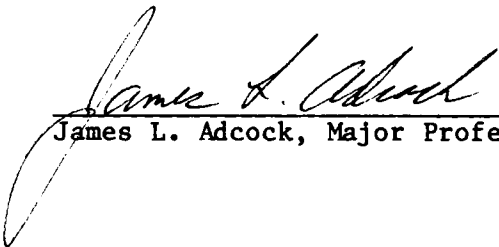
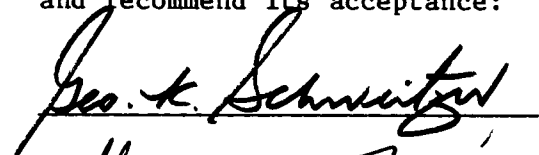
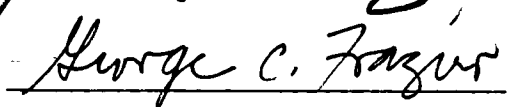
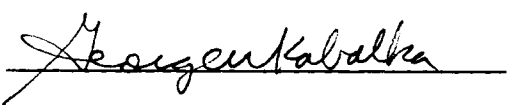


To the Graduate Council:

I am submitting herewith a dissertation written by Mark Lester Robin entitled "Aerosol Direct Fluorination: Syntheses of Perfluoro-ketones." 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

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:


The Graduate School

AEROSOL DIRECT FLUORINATION: SYNTHESSES OF PERFLUOROKETONES

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Mark Lester Robin

August 1983

DEDICATION

To my father and mother, Lester and Margaret Robin.

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 Mr. George McGhee for typing the dissertation.

The financial assistance from the Office of Naval Research and the Department of Chemistry, in the form of an ARCO Fellowship, is gratefully acknowledged.

Finally, I wish to acknowledge the patience and understanding of my wife, Debra, whose love and support have made this all worthwhile.

ABSTRACT

A series of perfluoroketones has been synthesized utilizing the aerosol direct fluorination method. The perfluoroketones are obtained directly from the hydrocarbon analog in the case of acyclic ketones, and in a two-step process from the corresponding methyl ether or ethylene glycol ketal in the case of cyclic ketones. Aerosol direct fluorination of the hydrocarbon analog produced the following perfluoroketones directly: F-3-pentanone, F-2-heptanone, F-3-heptanone, F-4-heptanone, F-2-butanone, F-acetone, and F-3,3-dimethyl-2-butanone. Aerosol direct fluorination of 2,2,4,4-tetramethyl-3-pentanone produced F-2,2,5-trimethyl-3-hexanone, a rare example of a skeletal rearrangement occurring during aerosol fluorination. Aerosol direct fluorination of methoxycyclopentane and methoxycyclohexane produced the perfluorinated analogs, which were then hydrolyzed in 100% sulfuric acid to F-cyclopentanone and F-cyclohexanone, respectively. Aerosol direct fluorination of the ethylene glycol ketals of cyclopentanone and cyclohexanone produced the perfluorinated analogs, which could also be hydrolyzed in 100% sulfuric acid to F-cyclopentanone and F-cyclohexanone, respectively, the first example of the use of a protecting group in direct fluorination. The perfluoroketones were characterized by infrared spectrophotometry, electron-impact and chemical ionization mass spectroscopy, and ^{19}F nuclear magnetic resonance spectroscopy.

In the course of the syntheses the basic aerosol fluorination system was modified to produce a more versatile system. The

modifications have made possible the aerosol direct fluorination of both solid and high boiling liquid hydrocarbon materials on a routine basis.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
A. Direct Fluorination Methods	1
B. Development of the Aerosol Direct Fluorination Process	3
C. The Synthesis of Perfluoroketones	6
D. Statement of Problem	12
II. EXPERIMENTAL PROCEDURES	13
A. Basic Aerosol Fluorination System	13
B. Modified Aerosol Fluorination System	27
C. Materials	31
D. Characterization of Compounds	34
E. Aerosol Fluorination of 3-Pentanone	35
F. Aerosol Fluorination of 4-Heptanone	38
G. Aerosol Fluorination of Cyclopentanone	38
H. Aerosol Fluorination of Cyclohexanone	41
I. Aerosol Fluorination of 3-Heptanone	43
J. Aerosol Fluorination of 2-Heptanone	44
K. Aerosol Fluorination of 2-Butanone	45
L. Aerosol Fluorination of Acetone	45
M. Aerosol Fluorination of Methoxycyclopentane	46
N. Hydrolysis of <u>F</u> -Methoxycyclopentane	47
O. Aerosol Fluorination of Methoxycyclohexane	48
P. Hydrolysis of <u>F</u> -Methoxycyclohexane	49
Q. Aerosol Fluorination of 1,4-Dioxaspiro[4.4]nonane	50
R. Hydrolysis of <u>F</u> -1,4-Dioxaspiro[4.4]nonane	51

CHAPTER	PAGE
S. Aerosol Fluorination of 1,4-Dioxaspiro[4.5]decane	52
T. Hydrolysis of <u>F</u> -1,4-Dioxaspiro[4.5]decane	52
U. Aerosol Fluorination of 3,3-Dimethyl-2-butanone	53
V. Aerosol Fluorination of 2,2,4,4-Tetramethyl-3-pentanone . . .	54
III. RESULTS AND DISCUSSION	56
A. General Results	56
B. Synthesis of <u>F</u> -3-Pentanone	63
C. Synthesis of <u>F</u> -4-Heptanone	66
D. Aerosol Fluorination of Cyclopentanone	69
E. Synthesis of <u>F</u> -3-Heptanone	71
F. Synthesis of <u>F</u> -2-Heptanone	74
G. Synthesis of <u>F</u> -2-Butanone	76
H. Synthesis of <u>F</u> -Acetone	77
I. Synthesis of <u>F</u> -Methoxycyclopentane	79
J. Synthesis of <u>F</u> -1,4-Dioxaspiro[4.4]nonane	80
K. Synthesis of <u>F</u> -Cyclopentanone	81
L. Synthesis of <u>F</u> -Methoxycyclohexane	83
M. Synthesis of <u>F</u> -1,4-Dioxaspiro[4.5]decane	84
N. Synthesis of <u>F</u> -Cyclohexanone	85
O. Synthesis of <u>F</u> -3,3-Dimethyl-2-butanone	87
P. Aerosol Fluorination of 2,2,4,4-Tetramethyl-3-pentanone:	
A Skeletal Rearrangement	89
Q. Miscellaneous Aerosol Fluorinations	91
IV. SUMMARY	93
LIST OF REFERENCES	95

CHAPTER	PAGE
APPENDICES	103
APPENDIX A. AEROSOL FLUORINATION PARAMETERS	104
APPENDIX B. CHARACTERIZATION OF COMPOUNDS	119
VITA	139

LIST OF TABLES

TABLE	PAGE
1. Syntheses of Perfluoroketones	10
A-1. Aerosol Fluorination of 3-Pentanone	105
A-2. Aerosol Fluorination of 4-Heptanone	106
A-3. Aerosol Fluorination of Cyclopentanone	107
A-4. Aerosol Fluorination of Cyclohexanone	108
A-5. Aerosol Fluorination of 3-Heptanone	109
A-6. Aerosol Fluorination of 2-Heptanone	110
A-7. Aerosol Fluorination of 2-Butanone	111
A-8. Aerosol Fluorination of Acetone	112
A-9. Aerosol Fluorination of Methoxycyclopentane	113
A-10. Aerosol Fluorination of Methoxycyclohexane	114
A-11. Aerosol Fluorination of 1,4-Dioxaspiro[4.4]nonane	115
A-12. Aerosol Fluorination of 1,4-Dioxaspiro[4.5]decane	116
A-13. Aerosol Fluorination of 3,3-Dimethyl-2-butanone	117
A-14. Aerosol Fluorination of 2,2,4,4-Tetramethyl-3-pentanone . . .	118
B-1. Characterization of <u>F</u> -3-Pentanone	120
B-2. Characterization of <u>F</u> -4-Heptanone	121
B-3. Characterization of <u>F</u> -Pentanoyl Fluoride	122
B-4. Characterization of <u>F</u> -3-Heptanone	123
B-5. Characterization of <u>F</u> -2-Heptanone	124
B-6. Characterization of <u>F</u> -2-Butanone	125
B-7. Characterization of <u>F</u> -Methoxycyclopentane	126
B-8. Characterization of <u>F</u> -Cyclopentanone	127
B-9. Characterization of <u>F</u> -Methoxycyclohexane	128

TABLE	PAGE
B-10. Characterization of <u>F</u> -Cyclohexanone	129
B-11. Characterization of <u>F</u> -1,4-Dioxaspiro[4.4]nonane	130
B-12. Characterization of <u>F</u> -1,4-Dioxaspiro[4.5]decane	131
B-13. Characterization of <u>F</u> -3,3-Dimethyl-2-butanone	132
B-14. Characterization of 3-Difluoromethyl- <u>F</u> -3-methyl-2-butanone	133
B-15. Characterization of 3,3-Bis(difluoromethyl)- <u>F</u> -2-butanone	134
B-16. Characterization of <u>F</u> -2,2,5-Trimethyl-3-hexanone	135
B-17. Characterization of <u>F</u> -Adamantane	136
B-18. Characterization of <u>F</u> -Trimethyl Orthoformate	137
B-19. Characterization of <u>F</u> -Tetramethyl Orthocarbonate	138

LIST OF FIGURES

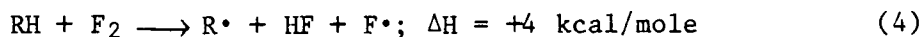
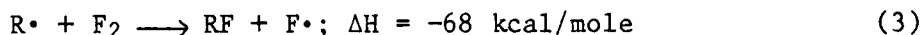
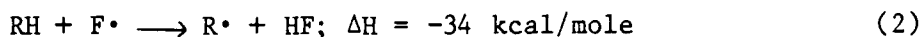
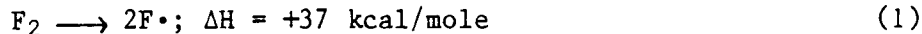
FIGURE	PAGE
1. Basic Aerosol Fluorination System	14
2. Hydrocarbon Evaporator Device	17
3. Aerosol Generator No. 1	18
4. Aerosol Generator No. 2	19
5. Hydrocarbon Inlet Tube	21
6. Reactor Module No. 1: Outer Unit	22
7. Reactor Module No. 1: Staging Insert	23
8. Reactor Module Cooling System	25
9. Photochemical Stage	26
10. Modified Aerosol Fluorination System	28
11. Aerosol Generator No. 3	30
12. Reactor Module Design No. 2	32
13. 3-Pentanone Throughputs	36
14. 4-Heptanone Throughputs	39
15. Cyclopentanone Throughputs	40
16. Cyclohexanone Throughputs	42

CHAPTER I

INTRODUCTION

A. Direct Fluorination Methods

Since the time of the initial attempts at direct fluorination by Moissan,¹ various methods have been developed in hopes of moderating the reaction of fluorine with organic compounds. Moissan's main observation was that combustion occurred upon the contact of fluorine with organic materials, and it is the dissipation of the large amounts of heat generated which constitutes the major obstacle to successful direct fluorination. It is generally accepted that direct fluorination proceeds via a radical chain mechanism:²



The low dissociation energy of fluorine combined with the relatively large amount of heat evolved in the radical chain process account for the fact that, unless heat is rapidly and efficiently dissipated, combustion can occur upon the contact of fluorine with organic materials. Inefficient removal of heat leads to extensive fragmentation of the carbon skeleton, and for this reason the production of perfluorinated species from the hydrocarbon analogs becomes increasingly difficult as the number of carbon atoms in the hydrocarbon starting material increases. The production of perfluorinated compounds via

the direct fluorination of hydrocarbons containing more than five carbon atoms presents serious problems.

To deal with the problem of heat dissipation, three methods were originally developed. The first method, primarily due to the work of Bockemüller,³ involved dissolving the organic compound in an inert solvent (e.g. CCl_4) and bubbling a mixture of nitrogen and fluorine into the cold solution. The method does not yield the perfluorinated analog, however, but is usually limited to the production of the mono- or di-substituted species. The second and most important direct fluorination method was developed by Bigelow and co-workers^{4,5} and employs a reactor packed with solid metal (e.g. copper gauze or shot) and a nitrogen-diluted fluorine stream. Employing this "catalytic" method Bigelow was able to successfully prepare fluorocarbons from the saturated hydrocarbon analogs, obtaining yields of purified perfluorocarbons as high as 62 percent for n-heptane. This vapor phase process of fluorination over a metal packing was extended by Cady⁶ and also by Smith, Musgrave, and Haszeldine.⁷⁻¹⁰ The principal function of the metal catalyst in these reactions appears to be the dispersion of the heat of reaction, and whether or not any catalytic function is actually provided is questionable.² The third direct fluorination method, the so-called "jet-fluorination" method,¹¹ utilizes concentric tubes for introducing separate gas streams and rapidly removing products from the reaction zone. Employing this apparatus Bigelow produced F-ethane (perfluoroethane) in an 85 percent yield, with little or no cracking or polymerization. The method has found little application to the production of perfluorocarbons, however, and

the predominant direct fluorination method remained the "catalytic" method up to the 1970's.

