-CF_2-O-CF_2-CF_2-O-CF_2-CF_2-O-CF_3

A C B

ϕ_A = -55.93 ppm (t); 3 J_{ac} = 9.16 Hz

ϕ_B = -89.27 ppm (s); 4

ϕ_C = -91.31 ppm (d); 2

TABLE B4

CHARACTERIZATION OF F-TETRAETHYLENE GLYCOL DIMETHYL ETHER

Infrared (cm^{-1})

1280(s), 1235(vs), 1215(s), 1190(s), 1150(s), 1125(s), 1020(m), 895(w), 835(w), 750(w), 720(w),

---

Mass Spectra [m/e (int.) formula]:

CI (CH_4):

185(37) C_3F_7O; 135(32)C_2F_5O; 121(13)CF_4O_2H; 119(100)C_2F_6; 117(51)C_5F_3; 105(9)C_4F_3; 103(63)C_2F_4OH; 101(97)CF_4O_2; 99(6)$C_4F_2O_2$; 97(38)C_2F_3O; 95(5)C_5FO; 87(6)C_3F_2O; 77(13)$C_2O_2FH_2$; 75(13)C_2O_2F; 69(29)CF_3; 67(11)CF_2OH;

EI (70eV):

119(2)C_2F_5; 100(16)C_2F_4; 69(100)CF_3; 50(13)CF_2;

---

^{19}F NMR [ϕ_{CFCl_3} = 0.0 PPM; ϕ (mult.); integral]:

CF_3-O-CF_2-CF_2-O-CF_2-CF_2-O-CF_2-CF_2-O-CF_2-CF_2-O-CF_3

A C B

ϕ_A = -55.97 ppm (t); 3 J_{ac} = 9.16 Hz

ϕ_B = -89.34 ppm (s); 6

ϕ_C = -91.35 ppm (d); 2

TABLE B5

CHARACTERIZATION OF F-BORNYL METHYL ETHER

Infrared (cm^{-1}):

1320(m), 1275(s), 1240(s), 1190(s), 1175(m), 1135(m), 1115(m), 1060(m), 1020(m), 990(m), 950(w), 720(m).

^{19}F NMR [$\emptyset_{CFCl_3}$ = 0.0 ppm]:

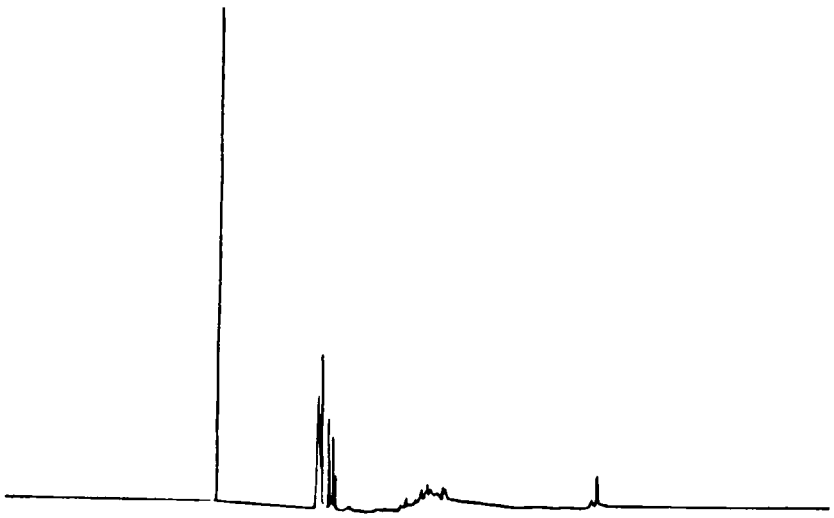


TABLE B6

CHARACTERIZATION OF F-CYCLOHEXENE OXIDE

Mass Spectra [m/e (int.) formula]:

CI(CH_4):

279(40)$C_6F_{10}OH$; 259(24)C_6F_9O; 231(22)C_5F_9; 228(33)C_5F_8O;
131(16)C_3F_5; 103(34)C_4F_2OH; 101(56)C_2F_4H; 97(20)C_2F_3O;
69(17)CF_3; 59(100)C_2FO

^{19}F NMR [$\emptyset_{CFCl_3}$ = 0.0 ppm; $\emptyset$ (mult.): integral]:

$\emptyset_a$ = -118.60 ppm	$\emptyset_d$ = -123.54 ppm	$\emptyset_g$ = -130.75 ppm
$\emptyset_b$ = -120.80 ppm	$\emptyset_e$ = -125.97 ppm	$\emptyset_h$ = -166.74 ppm
$\emptyset_c$ = -122.49 ppm	$\emptyset_f$ = -127.50 ppm	$\emptyset_i$ = -175.40 ppm

TABLE B7

CHARACTERIZATION OF F-METHYL-2,2-DIMETHYLPROPANOATE

Infrared (cm^{-1}):

1820(m), 1265(s), 1220(m), 1170(m), 1125(s), 990(m), 835(w)

Mass Spectra [m/e (int.) formula]:

CI (CH_4):

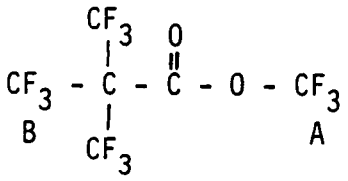
176(18)C_3F_7OH, $C_4F_5O_2H$; 160(100)C_4F_5OH; 158(10)$C_4F_4O_2H_2$;
151(6)C_3F_6H; 146(6)C_6F_3OH; 138(6)$C_4F_3O_2H$; 136(13)C_4F_5OH;
132(9)C_3F_5H; 70(19)CF_3H.

EI (70EV):

247(15)C_5F_9O; 159(12)C_4F_5O; 135(13)C_2F_5O; 69(100)CF_3

---

^{19}F NMR [ϕ_{CFCL_3} = 0.0 PPM; ø (mult.); integral]:



ϕ_A = -58.57 ppm (s); 1

ϕ_B = -63.64 ppm (s); 3

TABLE B8

CHARACTERIZATION OF F-METHYL-2-METHYLPROPANOATE

Infrared (cm^{-1}):

1820(m), 1350(m), 1305(s), 1250(s), 1165(s), 1140(s), 1090(s), 1040(m), 1020(s), 990(m), 835(m).

Mass Spectra [m/e (int.) formula]:

CI(CH_4):

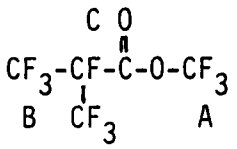
179(100)C_4F_6OH; 175(6)C_3F_7O, $C_4F_5O_2$; 167(6)C_3F_6OH; 161(19)$C_4F_5OH_2$; 159(6)C_4F_5O; 157(21)$C_4F_4O_2H$; 69(11)CF_3

EI(70eV):

197(12)C_4F_7O; 178(16)C_4F_6O; 169(9)C_3F_7; 113(8)$C_2F_3O_2$; 85(16)CF_3O; 69(100)CF_3; 50(26)CF_2

---

^{19}F NMR [$\emptyset_{CFCl_3}$ = 0.0 ppm; $\emptyset$ (mult.); integral]:



$\emptyset_A$ = -58.46 ppm (s); 3

$\emptyset_B$ = -74.57 ppm (d); 6

$\emptyset_C$ =-182.2 ppm (m); 1

TABLE B9

CHARACTERIZATION OF F-METHYL PROPANOATE

Infrared (cm^{-1}):

1810(m), 1335(m), 1270(s), 1245(s), 1220(s), 1160(s), 1120(s), 1020(s), 835(w).

Mass Spectra [m/e (int.) formula]:

CI(CH_4):

214(100)$C_4F_7O_2H$; 197(23)C_4F_7O; 147(28)C_3F_5O; 129(7)C_3F_4OH; 119(6)C_2F_5; 115(13)$C_2F_3O_2H_2$

EI(70eV):

147(15)C_3F_5O; 119(75)C_2F_5; 100(7)C_2F_4; 85(10)CF_3O; 69(100)CF_3; 50(49)CF_2

---

^{19}F NMR [ϕ_{CFCl_3} = 0.0 ppm; ø (mult.); integral]:

$$\underset{B}{CF_3}\text{-}\underset{C}{CF_2}\text{-}\overset{\overset{O}{\|}}{C}\text{-O-}\underset{A}{CF_3}$$

ϕ_A = -59.22 ppm (s); 3

ϕ_B = -83.73 ppm (s); 3

ϕ_C = -91.69 ppm (s); 2

TABLE B10

CHARACTERIZATION OF F-ETHYL PROPANOATE

Infrared (cm^{-1}):

1830(m), 1270(m), 1230(s), 1160(s), 1120(s), 1095(s), 1015(s).

Mass Spectra [m/e (int.) formula]:

CI(CH_4):

283(100)$C_5F_{10}O_2H$; 233(9)$C_4F_8O_2$; 183(40)$C_3F_6O_2H$; 147(19)C_3F_5O; 119(31)C_2F_5; 69(5)CF_3

EI(70eV):

147(14)C_3F_5O; 119(100)C_2F_5; 69(31)CF_3

---

^{19}F NMR [$\emptyset_{CFCl_3}$ = 0.0 ppm; $\emptyset$ (mult.); integral]:

$$\underset{B}{CF_3}\text{-}\underset{D}{CF_2}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\underset{C}{CF_2}\text{-}\underset{A}{CF_3}$$

$\emptyset_A$ = -83.76 ppm (s); 3

$\emptyset_B$ = -87.42 ppm (s); 3

$\emptyset_C$ = -92.45 ppm (s); 2

$\emptyset_D$ = -122.61 ppm (s); 2

TABLE B11

CHARACTERIZATION OF F-ISOPROPYL PROPANOATE

Infrared (cm^{-1}):

1835(m), 1335(m), 1300(s), 1240(s), 1220(s), 1170(s), 1130(s), 1105(s), 940(w).