The next major advance in direct fluorination technology was the result of the work of Lagow and co-workers.¹² In these studies a cryogenic reactor is employed to create a temperature gradient along the reactor length; as the reactants become more than 50 percent fluorinated, their volatility increases and they can move through the reactor more rapidly. The process also employs the high dilution of fluorine with helium, which also acts as a heat sink. This low-temperature gradient ("LTG") process, in contrast to the previously discussed direct fluorination methods, is generally useful for the fluorination of compounds containing functional groups as well as for hydrocarbons. The method has been successful in the perfluorination of highly branched hydrocarbons,^{13,14} hydrocarbon ethers,¹⁵ esters,¹⁶ acid fluorides,^{16,17} acid anhydrides,¹⁸ and cyclic amines.¹⁹ While the ability to completely fluorinate molecules containing functional groups with elemental fluorine was a major development in direct fluorination technology, the method has the disadvantages that it is a batch process, suitable in general only for small scale synthesis, and works well only for molecules with appreciable solid state volatility.

B. Development of the Aerosol Direct Fluorination Process

A critical analysis of the LTG direct fluorination technique led to the establishment of a set of conditions believed to be capable of

providing a high yield of fluorinated material from hydrocarbon starting materials:²⁰

1. Fluorination of molecules in the crystalline state.
2. High reactant surface area.
3. Low initial temperature.
4. High initial fluorine dilution.
5. Efficient dissipation of reaction heat.

As previously mentioned, the major problem in direct fluorination is the dissipation of the large amounts of heat evolved. The use of a crystalline matrix serves to reduce radical recombinations and at the same time serves as an energy sink to aid in the dissipation of reaction energies. High reactant surface area would tend to promote uniform attack by fluorine on all reactant molecules. To reduce fragmentation, the overall reaction rate should be reduced through the use of low temperatures and high fluorine dilution. High fluorine dilution also helps to reduce the probability of simultaneous attack by fluorine molecules or radicals on adjacent molecular sites, which would lead to increased fragmentation. Efficient heat dissipation also reduces the probability of fragmentation, and prevents combustion from occurring.

In order to successfully produce perfluorinated materials, the above considerations must be extended somewhat, and reaction conditions modified. At the onset of fluorination a low initial temperature and a high dilution of fluorine are desirable, but as the degree of fluorination increases it is increasingly difficult to add additional fluorine to the now partially fluorinated species, since a greater percentage of

collisions become ineffective. A means of establishing temperature and fluorine concentration gradients is desired wherein the temperature and fluorine concentration may be increased as the reaction proceeds in time. A flow process is also desired, wherein the temperature and fluorine concentration gradient would be established along a reactor's length. The reactants would be moved down this length by a carrier or some alternate means. Two basic flow type processes were examined and rejected. A liquid reagent stream would not allow for uniform, rapid mixing with the reactive gaseous elemental fluorine, and a gaseous reactant, while mobile, offers no convenient method for reducing collisions between hydrocarbon radicals which would lead to the production of tars and oils.

A heterogeneous system wherein a suspended solid reactant is subjected to gaseous fluorine attack provides a solution. By employing an aerosol one may attain gas-like mobility and still retain crystallinity. The crystalline matrix serves as an energy sink and the aerosol particles have very high surface areas, permitting uniform attack by elemental fluorine. As these aerosol particles are swept down a reactor length by a carrier gas, a temperature and fluorine concentration gradient can be established, allowing for higher temperatures and fluorine concentrations as the molecule becomes further fluorinated. Very efficient heat dissipation may be achieved by using helium as the carrier gas. Multiple collisions of reactant particulates with helium dissipates heat rapidly as excess energy is continuously carried by the helium atoms to the reactor walls.

An early aerosol fluorinator designed on the basis of the above considerations, while resulting in the first successful fluorination of a solid phase particulate aerosol using elemental fluorine, was best suited to the production of partially fluorinated species.^{21,22} Perfluorinated species could be produced, but in general yields were low.

Successful perfluorination in good yields was achieved through the addition of a photochemical stage, providing activation of the elemental fluorine, to the basic design.^{23,24} Use of the photochemical stage allowed exceptionally high yields of perfluorinated products to be obtained as well as providing efficient fluorine utilization. The aerosol fluorination apparatus employing the photochemical stage resulted in the successful perfluorination of alkanes, ethers, cycloalkanes, ketals, and chlorides.²⁰ The aerosol direct fluorination apparatus will be discussed in detail in the Experimental section.

C. The Synthesis of Perfluoroketones

While a range of perfluoroketones has been synthesized, the methods involved are quite distinct from those employed to synthesize the hydrocarbon analogs and almost invariably involve the reaction of a highly fluorinated species. Neither direct nor indirect fluorination methods have provided routes to the perfluoroketones starting from the hydrocarbon analog. The Swarts reaction²⁵ and other reactions involving halogen exchange require preparation of the corresponding chlorocarbon prior to fluorination, and the higher perchlorocarbons are often difficult to prepare. Simons' electrochemical method²⁶⁻²⁹

operates in anhydrous hydrogen fluoride and hence the perfluoroketones are unattainable via the electrochemical method. The cobalt trifluoride process cleaves the ketones at an early stage in the reaction,^{30,31} and the milder reagent, potassium tetrafluorocobaltate (III), also leads exclusively to fragmentation products.³²

The first example of the complete fluorination of a ketone via elemental fluorine was the fluorination of acetone by Bigelow; employing the "catalytic" fluorination method he was able to produce F-acetone in poor yields.⁵ Methyl ethyl ketone and cyclopentanone were also perfluorinated via the "catalytic" method, but again the yields were poor.³¹

In general, the direct fluorination of organic compounds containing functional groups to their perfluorinated analogs is limited to the method of Lagow¹² and the aerosol direct fluorination method described herein. Whereas the LTG method of Lagow has been successful in the perfluorination of groups such as ethers,¹⁵ esters,¹⁶ and acid anhydrides,¹⁸ the production of perfluoroketones has not been achieved via the method.³³

Despite the failure of the more "common" fluorination techniques, a number of perfluoroketones have been prepared in varying yields, usually from highly fluorinated precursors. The parent compound of the series, F-acetone, is commercially available and may be prepared by a variety of methods, including exchange of chlorine in hexachloroacetone by fluorine using hydrogen fluoride in the presence of a chromium (V) or chromium (III) catalyst.^{34,35} Halogen exchange has also been employed in the synthesis of F-2-butanone from perchloro-2-butanone.³⁶

The decomposition over Lewis acid catalysts of perfluoroalkylene epoxides, prepared from the corresponding cyclic or acyclic perfluoroalkenes, constitutes another method for the production of perfluoroketones. For example, F-cyclopentanone^{37,38} F-acetone,³⁷⁻³⁹ F-cyclohexanone,³⁸⁻⁴⁰ F-2-methyl-3-pentanone,⁴¹ F-4-methyl-2-pentanone,⁴¹ F-3-hexanone,⁴² F-2-heptanone,^{42,43} F-2-butanone,⁴³ F-2-pentanone,⁴³ F-2-hexanone,⁴³ F-2-octanone,⁴³ and F-2,6,6-trimethyl-3-heptanone⁴⁴ have been prepared in this manner.

The fluoride ion catalyzed addition of perfluoroacyl fluorides to F-propene affords a route to perfluoroketones containing the branched perfluoroisopropyl group and has led to the syntheses of F-3-methyl-2-butanone,^{45,46} F-2-methyl-3-hexanone,^{45,46} F-2,4-dimethyl-3-pentanone,⁴⁵⁻⁴⁷ F-2-methyl-3-pentanone,⁴⁸ F-2-methyl-3-heptanone,⁴⁸ and F-2-methyl-3-nonanone.⁴⁸ Chambers et al.⁴⁹ have synthesized perfluoroketones containing the perfluoroisopropyl group and a perfluoroaryl group. For example, the reactions of F-propene with F-benzoyl fluoride, F-4-isopropylbenzoyl fluoride, and F-isonicotinoyl fluoride produced the corresponding perfluoroketones.

The reaction of perfluoroalkyl carboxylates with sodium alkoxides has led to the production of F-3-pentanone and F-4-heptanone.⁵⁰ The reactions of ethyl perfluorobutyrate with sodium,⁵¹ perfluoropropyl magnesium iodide,⁵² or perfluoropropyl lithium⁵³ have also produced F-4-heptanone. Perfluoroacyl chlorides have been reacted with perfluoropropyl zinc iodide⁵⁴ to produce F-2-pentanone and F-4-heptanone; with perfluoropropyl magnesium iodide⁵⁵ to produce F-2-pentanone, F-3-hexanone, and F-4-heptanone; and with

perfluoromethyl magnesium iodide⁵⁶ to produce F-acetone and F-2-pentanone.

The oxidation of a perfluoroalkene has in several cases produced a perfluoroketone: F-acetone,⁵⁷ F-2-pentanone,⁵⁸ and F-acetylcyclohexane⁵⁸ were prepared via the oxidation with aqueous potassium permanganate of F-2-methylpropene, F-2-methyl-1-pentene, and F-2-cyclohexylpropene, respectively. The action of lead tetrafluoride on ethylbenzene, followed by neutralization and treatment with water, was also reported to produce F-acetylcyclohexane.⁵⁹

Delfino and Shreeve⁶⁰ have reported the synthesis of F-2-butanone via the reaction of F-2-fluorosulfatobutane at 70°C in the presence of cesium or potassium fluoride. In a similar fashion, F-4-methyl-2-heptanone has been prepared from F-2-chlorosulfato-4-methylheptane.⁶¹

F-Cyclobutanone,⁶² F-cyclopentanone,⁶³ F-cyclohexanone,⁶³ F-cycloheptanone,⁶⁴ and F-cyclooctanone⁶⁵ have been prepared via the acid hydrolysis of the corresponding methyl perfluorocycloalkyl ethers. F-cyclopentanone and F-cyclohexanone have also been prepared by potassium fluoride-tetramethylene sulfone metathesis of the corresponding 1,1-dichloroperfluorocycloketone^{66,67} or 1,2-dichloroperfluorocycloalkylene epoxide.^{66,68}

Table 1 lists the syntheses of a number of perfluoroketones and includes all the known perfluoroketones of ten or fewer carbons.

TABLE 1
SYNTHESES OF PERFLUOROKETONES

Synthesis	Ref.
$\text{CCl}_3\overset{\text{O}}{\parallel}\text{CCCl}_3 \xrightarrow[\text{Cr catalyst}]{\text{HF}} \text{CF}_3\overset{\text{O}}{\parallel}\text{CCF}_3$	34,35
$\text{Cl}_3\overset{\text{O}}{\parallel}\text{CCCl}_2\text{CCl}_3 \xrightarrow[\text{Cr catalyst}]{\text{HF}} \text{CF}_3\overset{\text{O}}{\parallel}\text{CCF}_2\text{CF}_3$	36
$\begin{array}{c} \text{CF} \diagup \text{O} \diagdown \text{CF} \\ \quad \quad \\ \text{CF}_2 - (\text{CF}_2)_n \end{array} \xrightarrow{\text{Al}_2\text{O}_3} \begin{array}{c} \text{CF} - \text{C}=\text{O} \\ \quad \quad \\ \text{CF}_2 - (\text{CF}_2)_n \end{array} \quad n=2,3$	37-40
$(\text{CF}_3)_2\text{CF} \diagup \text{O} \diagdown \text{CF} \text{CF}_3 \xrightarrow{\text{SbF}_5} (\text{CF}_3)_2\text{CF} \text{CF}_2 \overset{\text{O}}{\parallel} \text{CF}_3$	41
$\text{Cl}(\text{CF}_2)_n \text{CF} \diagup \text{O} \diagdown \text{CF}_2 \xrightarrow{\text{SbF}_5} \text{F}(\text{CF}_2)_n \overset{\text{O}}{\parallel} \text{CF}_3 \quad n=2-6$	43
$\text{R}_f \overset{\text{O}}{\parallel} \text{CF} + \text{CF}_3\text{CF}=\text{CF}_2 \xrightarrow{\text{F}^-} \text{R}_f \overset{\text{O}}{\parallel} \text{CCF}(\text{CF}_3)_2$	45-49
$\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5, n\text{-C}_3\text{F}_7, (\text{CF}_3)_2\text{CF},$ $n\text{-C}_4\text{F}_9, c\text{-C}_4\text{F}_7, n\text{-C}_6\text{F}_{13}, c\text{-C}_6\text{F}_5$	
$\text{R}_f \text{COOC}_2\text{H}_5 + \text{NaOC}_2\text{H}_5 \longrightarrow (\text{R}_f)_2\text{CO}$	50
$\text{R}_f = \text{C}_2\text{F}_5, n\text{-C}_3\text{F}_7$	
$\text{C}_3\text{F}_7\text{COOC}_2\text{H}_5 + \text{Na} \longrightarrow (\text{C}_3\text{F}_7)_2\text{CO}$	51
$\text{C}_3\text{F}_7\text{COOC}_2\text{H}_5 + \text{C}_3\text{F}_7\text{MgI} \longrightarrow (\text{C}_3\text{F}_7)_2\text{CO}$	52
$\text{C}_3\text{F}_7\text{COOC}_2\text{H}_5 + \text{C}_3\text{F}_7\text{Li} \longrightarrow (\text{C}_3\text{F}_7)_2\text{CO}$	53

TABLE 1 (Continued)

Synthesis	Ref.
$\text{R}_f\overset{\text{O}}{\parallel}\text{CCl} + \text{C}_3\text{F}_7\text{ZnI} \longrightarrow \text{R}_f\overset{\text{O}}{\parallel}\text{CC}_3\text{F}_7$ $\text{R}_f = \text{CF}_3, \text{n-C}_3\text{F}_7$	54
$\text{R}_f\overset{\text{O}}{\parallel}\text{CCl} + \text{C}_3\text{F}_7\text{MgI} \longrightarrow \text{R}_f\overset{\text{O}}{\parallel}\text{CC}_3\text{F}_7$ $\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5, \text{n-C}_3\text{F}_7$	55
$\text{R}_f\overset{\text{O}}{\parallel}\text{CCl} + \text{CF}_3\text{MgI} \longrightarrow \text{R}_f\overset{\text{O}}{\parallel}\text{CCF}_3$ $\text{R}_f = \text{CF}_3, \text{n-C}_3\text{F}_7$	56
$\text{R}_f\text{CF}_3\text{C}=\text{CF}_2 \xrightarrow{\text{KMnO}_4} \text{R}_f\overset{\text{O}}{\parallel}\text{CCF}_3$ $\text{R}_f = \text{CF}_3, \text{n-C}_3\text{F}_7, \text{c-C}_6\text{F}_{11}$	57, 58
$\text{CF}_3\text{CF}(\text{SO}_3\text{X})\text{R}_f \xrightarrow{\text{KF}} \text{CF}_3\overset{\text{O}}{\parallel}\text{CR}_f$ $\text{X} = \text{F}, \text{Cl}$ $\text{R}_f = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7\text{CF}(\text{CF}_3)\text{CF}_2$	60, 61
$\begin{array}{c} \text{CF}_2 - \text{CF} - \text{OCH}_3 \\ \qquad \\ \text{CF}_2 - (\text{CF}_2)_n \end{array} \xrightarrow[2. \text{P}_2\text{O}_5]{1. \text{100\% H}_2\text{SO}_4} \begin{array}{c} \text{CF}_2 - \overset{\text{O}}{\parallel}\text{C} \\ \qquad \\ \text{CF}_2 - (\text{CF}_2)_n \end{array} \quad n = 1-5$	62-65
$\begin{array}{c} \text{CF}_2 - \overset{\text{O}}{\parallel}\text{C} \\ \qquad \\ (\text{CF}_2)_n - \text{CCl}_2 \end{array} \xrightarrow{\text{KF-TMS}} \begin{array}{c} \text{CF}_2 - \overset{\text{O}}{\parallel}\text{C} \\ \qquad \\ (\text{CF}_2)_n - \text{CF}_2 \end{array} \quad n = 2, 3$	66, 67
$\begin{array}{c} \text{CF}_2 - \text{C} \begin{array}{l} \nearrow \text{Cl} \\ \searrow \text{O} \end{array} \\ \qquad \\ (\text{CF}_2)_n - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{Cl} \end{array} \end{array} \xrightarrow{\text{KF-TMS}} \begin{array}{c} \text{CF}_2 - \overset{\text{O}}{\parallel}\text{C} \\ \qquad \\ (\text{CF}_2)_n - \text{CF}_2 \end{array} \quad n = 2, 3$	66, 68

D. Statement of Problem

Although the methods described above have produced perfluoroketones in selected cases, a more general method for the production of perfluoroketones would be desirable. The purpose of this investigation is to provide a route to the perfluoroketones from the relatively inexpensive hydrocarbon analogs via the aerosol direct fluorination process. Extension of the process to the production of perfluoroketones would comprise an important advance in direct fluorination technology.

CHAPTER II

EXPERIMENTAL PROCEDURES

A. Basic Aerosol Fluorination System

The basic aerosol fluorination system is shown schematically in Figure 1. A bed of sodium fluoride (A) in a heavy gauge nickel combustion boat (Fisher Scientific) is heated to approximately 850°C (iron-constantan thermocouple) in a stainless steel oven tube located inside an electric furnace (Hoskins Electric Furnace Company, model FD-303A). Finely dispersed sodium fluoride particles (average radius 17.5 Å⁶⁹) sublime into a helium carrier gas and are cooled to near -196°C by passing through a liquid nitrogen cooled heat exchanger (B). The chilled stream is mixed with a second gas stream containing hydrocarbon vapor within the body of the aerosol generator (C). The hydrocarbon vapor, in a stream produced by the evaporator device (D), condenses into aggregates around the chilled sodium fluoride particles. The chilled aerosol is then passed through the reactor modules (E,F,G) where it is mixed with elemental fluorine. Following the last reactor module is an endcap (H), a series of coils (I,I') which may be heated if desired, and a water-cooled flow type photochemical stage (J) which provides activation of the elemental fluorine. The products then flow through a brass scrubber (K) filled with sodium fluoride pellets to facilitate removal of hydrogen fluoride and are collected in the liquid nitrogen cooled product trap (L). Excess fluorine is removed by passing the gas stream through a brass cylinder filled with activated alumina.

Figure 1. Basic Aerosol Fluorination System.

A heated bed of sodium fluoride (A) sublimates 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 evaporator device (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), a series of coils (I,I'), and a water-cooled photochemical stage (J). Hydrogen fluoride is removed in the scrubber (K) and the products collected in the liquid nitrogen cooled product trap (L). Excess fluorine is removed by passing the gas stream through an alumina trap.

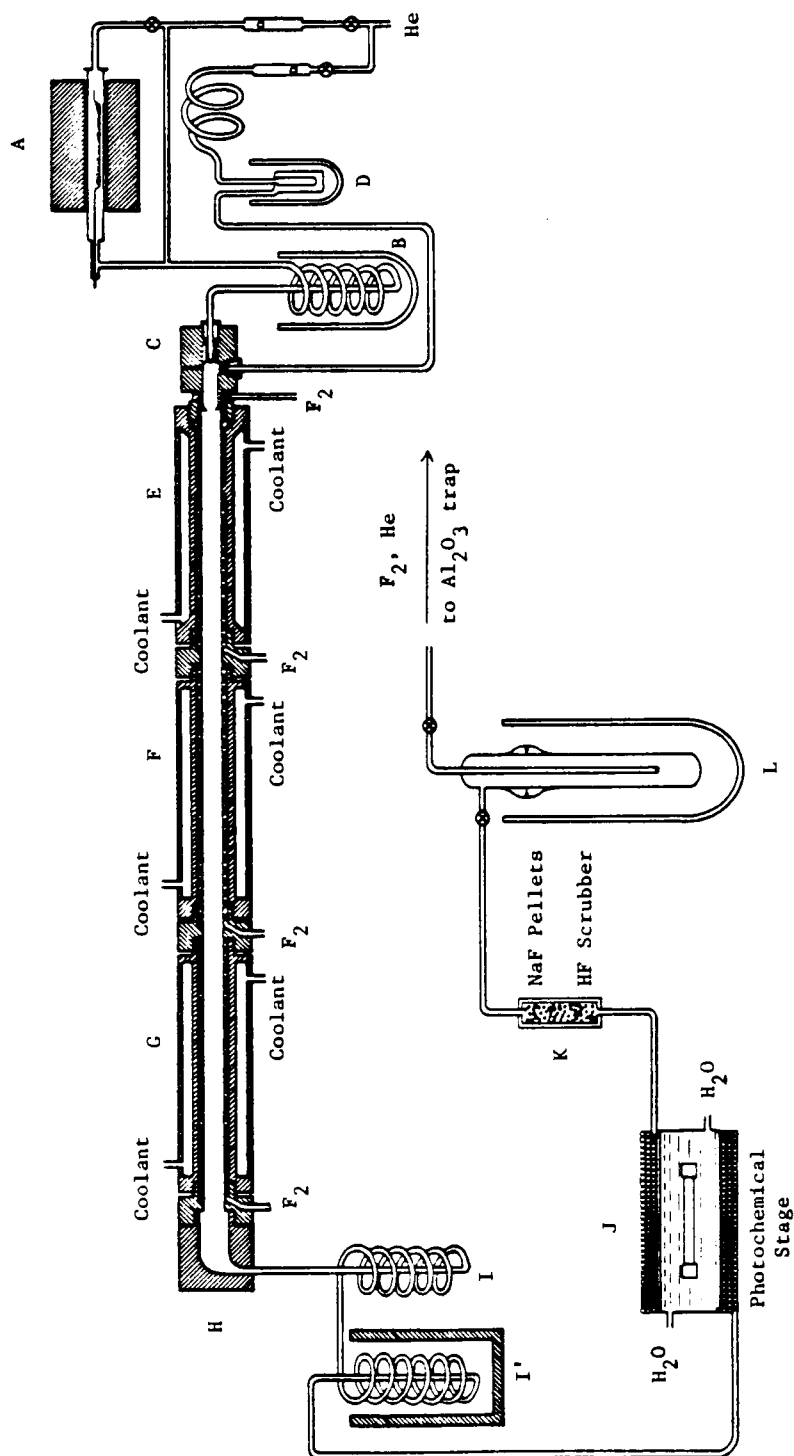
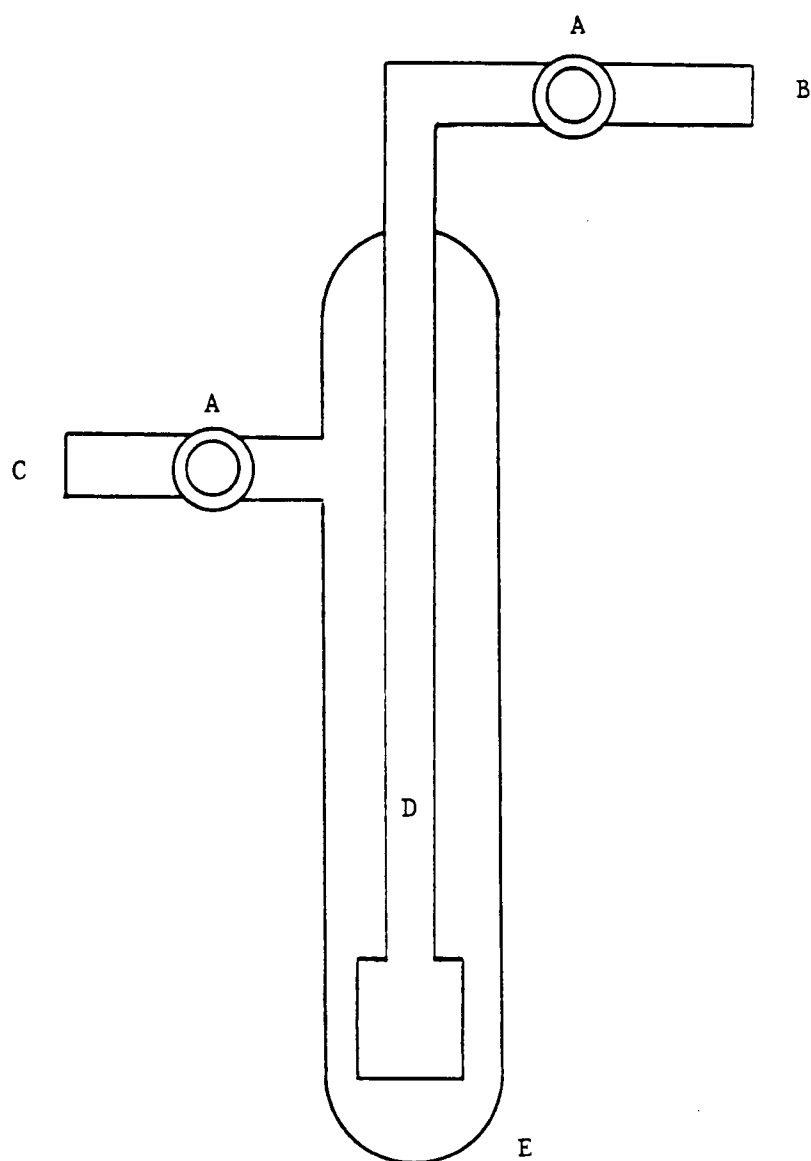


Figure 1.

The hydrocarbon evaporator device is shown schematically in Figure 2. The evaporator is constructed from a 30 mm Pyrex tube and a 1/4 inch medium wall gas filtering tube (Fisher Scientific). The inlet and outlet are constructed of 1/4 inch medium wall Pyrex tubing to allow connection of the device to the system via standard Ultratorr fittings. Teflon stopcocks (Kontes Scientific Glassware) are employed in all glassware. Approximately 20 ml of hydrocarbon are placed in the evaporator and the desired throughput (typically 2-5 mmol/hr) is obtained by adjusting the evaporator temperature and/or the helium flow through the device. The evaporator is held at a selected temperature by immersing it in an appropriate cold bath.

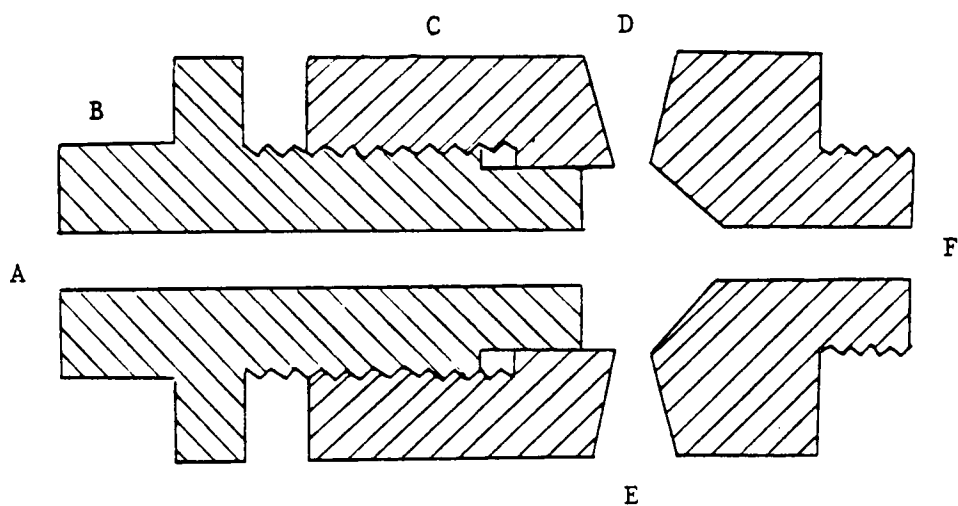
Two types of aerosol generators were employed, neither offering any observable advantage over the other. The aerosol generators are shown schematically in Figures 3 and 4. The chilled sodium fluoride stream enters at the rear through a Teflon insert which serves as insulation to prevent heating of the chilled stream. The sodium fluoride stream is then mixed with the hydrocarbon vapor entering from the side. A third inlet is provided to allow balancing of the flows within the generator with a helium stream.