Mass Spectra [m/e (int.) formula]:

CI(CH_4):

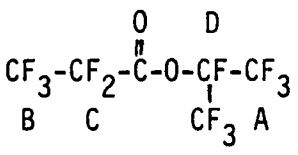
313(3)$C_5F_{11}O_2$; 234(11)C_4F_9O; 233(100)$C_4F_8O_2H$; 167(14)C_3F_6OH; 147(36)C_3F_5; 119(50)C_2F_5; 117(24)C_2F_4OH; 97(58)C_2F_3O; 69(55)CF_3

EI(70eV):

169(19)C_3F_7; 147(17)C_3F_5O; 119(100)C_2F_5; 69(90)CF_3

---

^{19}F NMR [ϕ_{CFCl_3} = 0.0 ppm; ϕ (mult.); integral]:



ϕ_A = -79.46 ppm (s); 6

ϕ_B = -83.55 ppm (s); 3

ϕ_C = -122.03 ppm (s); 2

ϕ_D = -142.93 ppm (s); 1

TABLE B12

CHARACTERIZATION OF F-TERTIARYBUTYL PROPANOATE

Infrared (cm^{-1}):

1830(m), 1330(w), 1270(s), 1230(s), 1160(m), 1130(s), 1090(m), 1005(s), 980(s), 805(w).

Mass Spectra [m/e (int.) formula]:

CI(CH_4):

198(48)C_4F_7OH; 182(10)C_4F_7H; 180(9)$C_4F_6OH_2$; 170(12)C_3F_7H; 166(14)C_3F_6O; 164(13)$C_3F_5O_2H$; 148(68)C_3F_5OH; 146(23)$C_3F_4O_2H_2$; 132(32)C_3F_5H; 120(81)C_2F_5H; 117(6)C_2F_4OH; 101(13)C_2F_4H; 97(28)C_2F_3O; 94(21)$C_2F_2O_2$; 91(7)C_3F_2OH; 79(5)C_2F_2OH; 77(7)$C_2O_2FH_2$; 69(100)CF_3; 65(8)CO_2FH_2

EI(70eV):

147(19)C_3F_5O; 131(10)C_3F_5; 119(81)C_2F_5; 100(6)C_2F_4; 97(8)C_2F_3O 69(100)CF_3

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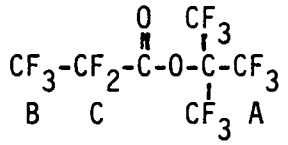
^{19}F NMR [ϕ_{CFCl_3} = 0.0 ppm; ϕ (mult.); integral]:



ϕ_A = -70.48 ppm (s); 9

ϕ_B = -83.58 ppm (s); 3

ϕ_C = -121.52 ppm (s); 2

TABLE B13

CHARACTERIZATION OF F-METHYL 2-METHOXYPROPANOATE

Infrared (cm^{-1}):

1830(m), 1285(s), 1250(s), 1230(s), 1175(m), 1145(m), 1125(m)
1025(m).

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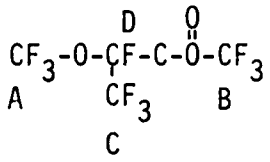
^{19}F NMR [ϕ_{CFCl_3} = 0.0 ppm; ø(mult.); integral]:



ϕ_A = -55.44 ppm (d); 3 J_{AD} = 7.33 Hz

ϕ_B = -58.53 ppm (s); 3 J_{CD} = 2.44 Hz

ϕ_C = -81.63 ppm (d); 3

ϕ_D = -133.50 ppm (m); 1

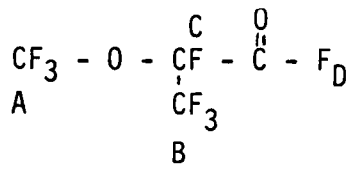
TABLE B14

CHARACTERIZATION OF F-2-METHOXYPROPANOYL FLUORIDE

Infrared (cm^{-1}):

1875(s), 1330(m), 1280(s), 1220(vs), 1150(s), 1120(s), 1090(m), 1000(s), 895(w), 835(m).