To prevent condensation of the hydrocarbon vapor on the generator walls, the entire aerosol generator body is heated. A layer of asbestos paper is wrapped around the generator body, and over this is wound approximately five feet of 26 gauge nichrome wire in such a manner as to allow connection to an external voltage source. The entire generator body is then coated with a synthetic porcelain,



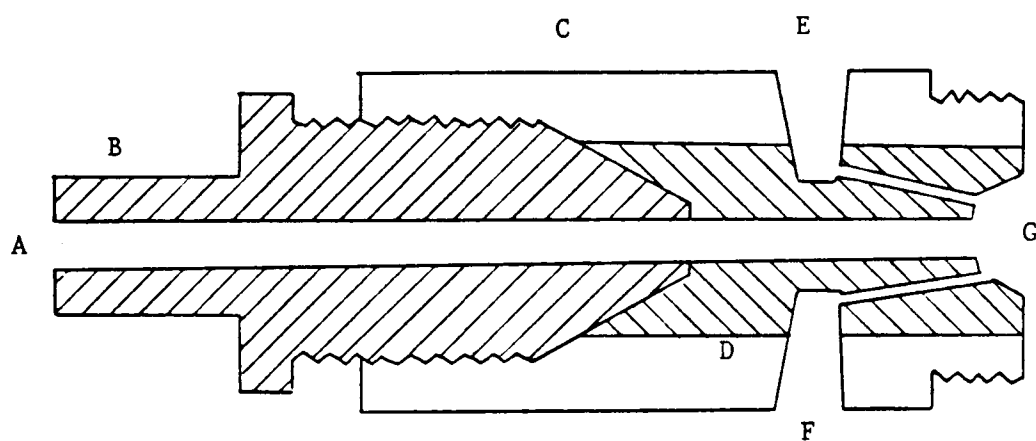
- Legend:
- A. Stopcock.
 - B. Helium inlet.
 - C. Outlet.
 - D. Gas filtering tube.
 - E. 30 mm Pyrex tube.

Figure 2. Hydrocarbon Evaporator Device.



Legend: A. Nucleating particle inlet.
B. Teflon insert.
C. Generator body (brass).
D. Hydrocarbon inlet.
E. Helium inlet.
F. Outlet.

Figure 3. Aerosol Generator No. 1.



- Legend:
- A. Nucleating particle inlet.
 - B. Teflon insert.
 - C. Generator body (brass).
 - D. Teflon insert.
 - E. Hydrocarbon inlet.
 - F. Helium inlet.
 - G. Outlet.

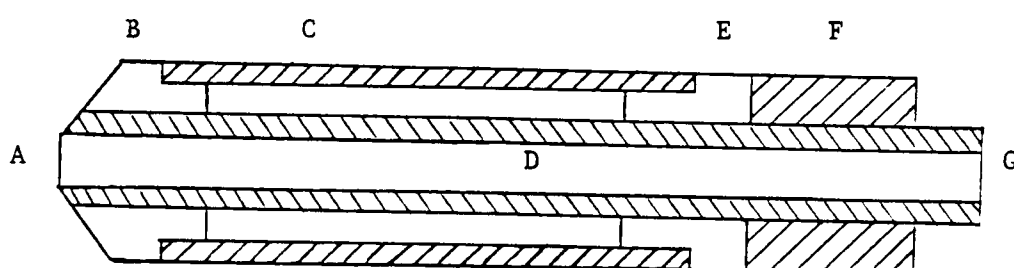
Figure 4. Aerosol Generator No. 2.

Sauereisen (Sauereisen Cements Company), which provides good thermal and electrical insulation.

Aerosol generator no. 1 employs a heated hydrocarbon inlet tube. This hydrocarbon inlet tube extends into the aerosol generator body through a male Ultratorr fitting screwed into the generator body, and is heated via connection to an external voltage source to prevent condensation of the hydrocarbon vapor prior to its entering the mixing chamber of the aerosol generator. The inlet consists of a stainless steel tube within a copper tube as shown schematically in Figure 5. The design allows the inner tube to be heated in order to prevent condensation of the hydrocarbon vapor while the outer copper tube remains relatively cool to prevent warming of the chilled sodium fluoride stream. No such heated inlet tube is provided in the case of aerosol generator no. 2 and no changes in system efficiency were observed; in this design the hydrocarbon enters the generator directly from the evaporator device.

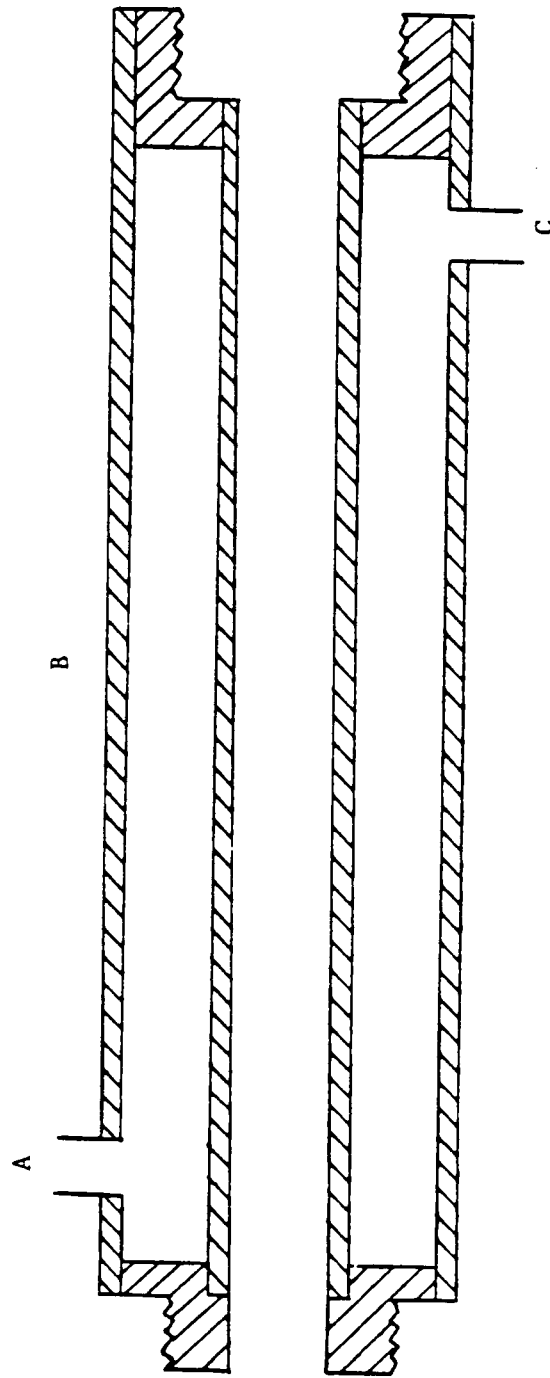
The reactor modules consist of an outer unit and a staging insert, both constructed of Monel, as shown schematically in Figures 6 and 7. The staging insert is constructed in such a manner that 0.025 inch holes drilled along the insert's inner surface in a corkscrew fashion allow a uniform concentration gradient of fluorine to be established along the module length.

The reactor modules are cooled by an integral heat exchanger. A freon reservoir is cooled to approximately -78°C with a dry ice/methanol solution and the chilled freon pumped to the desired module (Eastman/Iwaki mag-drive pump, model MD-15T) via a diverter unit.



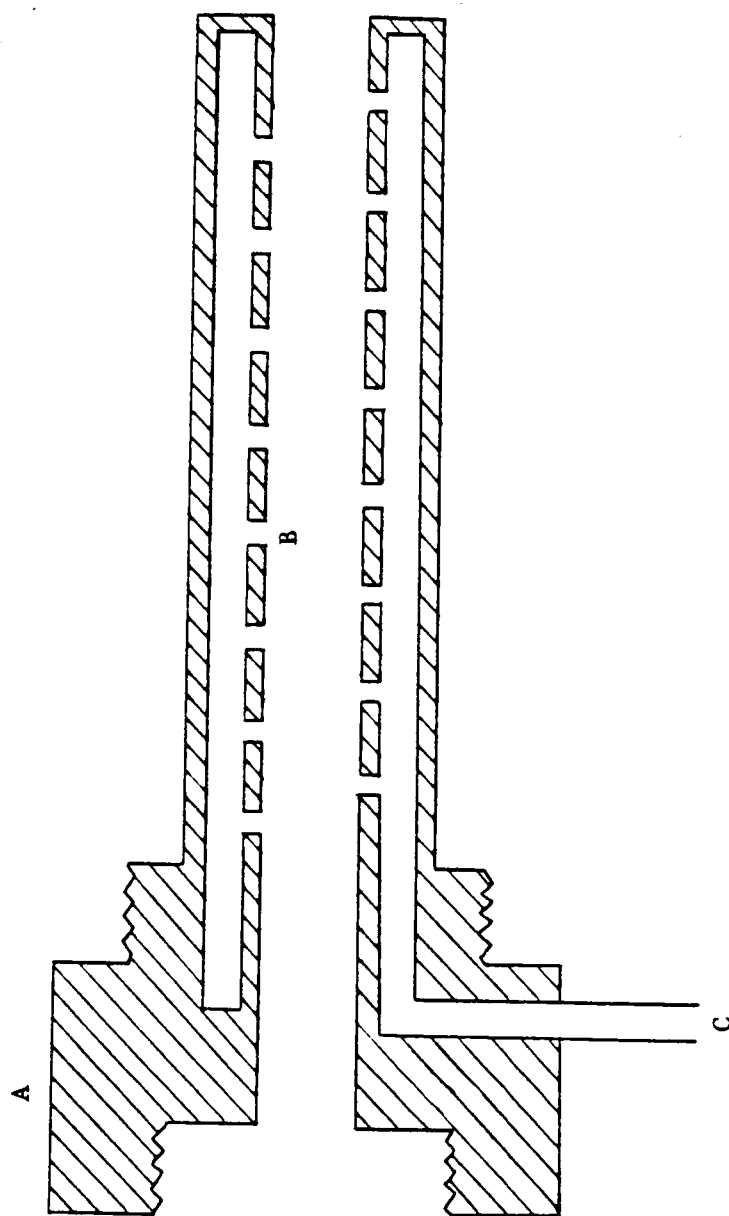
- Legend:
- A. Outlet.
 - B. Brass nozzle.
 - C. Copper tube.
 - D. Stainless steel tube.
 - E. Teflon spacer.
 - F. Copper tube.
 - G. Inlet.

Figure 5. Hydrocarbon Inlet Tube.



Legend: A. Coolant inlet.
 B. Unit body.
 C. Coolant outlet.

Figure 6. Reactor Module No. 1: Outer Unit.



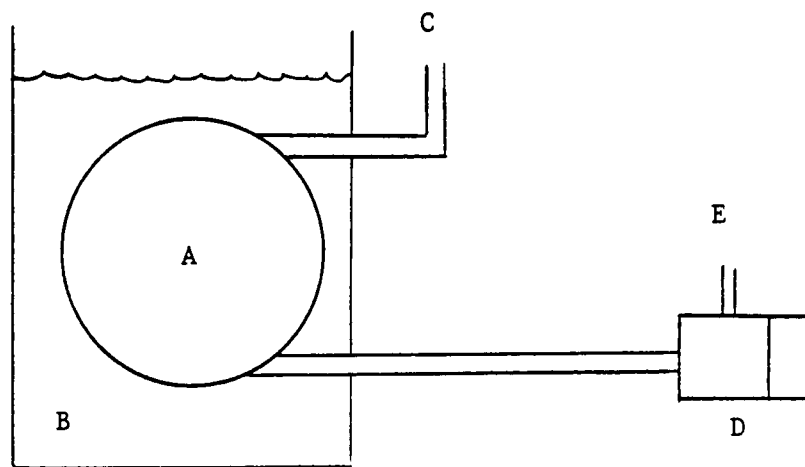
Legend: A. Unit body.
B. 0.025" holes.
C. Fluorine inlet.

Figure 7. Reactor Module No. 1: Staging Insert.

Figure 8 shows the design of the cooling system. Temperature control is obtained via solenoid valves (Asco) located at each module, and the associated control electronics. Module temperatures are monitored on a Bendix I/C type T/C model 302 pyrometer or GE type D053 temperature gauge connected to a thermocouple wire in a thin-walled stainless steel thermocouple probe extending into the cooling jacket of each module.

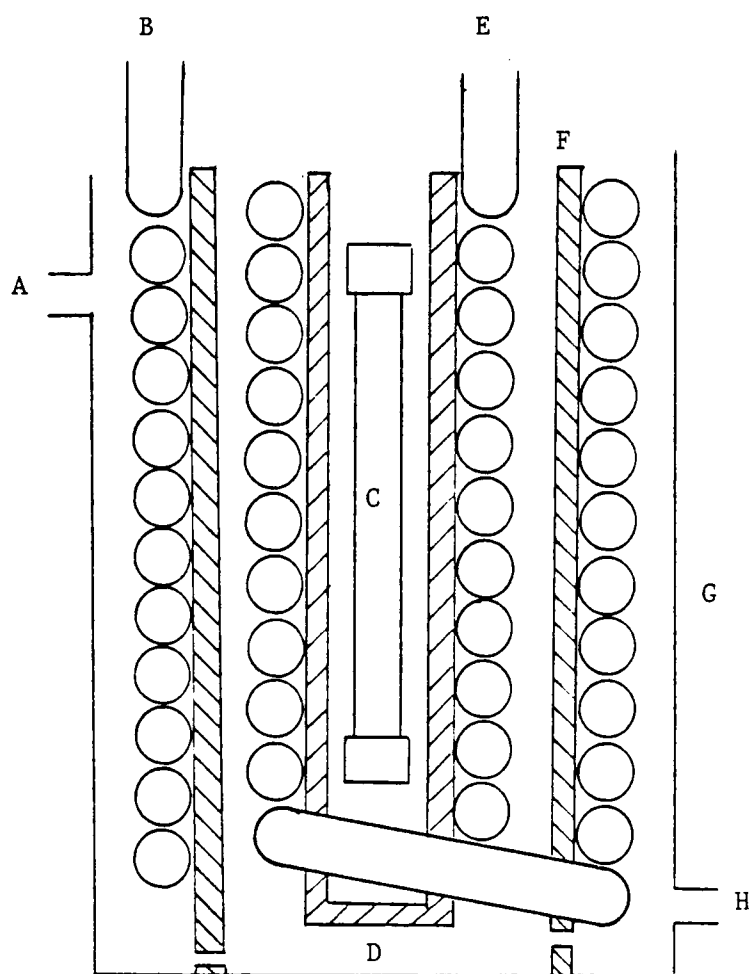
The photochemical stage provides activation of the elemental fluorine and is shown schematically in Figure 9. The stage consists of approximately 10 meters of 0.015 inch wall, 3/8 inch i.d. FEP Teflon tubing, one layer wrapped around a 50 mm x 390 mm quartz immersion well (Ace Glass) containing a 550 watt medium pressure mercury arc lamp (Hanovia), and a second layer wrapped concentrically around an overlying 75 mm Pyrex tube. Reactants flow through the stage in such a manner that they are initially exposed to Pyrex-filtered wavelengths (> 300 nm) and then encounter the more energetic ultraviolet wavelengths (FEP cutoff at approximately 225 nm^{23}) before leaving the stage. All FEP tubing is maintained at approximately $20\text{--}25^\circ\text{C}$ by positive water circulation over all surfaces.

Connections between the various sections of the aerosol direct fluorination system are accomplished via copper or Teflon tubing and standard Swagelok fittings. Fluorine flows are monitored with a Hastings mass flowmeter (model LF-20X) and Hastings mass flow transducers (model LF-20X, types F-100M and F-20M). Before entering the reactor modules, the fluorine flows are diluted with helium in a gas manifold. All helium flows are monitored with Matheson rotameters



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

Figure 8. Reactor 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.

(types 600 or 603), and Whitey valves (model SS1KS4 for He, M1KS4 or M21RS4 for F₂) are employed for the control of all flows.

B. Modified Aerosol Fluorination System

The modified aerosol fluorination system is shown schematically in Figure 10. This system employs a flash evaporator/sublimator unit allowing the handling of solids or nonvolatile liquids, and also employs a modified reactor module design. The remaining components of the system are identical to those in the basic system.

The modified aerosol generator, adapted to a flash evaporator/sublimator unit is shown schematically in Figure 11. Chilled sodium fluoride particles in a helium stream enter one side of the aerosol generator and are mixed with the hydrocarbon vapor in the hydrocarbon carrier stream from the evaporator/sublimator. The hydrocarbon carrier consists of one upper (primary) and a lower (secondary) helium flow entering the evaporator/sublimator body at the top and bottom, respectively. Liquid hydrocarbon is delivered from a Precision Sampling Corporation "Pressure-Lok" syringe driven by a Sage model 341a syringe pump, and enters at the bottom of the evaporator/sublimator unit. In the case of a solid hydrocarbon, the unit is filled with the solid material and helium enters at both bottom inlets.

The flash evaporator/sublimator is a stainless steel cylinder adapted to an inline filter (Nupro SS-4TF2-2BP4-2) containing a two micron filter element. The entire unit is wrapped in asbestos paper, wound with nichrome wire to permit resistive heating, and covered with

Figure 10. Modified Aerosol Fluorination System.

A heated bed of sodium fluoride (A) sublimates 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/sublimator unit (D) and the aerosol passed through the reactor modules (E,F,G) where it is mixed with fluorine. Following the last module is an endcap (H), a series of coils (I,I'), and a water-cooled photochemical stage (J). Hydrogen fluoride is removed in the scrubber (K) and the products collected in the liquid nitrogen cooled product trap (L). Excess fluorine is removed by passing the gas stream through an alumina trap.

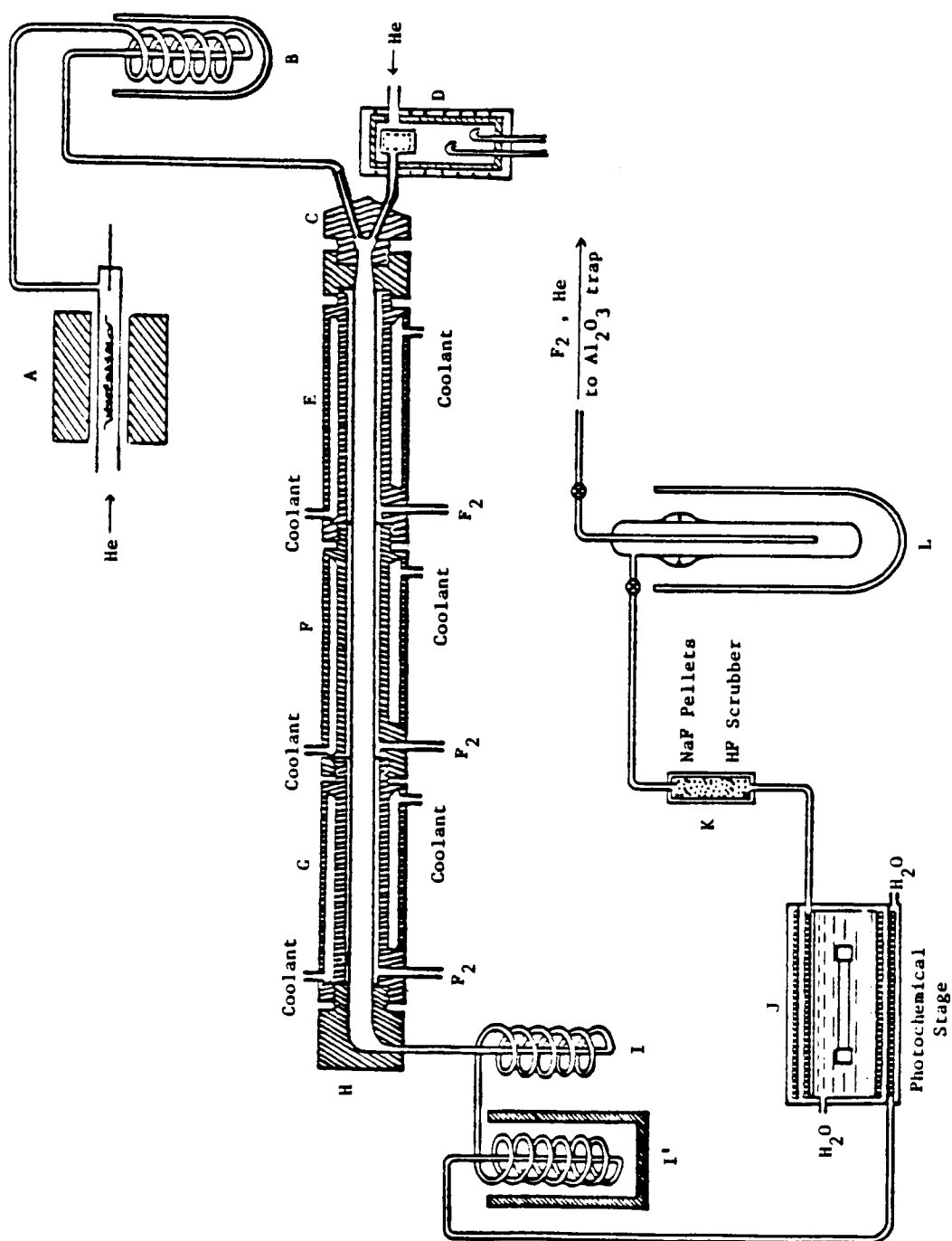
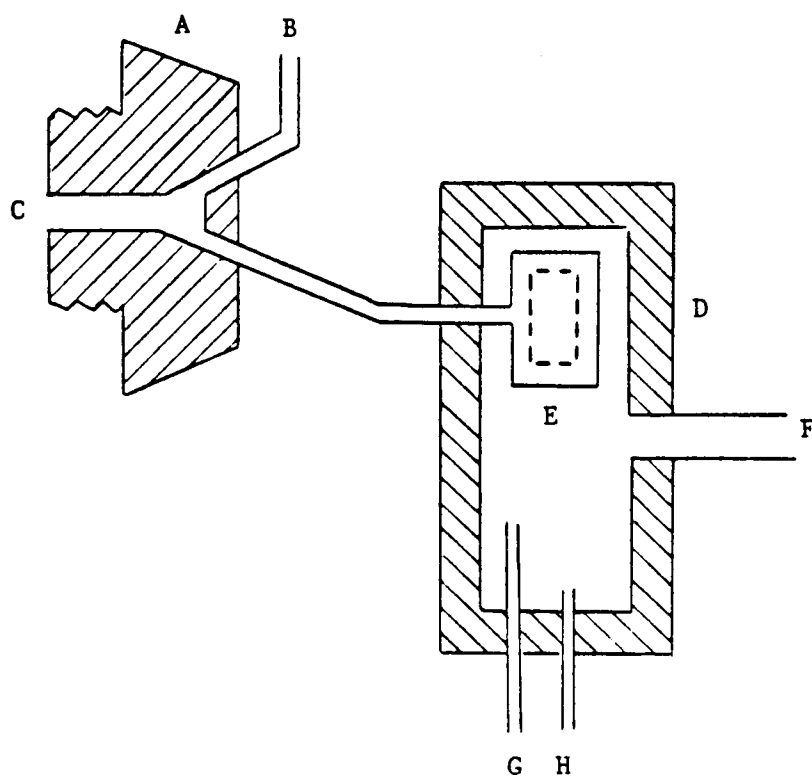


Figure 10.



- Legend:
- A. Generator body (brass).
 - B. Helium inlet.
 - C. Outlet to reactor modules.
 - D. Evaporator/sublimator body.
 - E. Filter.
 - F. Primary helium inlet.
 - G. Secondary helium inlet.
 - H. Hydrocarbon or tertiary helium inlet.

Figure 11. Aerosol Generator No. 3.

synthetic porcelain. A thermocouple wire soldered to the device's body allows monitoring of the evaporator/sublimator temperature.

The modified reactor module design is shown schematically in Figure 12. The modules are constructed of Monel, and fluorine enters the reaction region through a 3/4 inch diameter two micron porous Monel filter element.

C. Materials

All materials used were reagent grade and were used as received except where otherwise noted.

Acetone-Fisher Scientific; dried over anhydrous CaSO_4 , distilled and stored over molecular sieves.

Adamantane-Aldrich Chemical (99%).

Alumina-Alcoa Chemicals (activated).

Benzene-Fisher Scientific.

2-Butanone-Mallinckrodt Chemical.

Calcium Hydride-Alpha Products (anhydrous).

Calcium Sulfate-W. A. Hammond Drierite Company (anhydrous).

Carbon Tetrachloride-Fisher Scientific; dried over molecular sieves.

Cyclohexanol-Fisher Scientific.

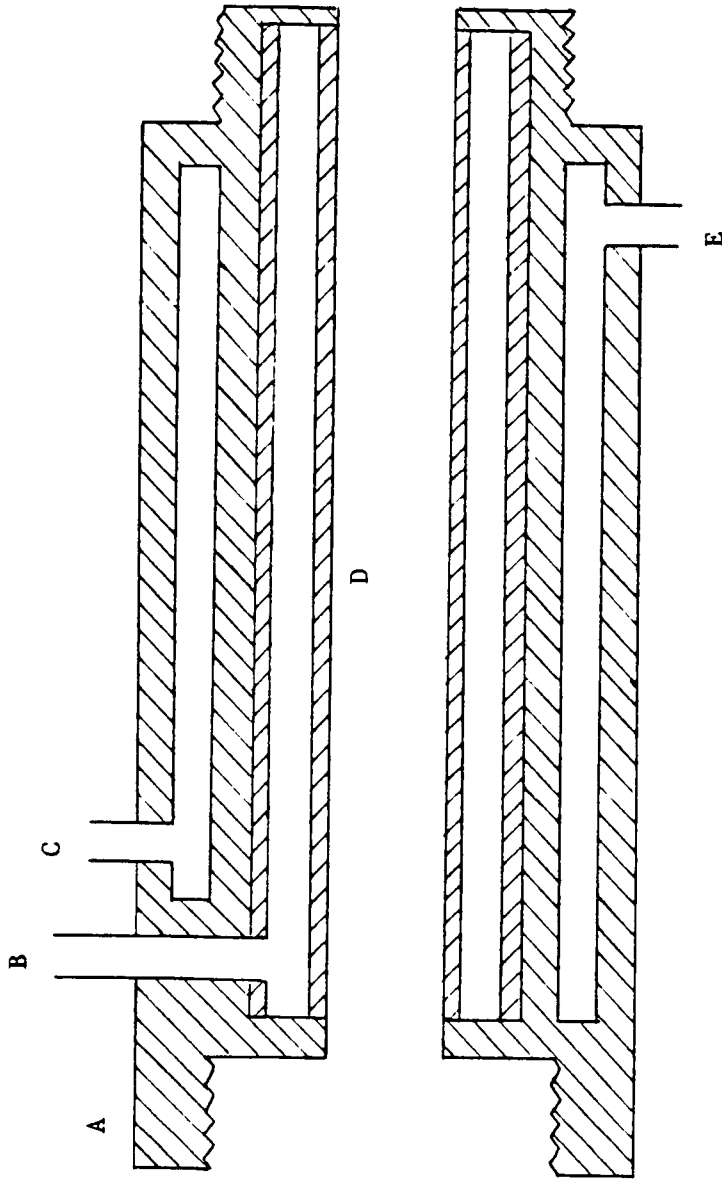
Cyclohexanone-Fisher Scientific.