^{19}F NMR [ϕ_{CFCl_3} = 0.0 ppm; ϕ(mult.); integral]:



ϕ_A = -56.17 ppm (t); 3 J_{BD} = 8.80 Hz

ϕ_B = -58.60 ppm (d·d); 3 J_{BC} = 2.20 Hz

ϕ_C = -82.12 ppm (m); 2 J_{AC} = 440 Hz

ϕ_D = + 26.96 ppm (m); 1 J_{AD} = 1.47 Hz

TABLE B15

CHARACTERIZATION OF F-2-HYDRYL-2,4-DIMETHYLPENTANE

Mass Spectra [m/e(int.)formula]:

CI(CH_4):

350(100)C_7F_{14}; 262(13)C_6F_{10}.

EI(70 eV):

262(23)C_6F_{10}; 200(24)C_4F_8; 150(11)C_3F_6; 131(11)C_3F_5;
112(31)C_2F_4; 69(100)CF_3.

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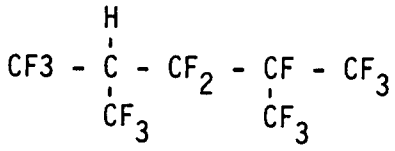
^1H NMR [$\emptyset_{TMS}$ = 0.0 ppm; $\emptyset$(mult.)]



$\emptyset$ = 3.96 ppm(m)

TABLE B16

CHARACTERIZATION OF F-2,4-DIHYDRYL-2,4-DIMETHYLPENTANE

Mass Spectra [m/e (int.) formula]:

CI (CH_4):

333(100)$C_7F_{13}H_2$; 313(12)$C_7F_{12}H$; 263(11)$C_6H_{10}F$; 245(17)$C_6F_9H_2$;

201(29)C_4F_8H; 113(21)C_3F_4H

EI (70eV):

208(97)C_4H_8H; 132(21)C_3F_5H; 113(75)C_3F_4H; 69(100)CF_3;

51(11)CF_2H

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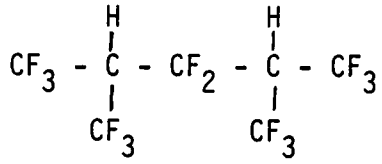
^1H NMR [$\emptyset_{TMS}$ = 0.0 ppm; $\emptyset$ (mult.)]



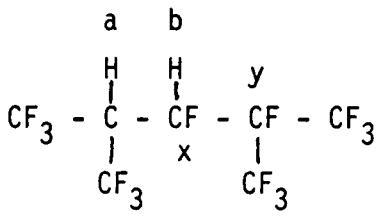
$\emptyset$ = 3.88 ppm (m)

J_{HF} = 8 Hz

TABLE B17

CHARACTERIZATION OF F-2,3-DIHYDRYL-2,4-DIMETHYLPENTANE

^{1}H NMR [$\emptyset_{TMS}$ = 0.0 ppm; $\emptyset$ (multi); integral];



$\emptyset_a$ = 3.58 ppm (m); 1

$\emptyset_b$ = 5.48 ppm (d·d); 1

J_{bx} = 44 Hz

J_{by} = 20 Hz

TABLE B18

CHARACTERIZATION OF F-3-HYDRYL-2,4-DIMETHYLPENTANE

Mass Spectra [m/e (int.) formula]:

CI(CH_4):

350(13)C_7F_{14}; 263(64)$C_6F_{10}H$; 121(25)$C_2F_5H_2$; 119(97)C_2F_5;

117(100)C_5F_3; 101(99)C_2F_4H; 69(91)CF_3

EI (70eV):

131(10)C_3F_5; 112(28)C_3F_4; 69(100)CF_3

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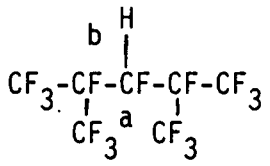
^1H NMR [$\emptyset_{TMS}$ = 0.0 PPM; $\emptyset$ (mult.)]



$\emptyset$ = 5.55 ppm (d·t)

J_{Ha} = 45 Hz

J_{Hb} = 10 Hz

TABLE B19

CHARACTERIZATION OF MONOFLUOROBENZENE

Infrared (cm^{-1}):

3020(s), 1585(s), 1480(s), 1215(s), 795(w), 730(s)

Mass Spectra [m/e(int.)formula]:

CI(CH_4):

98(6)C_6H_7F; 97(100)C_6H_6F; 96(12)C_6H_5F; 93(20)C_6FH_2; 79(42)C_6H_7

EI(70 eV):

96(6)C_6H_5F; 95(100)C_6H_4F, 94(10)C_6H_3F; 77(31)C_6H_5; 76(9)C_6H_4; 70(19)C_4FH_3; 50(10)C_3H_2

VITA

Myron Lee Cherry was born in Centerville, Tennessee. He graduated from Hickman County High School and later received a Bachelor of Science degree in chemistry from Austin Peay State University in 1979. He entered the Graduate School of The University of Tennessee, Knoxville, in September 1979. He is married to the former Ann Lazenby. They have two children, Michael and Kimberly.