Cyclopentanol-Aldrich Chemical (99%).

Cyclopentanone-Aldrich Chemical (99+%).

Deuteriochloroform-Aldrich Chemical (99.8 atom %).

3,3-Dimethyl-2-butanone (Pinacolone) — Aldrich Chemical.



- Legend: A. Module body.
B. Fluorine inlet.
C. Coolant inlet.
D. Porous Monel filter element.
E. Coolant outlet.

Figure 12. Reactor Module Design No. 2.

Ethyl Ether-Fisher Scientific (anhydrous).
Ethylene Glycol-Fisher Scientific.
Fluorine-Air Products.
Freon 11-Allied Chemical (Genetron 11).
2-Heptanone-Aldrich Chemical (98%).
3-Heptanone-Aldrich Chemical (98%).
4-Heptanone-Aldrich Chemical (98%).
Hydrochloric Acid-Fisher Scientific (concentrated).
Methanol-distilled drum grade.
Methyl Iodide-Aldrich Chemical (99%).
Molecular Sieves-Fisher Scientific (4Å).
Nitrogen (gas)-Burdett Oxygen Company.
Pentane-Fisher Scientific.
3-Pentanone-Chemical Samples Company (99%).
Perfluoropentane-PCR Research Chemicals.
Potassium Carbonate-Fisher Scientific (anhydrous).
Sodium-Fisher Scientific.
Sodium Fluoride-Fisher Scientific.
Sodium Fluoride Pellets-Harshaw Chemical Company.
Sodium Hydroxide-Fisher Scientific.
Sulfuric Acid-Fisher Scientific (fuming, 30% SO₃).
Tetramethyl Orthocarbonate-Aldrich Chemical.
2,2,4,4-Tetramethyl-3-pentanone (Pivalone) - Fluka Chemicals.
Tetramethylsilane-Mallinckrodt Chemical (nmr grade).
para-Toluene Sulfonic Acid-Eastman Chemical (practical).
Xylene-Fisher Scientific; dried over sodium.

D. Characterization of Compounds

Workup of products, following removal of hydrogen fluoride, consisted of vacuum line fractionation, infrared assay of fractions, and gas chromatographic separation of materials. Characterizations were made by vapor phase infrared spectrophotometry, electron-impact and chemical ionization mass spectrometry, ^1H and ^{19}F nuclear magnetic resonance (nmr) spectroscopy, and elemental analysis. Product distributions and percent yields were determined by gas chromatographic assay (cut and weigh method).

Vacuum Line. An all glass vacuum system with Teflon stopcocks (Kontes Scientific Glassware) was employed. A Welch Duo-seal vacuum pump (model 1402B) was used, and all transfers, fractionations, etc., performed at approximately 3 microns of mercury (Hastings vacuum gauge, model VT-5B).

Gas Chromatography. Gas chromatographic separations were performed on a Bendix model 2300 gas chromatograph (subambient, multi-controller) employing a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh acid-washed Chromosorb P conditioned at 225°C (12 hours) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber stationary phase on acid-washed Chromosorb P conditioned at 250°C (12 hours). The carrier gas was helium (60 cc/min). Injections were made using standard microliter syringes (Hamilton) or in the case of extremely volatile materials with Precision Sampling Corporation "Pressure-Lok" syringes. All retention times (t_R) were measured relative to the time of injection.

Infrared Spectra. All infrared spectra were recorded as gases in a gas cell (path length 10 centimeters) with potassium chloride optics or as neat liquids between potassium chloride plates. Spectra were recorded on a Perkin Elmer model 1330 infrared spectrophotometer.

Mass Spectra. Mass spectra were taken on a Hewlett-Packard GC/MS (5710A GC, 5980 MS, 5934A computer); electron-impact mass spectrometry was performed at 70 eV and chemical ionization mass spectrometry employed a methane plasma.

Nuclear Magnetic Resonance. ^1H and ^{19}F nmr spectra were taken with a JEOL FX90Q (omniprobe) nmr spectrometer operating at 89 MHz for ^1H and 84 MHz for ^{19}F . Spectra were recorded with tetramethylsilane (TMS) as internal standard for ^1H and in CDCl_3 with 1% CFCl_3 internal standard for ^{19}F .

Elemental Analysis. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

E. Aerosol Fluorination of 3-Pentanone

Throughputs for 3-pentanone were determined by cooling approximately 20 ml of the material in the evaporator device to 0°C (ice bath) and, for a given helium flow through the device, weighing the amount of 3-pentanone collected in a liquid nitrogen cooled trap over a given time interval. Results of the throughput experiments are shown in Figure 13. At 0°C the vapor pressure of 3-pentanone is such that a 70 cc/min flow of helium through 20 ml of the material in the evaporator device produced a throughput of 2.2 mmol/hr.

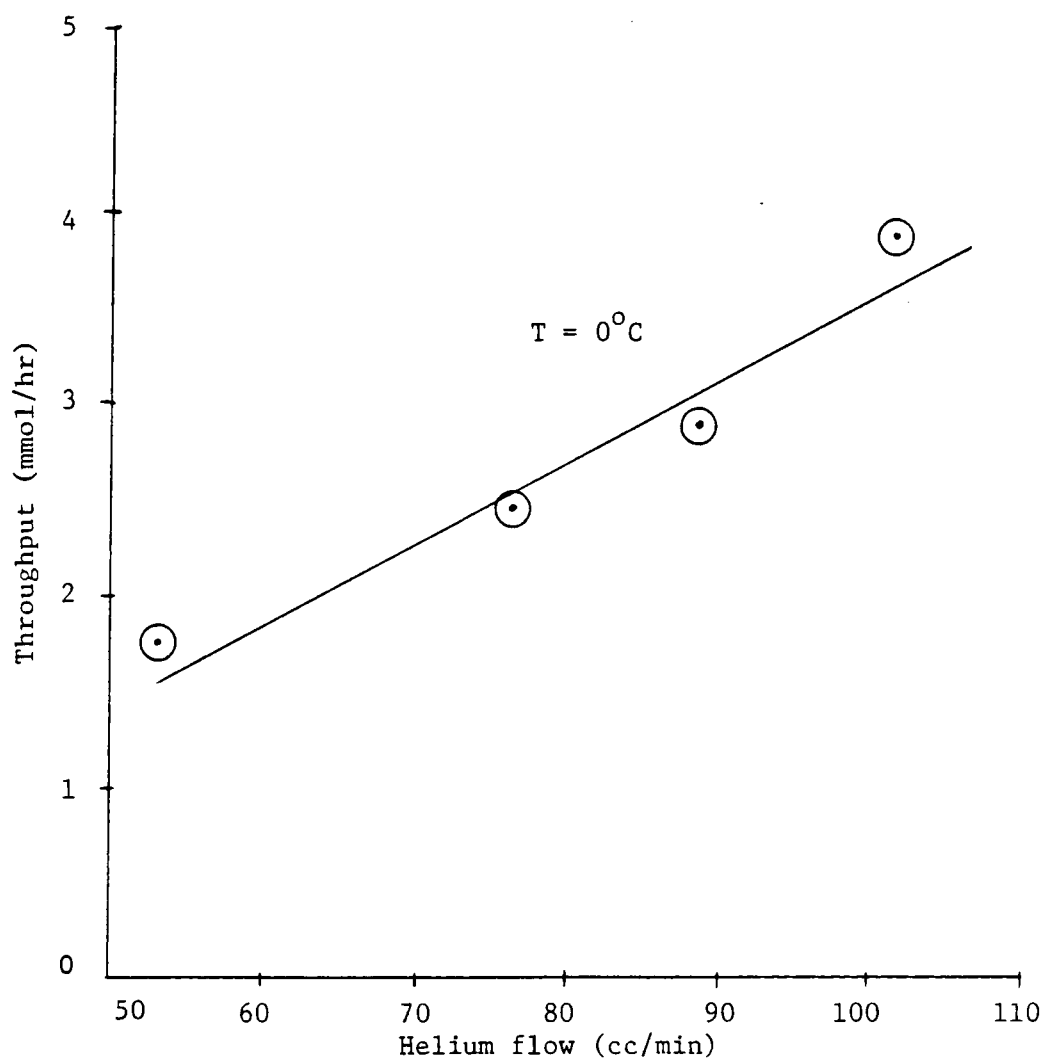


Figure 13. 3-Pentanone Throughputs.

The aerosol fluorination of 3-pentanone was conducted with the basic aerosol fluorination system. Details of the aerosol fluorination parameters are given in Table 1, Appendix A. At the end of the reaction the products were transferred to the vacuum line and fractionated through -131°C (pentane) and -196°C (liquid nitrogen) cold traps. The -196°C trap contents, which included species such as CF_4 and COF_2 (infrared assay of fraction), were discarded. The -131°C trap contents, which constituted the majority of products, were collected, weighed, and separated on the QF-1 gas chromatographic column with the temperature program: -5°C , 2 min; $1^{\circ}\text{C}/\text{min}$ to 10°C ; 10°C , 1 min; $20^{\circ}\text{C}/\text{min}$ to 180°C . The major product was F-3-pentanone ($t_R = 16$ min) which constituted 53% (0.113 g, 0.42 mmol), 62% (0.198 g, 0.74 mmol), and 71% (0.271 g, 1.02 mmol) of the total products collected by weight for reactions 1, 2, and 3, respectively. Without correcting for unreacted or partially reacted materials, the percent yields of F-3-pentanone based on the throughput of 3-heptanone (8.8 mmol) for reactions 1, 2, and 3 were 5%, 8%, and 12%, respectively. The characterization of F-3-pentanone is given in Table 1, Appendix B. Also isolated from the reactions was F-n-propane ($t_R = 12$ min), identified from its infrared spectrum.⁷⁰ The percent distributions of F-n-propane for reactions 1, 2, and 3 were 26% (0.056 g, 0.30 mmol), 14% (0.045 g, 0.24 mmole), and 13% (0.049 g, 0.26 mmol) of the total products collected by weight, respectively.

F. Aerosol Fluorination of 4-Heptanone

Throughputs for 4-heptanone at room temperature (23°C) were determined in the manner employed for 3-pentanone, and the results are shown in Figure 14. The vapor pressure of 4-heptanone at 23°C is such that a 165 cc/min flow of helium through approximately 20 ml of the material in the evaporator device produced a throughput of 2.5 mmol/hr.

The aerosol fluorination of 4-heptanone was conducted with the basic aerosol fluorination system. Details of the aerosol fluorination parameters are given in Table 2, Appendix A. Products from a four hour run were transferred to the vacuum line and worked up as for 3-pentanone. The -131°C cold trap contents (0.734 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 30°C, 1 min; 2°C/min to 60°C; 60°C, 1 min; 50°C/min to 180°C. The major product was F-4-heptanone (t_R = 14 min) which constituted 92% (0.675 g, 1.84 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials, the percent yield of F-4-heptanone based on the throughput of 4-heptanone (10.0 mmol) was 18%. The characterization of F-4-heptanone is given in Table 2, Appendix B; the infrared spectrum was identical to that appearing in the literature.⁵²

G. Aerosol Fluorination of Cyclopentanone

Throughputs for cyclopentanone at 23°C were determined as described above and the results are shown in Figure 15. The vapor pressure of cyclopentanone at 23°C is such that a 112 cc/min flow of

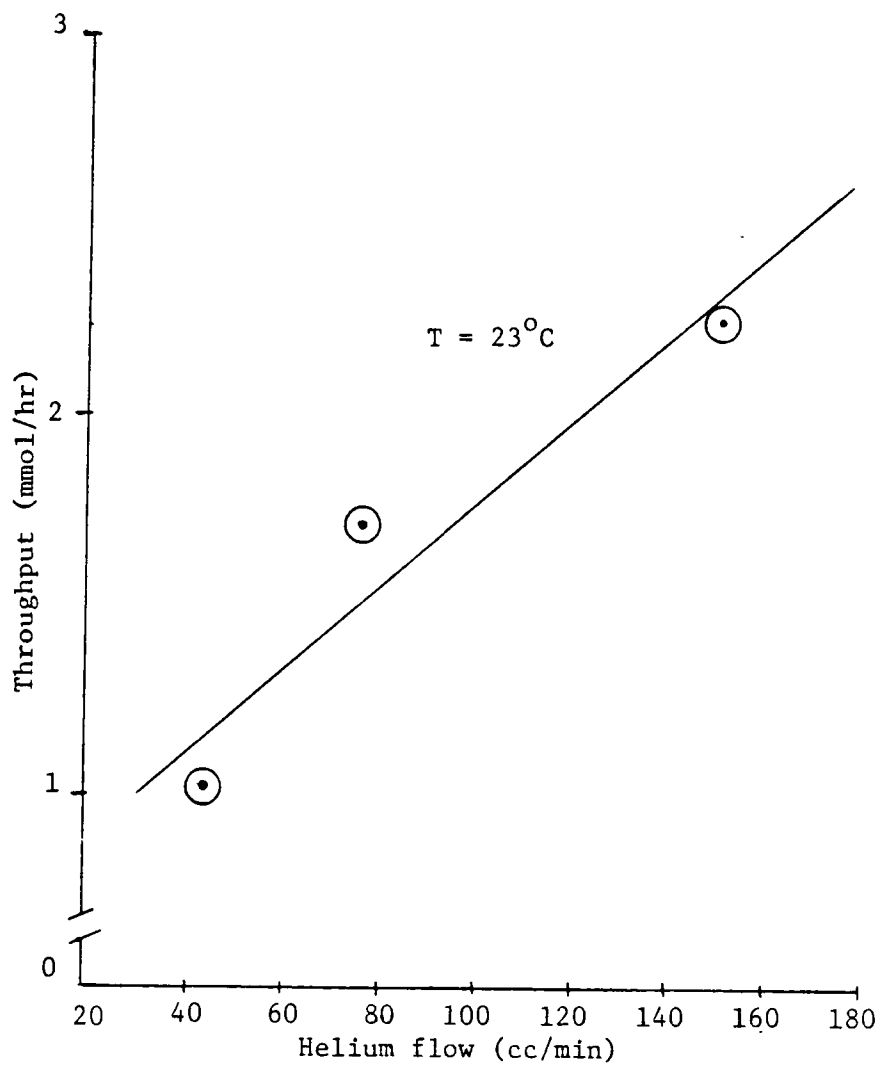


Figure 14. 4-Heptanone Throughputs.

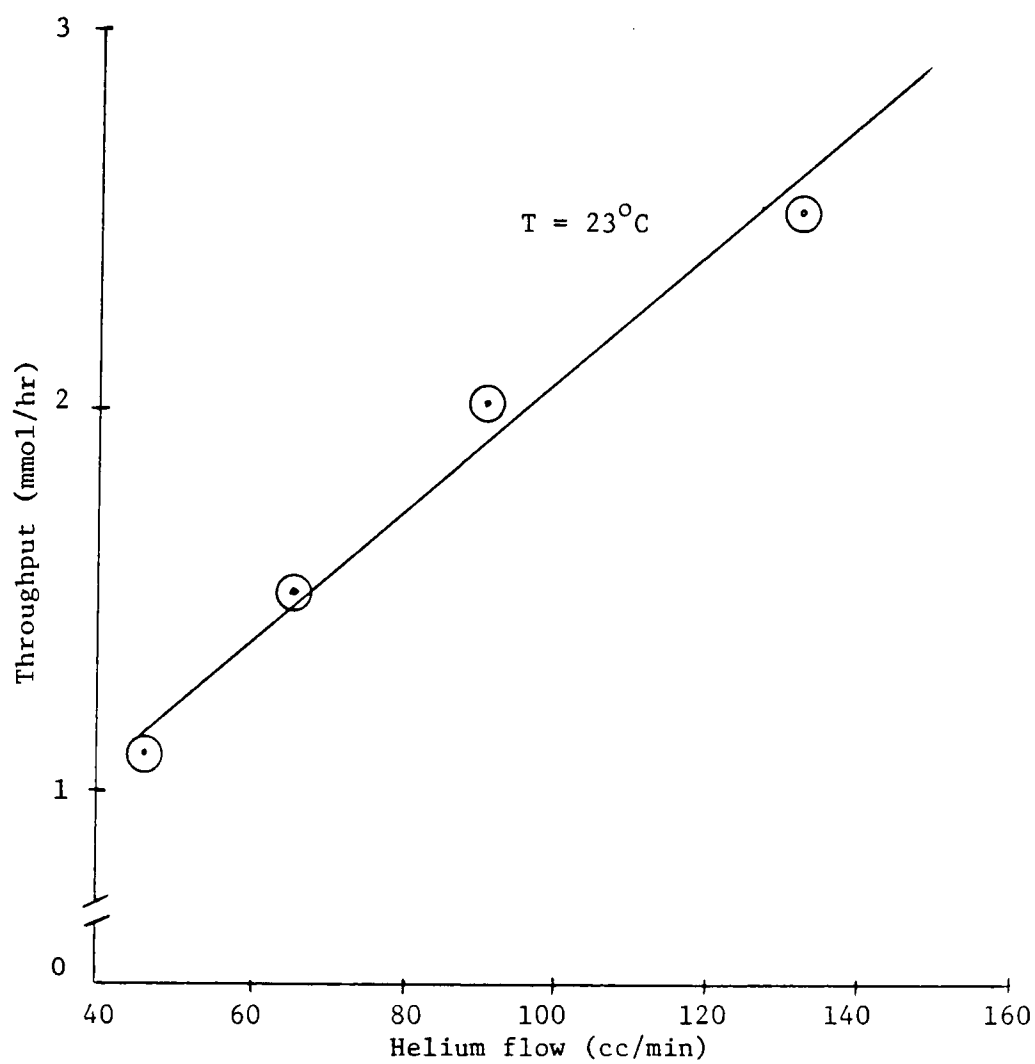


Figure 15. Cyclopentanone Throughputs.

helium through approximately 20 ml of material in the evaporator device produced a throughput of 2.3 mmol/hr.

The aerosol fluorination of cyclopentanone was conducted with the basic aerosol fluorination system. Details of the aerosol fluorination parameters are given in Table 3, Appendix A. Products from a three hour run were transferred to the vacuum line, and worked up as described above. The -131°C trap contents (0.620 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 10°C , 1 min; $1^{\circ}\text{C}/\text{min}$ to 30°C ; 30°C , 1 min; $20^{\circ}\text{C}/\text{min}$ to 180°C . The major products were F-pentanoyl fluoride ($t_R = 14$ min) and F-n-butane ($t_R = 7$ min) which constituted 61% (0.378 g, 1.42 mmol) and 11% (0.068 g, 0.29 mmol) of the total products collected by weight, respectively. Without correcting for unreacted or partially reacted materials, the percent yield of F-pentanoyl fluoride based on the throughput of cyclopentanone (6.9 mmol) was 21%. The characterization of F-pentanoyl fluoride is given in Table 3, Appendix B. The ^{19}F nmr spectrum of F-pentanoyl fluoride was in agreement with that appearing in the literature.⁷¹ F-n-Butane was identified from its infrared spectrum.⁷⁰

H. Aerosol Fluorination of Cyclohexanone

Throughputs for cyclohexanone at 23°C were determined as described above and the results are shown in Figure 16. The vapor pressure of cyclohexanone at 23°C is such that a 165 cc/min flow of helium through approximately 20 ml of material in the evaporator device produced a throughput of 1.9 mmol/hr.

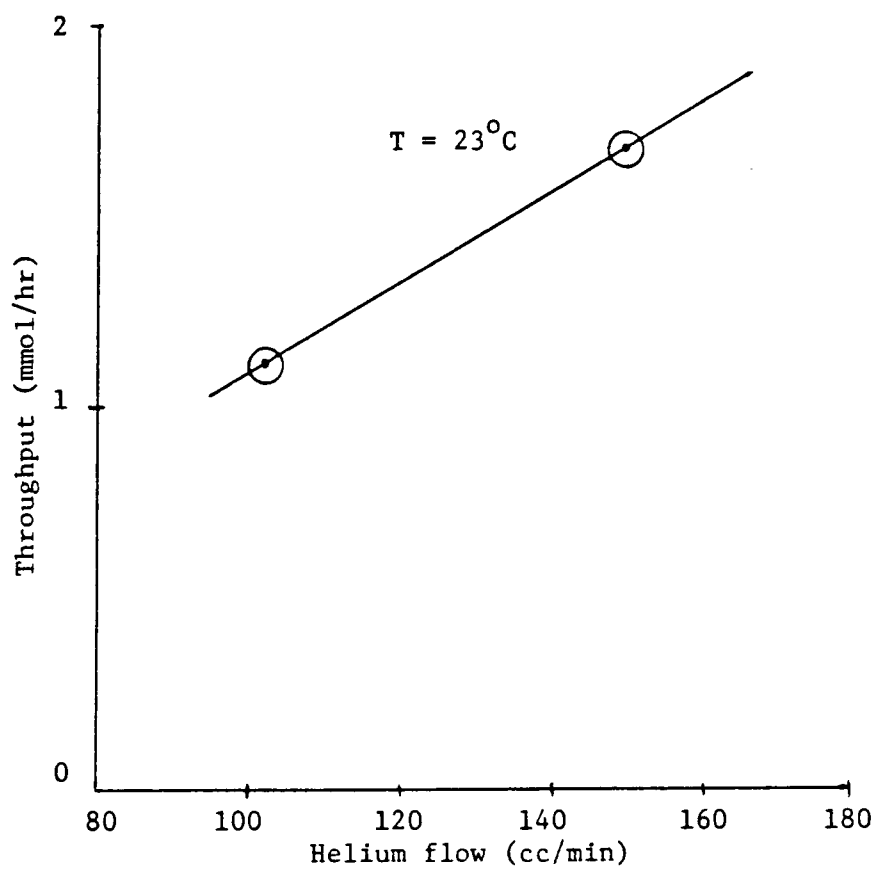


Figure 16. Cyclohexanone Throughputs.

The aerosol fluorination of cyclohexanone was conducted with the basic aerosol fluorination system. Details of the aerosol fluorination parameters are given in Table 4, Appendix A. In all cases, only a small amount of nonvolatile products were obtained which bled out slowly on the chromatographic columns. No traces of perfluorinated materials were found.

I. Aerosol Fluorination of 3-Heptanone

Due to the low volatility of 3-heptanone, aerosol fluorination utilizing the basic aerosol fluorination system was not possible. At the highest carrier flow allowed with the system, a sufficient throughput (at least 1 mmol/hr) of material was unattainable. Hence, the aerosol fluorination of 3-heptanone was conducted with the modified aerosol fluorination system. Details of the aerosol fluorination parameters are given in Table 5, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The contents of the -131°C trap were collected, weighed, and separated on the QF-1 gas chromatographic column with the temperature program: 25°C , 2 min; $1.5^{\circ}\text{C}/\text{min}$ to 60°C ; 60°C , 1 min; $50^{\circ}\text{C}/\text{min}$ to 180°C . The major products were F-3-heptanone ($t_R = 17$ min) and F-n-butane ($t_R = 7$ min). Percent distributions and percent yields of F-3-heptanone for the reactions are given in Table 5, Appendix A. For optimized aerosol fluorination parameters, F-3-heptanone constituted 59% (0.975 g, 2.66 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials, the percent yield of F-3-heptanone based on the

amount of 3-heptanone injected (21.0 mmol) was 13%. The characterization of F-3-heptanone is given in Table 4, Appendix B. F-n-Butane was identified from its infrared spectrum,⁷⁰ and constituted 9% (0.149 g, 0.63 mmol) of the total products collected by weight for the run under optimum conditions.

J. Aerosol Fluorination of 2-Heptanone

The aerosol fluorination of 2-heptanone was conducted with the modified aerosol fluorination system. A pump speed corresponding to 3.8 mmol/hr was established and 1.7 ml (12.2 mmol) 2-heptanone delivered over a 3.2 hour period. Details of the aerosol fluorination parameters are given in Table 6, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The contents of the -131°C trap (0.633 g) were collected and separated on the SE-52 gas chromatographic column with the temperature program: 0°C, 2 min; 1°C/min to 10°C; 10°C, 1 min; 20°C/min to 180°C. The major products were F-2-heptanone (t_R = 9 min) and F-n-pentane (t_R = 3.5 min) which constituted 55% (0.348 g, 0.95 mmol) and 26% (0.165 g, 0.57 mmol) of the total products collected by weight, respectively. Without correcting for unreacted or partially reacted materials, the percent yield of F-2-heptanone based on the amount of 2-heptanone injected (12.2 mmol) was 8%. The characterization of F-2-heptanone is given in Table 5, Appendix B. The ¹⁹F nmr spectrum of F-2-heptanone was in agreement with that appearing in the literature.⁴³ F-n-Pentane was identified from its infrared spectrum.⁷⁰

K. Aerosol Fluorination of 2-Butanone

The aerosol fluorination of 2-butanone was conducted with the modified aerosol fluorination system. A pump speed corresponding to 3.9 mmol/hr was established and 1.4 ml (15.6 mmol) 2-butanone delivered over a 4 hour period. Details of the aerosol fluorination parameters are given in Table 7, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The contents of the -131°C trap (1.553 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 0°C , 2 min; $1^{\circ}\text{C}/\text{min}$ to 10°C ; 10°C , 1 min; $20^{\circ}\text{C}/\text{min}$ to 180°C . The major product was F-2-butanone ($t_R = 11.5$ min) which constituted 20% (0.311 g, 1.44 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials, the percent yield of F-2-butanone based on the amount of 2-butanone injected (15.6 mmol) was 9%. The characterization of F-2-butanone is given in Table 6, Appendix B. The infrared and ^{19}F nmr spectra of F-2-butanone were in agreement with those found in the literature.^{43,60}

L. Aerosol Fluorination of Acetone

The aerosol fluorination of acetone was conducted with the modified aerosol fluorination system. A pump speed corresponding to 5.1 mmol/hr was established and 1.5 ml (20.4 mmol) acetone delivered over a 4 hour period. Details of the aerosol fluorination parameters are given in Table 8, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The -131°C trap contents (0.309 g) were collected and separated on the SE-52 gas chromatographic column with the temperature program: -40°C , 2 min; $1^{\circ}\text{C}/\text{min}$ to -30°C ; -30°C , 1 min; $20^{\circ}\text{C}/\text{min}$ to 180°C . The major product was F-acetone ($t_R = 3.5$ min) which constituted 48% (0.148 g, 0.89 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials the percent yield of F-acetone based on the amount of acetone injected (20.4 mmol) was 4%. F-Acetone was identified from its infrared spectrum.^{72,73}

M. Aerosol Fluorination of Methoxycyclopentane

Methoxycyclopentane was prepared by the method of Vogel.⁷⁴ Freshly cut sodium (15.5 g, 0.67 mol) and 350 ml of sodium-dried xylene were placed in a 1000-ml three-neck flask fitted with a stirrer and condenser and the contents heated with an oil bath. When all the sodium had melted, the stirrer was started and stirring continued until all the sodium was in the form of fine granules. The oil bath was then removed and stirring continued until the flask and contents cooled to room temperature. The xylene was then decanted off, and the solid "sodium sand" washed twice with 100 ml of anhydrous ether and covered with 150 ml anhydrous ether. To the sodium sand solution, 60 ml (0.67 mol) cyclopentanol in 75 ml anhydrous ether were added dropwise from an addition funnel over a two hour period, and the contents allowed to stand overnight. To the solid alkoxide were added 42 ml (0.67 mol) methyl iodide from an addition funnel over a two hour period. The

contents were then stirred for 30 minutes and the ether distilled off (heating mantle). The products were then distilled, yielding a large fraction of boiling point 100-105°C. Repeated distillation from sodium yielded 25.6 g (0.26 mol) pure methoxycyclopentane (bp 105°C, identical to literature value⁷⁴), a 39% yield.

The aerosol fluorination of methoxycyclopentane was conducted with the modified aerosol fluorination system. Details of the aerosol fluorination parameters are given in Table 9, Appendix A. Products were transferred to the vacuum line and worked up as described above. The contents of the -131°C trap were collected and separated on the QF-1 gas chromatographic column with the temperature program: 20°C, 10 min; 5°C/min to 100°C; 100°C, 1 min; 50°C/min to 180°C. The major product was F-methoxycyclopentane (t_R = 13 min) which constituted 38% (1.363 g, 4.31 mmol) and 57% (1.381 g, 4.37 mmol) of the total products collected by weight for the two reactions. Without correcting for unreacted or partially reacted materials the percent yields of F-methoxycyclopentane based on the throughput of methoxycyclopentane (34.4 mmol, 20.4 mmol, respectively) for the reactions were 13% and 21%, respectively. The characterization of F-methoxycyclopentane is given in Table 7, Appendix B. The ¹⁹F nmr and electron-impact mass spectra of F-methoxycyclopentane were in agreement with those appearing in the literature.⁷⁵

N. Hydrolysis of F-Methoxycyclopentane

F-Methoxycyclopentane (0.321 g, 1.02 mmol) was condensed onto an approximately equal volume of fuming sulfuric acid (30% SO₃) which had

been degassed and vacuum-stripped of SO_3 . The reaction tube (Pyrex) was then sealed off under vacuum and heated for 24 hours at 360°C in a tube furnace. The tube was then opened under vacuum and the contents fractionated through -131°C and -196°C cold traps. The contents of the -131°C trap (0.243 g) were dissolved in CCl_4 and separated on the SE-52 gas chromatographic column with the temperature program: -10°C , 5 min; $0.5^\circ\text{C}/\text{min}$ to 20°C . The products were identified as F-cyclopentanone ($t_R = 6.5$ min) and unreacted F-methoxycyclopentane ($t_R = 9.5$ min) which constituted 58% (0.141 g, 0.62 mmol) and 42% (0.102 g, 0.32 mmol) of the total products collected by weight, respectively. The percent yield of F-cyclopentanone based on F-methoxycyclopentane reacted was thus 88% (61% conversion). The characterization of F-cyclopentanone is given in Table 8, Appendix B. The infrared, ^{19}F nmr, and electron-impact mass spectra of F-cyclopentanone were in agreement with those appearing in the literature.^{63,66}

O. Aerosol Fluorination of Methoxycyclohexane

Methoxycyclohexane was prepared by the method of Vogel.⁷⁴ Proceeding as for the preparation of methoxycyclopentane, from 15.5 g (0.67 mol) sodium, 69 ml (0.67 mol) cyclohexanol, and 43 ml (0.69 mol) methyl iodide were isolated 17.5 g (0.15 mol) pure methoxycyclohexane (bp 133°C , identical to literature value⁷⁴), a 22% yield.

The aerosol fluorination of methoxycyclohexane was conducted with the modified aerosol fluorination system. A pump speed corresponding to 3.8 mmol/hr was established and 3.3 ml (25.5 mmol) delivered over a

6.7 hour period. Details of the aerosol fluorination parameters are given in Table 10, Appendix A.

The products were transferred to the vacuum line and worked up as described above. The contents of the -131°C trap (3.323 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 35°C , 10 min; $4^{\circ}\text{C}/\text{min}$ to 100°C ; 100°C , 1 min; $50^{\circ}\text{C}/\text{min}$ to 180°C . The major product was F-methoxycyclohexane ($t_R = 14$ min) which constituted 90% (2.991 g, 8.17 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials the percent yield of F-methoxycyclohexane based on the amount of methoxycyclohexane injected (25.5 mmol) was 32%. The characterization of F-methoxycyclohexane is given in Table 9, Appendix B. The ^{19}F nmr spectrum of F-methoxycyclohexane was in agreement with that appearing in the literature.⁷⁵

P. Hydrolysis of F-Methoxycyclohexane

F-Methoxycyclohexane (0.308 g, 0.84 mmol) was condensed onto an approximately equal volume of sulfuric acid which had been treated as described above. The reaction tube was then sealed under vacuum and heated for 14 hours at 340°C in a tube furnace. The tube was then opened under vacuum and the products fractionated through -131°C and -196°C cold traps. The -131°C trap contents (0.268 g) were collected, dissolved in CCl_4 , and separated on the SE-52 gas chromatographic column with the temperature program: 0°C , 10 min; $1^{\circ}\text{C}/\text{min}$ to 100°C . The products were identified as F-cyclohexanone ($t_R = 9$ min) and unreacted F-methoxycyclohexane ($t_R = 18$ min) which constituted 25%

(0.067 g, 0.24 mmol) and 75% (0.201, 0.55 mmol) of the total products collected by weight, respectively. The yield of F-cyclohexanone based on the amount of F-methoxycyclohexane reacted was thus 83% (28% conversion). The characterization of F-cyclohexanone is given in Table 10, Appendix B. The infrared, ^{19}F nmr, and electron-impact mass spectra of F-cyclohexanone were in agreement with those appearing in the literature.^{63,66}

Q. Aerosol Fluorination of 1,4-Dioxaspiro[4.4]nonane

1,4-Dioxaspiro[4.4]nonane was prepared by the method of Daignault and Eliel.⁷⁶ Cyclopentanone (21 ml, 0.24 mol), ethylene glycol (14 ml, 0.26 mol), para-toluenesulfonic acid (0.1 g), and 100 ml benzene were placed in a 200-ml flask fitted with a Dean-Stark trap. The mixture was then refluxed until the theoretical amount of water (4.3 ml) collected in the trap. The cooled reaction mixture was washed with 40 ml of 20% NaOH, followed by five 20 ml washings with water. The solution was dried over anhydrous potassium carbonate and the benzene removed with a rotary evaporator. Distillation yielded 16.1 g (0.13 mol) pure 1,4-dioxaspiro[4.4]nonane (bp 156°C, literature 155°C⁷⁷), a 54% yield.

The aerosol fluorination of 1,4-dioxaspiro[4.4]nonane was conducted with the modified aerosol fluorination system. A pump speed corresponding to 4.2 mmol/hr was established and 3.0 ml (25.2 mmol) 1,4-dioxaspiro[4.4]nonane delivered over a 6 hour period. Details of the aerosol fluorination parameters are given in Table 11, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The -131°C trap contents (1.651 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 30°C , 5 min; $5^{\circ}\text{C}/\text{min}$ to 100°C ; 100°C , 1 min; $50^{\circ}\text{C}/\text{min}$ to 180°C . The major product was F-1,4-dioxaspiro[4.4]nonane ($t_R = 15$ min) which constituted 74% (1.222g, 3.55 mmol) of the total products collected by weight. Without correcting for unreacted of partially reacted materials, the percent yield of F-1,4-dioxaspiro[4.4]nonane based on the amount of 1,4-dioxaspiro[4.4]nonane injected (25.2 mmol) was 14%. The complete characterization of F-1,4-dioxaspiro[4.4]nonane is given in Table 11, Appendix B.

R. Hydrolysis of F-1,4-Dioxaspiro[4.4]nonane

F-1,4-Dioxaspiro[4.4]nonane (0.156 g, 0.45 mmol) was condensed onto an approximately equal volume of sulfuric acid which had been treated as described above. The reaction tube was sealed off under vacuum and heated for 24 hours at 450°C in a tube furnace. The reaction tube was then opened under vacuum and the products fractionated through -131°C and -196°C cold traps. The -131°C trap contents (0.152 g) were collected, dissolved in CCl_4 , and separated on the SE-52 gas chromatographic column with the temperature program: -10°C , 5 min; $0.5^{\circ}\text{C}/\text{min}$ to 20°C . The products were identified as F-cyclopentanone ($t_R = 6.5$ min) and unreacted F-1,4-dioxaspiro[4.4]nonane ($t_R = 13$ min) which constituted 16% (0.024 g, 0.11 mmol) and 50% (0.076 g, 0.22 mmol) of the total products collected by weight, respectively. The percent yield of F-cyclopentanone based on the amount of

F-1,4-dioxaspiro[4.4]nonane reacted was thus 48% (24% conversion). Products were identified by comparison of their infrared spectra with those of known samples.

S. Aerosol Fluorination of 1,4-Dioxaspiro[4.5]decane

1,4-Dioxaspiro[4.5]decane (bp 180°C, identical to literature value⁷⁷), prepared by the method of Daignault and Eliel,⁷⁶ was fluorinated employing the modified aerosol fluorination system. A pump speed corresponding to 4.3 mmol/hr was established and 3.0 ml (21.5 mmol) delivered over a five hour period. Details of the aerosol fluorination parameters are given in Table 12, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The -131°C trap contents (1.280 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 50°C, 5 min; 2°C/min to 100°C; 100°C, 1 min; 50°C/min to 180°C. The major product was F-1,4-dioxaspiro[4.5]decane (t_R = 14 min) which constituted 76% (0.973 g, 2.47 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials, the percent yield of F-1,4-dioxaspiro[4.5]decane based on the amount of 1,4-dioxaspiro[4.5]decane injected (21.5 mmol) was 11%. The characterization of F-1,4-dioxaspiro[4.5]decane is given in Table 12, Appendix B.

T. Hydrolysis of F-1,4-Dioxaspiro[4.5]decane

F-1,4-Dioxaspiro[4.5]decane (0.198 g, 0.50 mmol) was condensed onto an approximately equal volume of sulfuric acid which had been

treated as described above. The reaction tube was sealed off under vacuum and heated for 18 hours at 500°C in a tube furnace. The reaction tube was then opened under vacuum and the contents fractionated through -131°C and -196°C cold traps. The -131°C trap contents (0.188 g) were collected, dissolved in CCl₄, and separated on the SE-52 gas chromatographic column with the temperature program: 0°C, 10 min; 1°C/min to 100°C. The products were identified as F-cyclohexanone (t_R = 9 min) and unreacted F-1,4-dioxaspiro[4.5]decane (t_R = 15 min) which constituted 27% (0.051 g, 0.18 mmol) and 68% (0.128 g, 0.32 mmol) of the total products collected by weight. The yield of F-cyclohexanone based on the amount of F-1,4-dioxaspiro[4.5]decane reacted was thus 100% (36% conversion). Products were identified by comparison of their infrared spectra with those of known samples.

U. Aerosol Fluorination of 3,3-Dimethyl-2-butanone

The aerosol fluorination of 3,3-dimethyl-2-butanone (pinacolone, tert-butyl methyl ketone) was conducted with the modified aerosol fluorination system. A pump speed corresponding to 2.8 mmol/hr was established and 0.8 ml (6.3 mmol) delivered over a 2.25 hour period. Details of the aerosol fluorination parameters are given in Table 13, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The -131°C trap contents (1.034 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 0°C, 2 min; 1°C/min to 10°C; 10°C, 1 min; 20°C/min to 180°C. The major products were F-3,3-dimethyl-2-butanone (t_R = 20 min),

3-difluoromethyl-F-3-methyl-2-butanone ($t_R = 25$ min), and 3,3-bis(difluoromethyl)-F-2-butanone ($t_R = 27$ min) which constituted 23% (0.238 g, 0.75 mmol), 25% (0.258 g, 0.86 mmol), and 13% (0.134 g, 0.48 mmol) of the total products collected by weight, respectively. Without correcting for unreacted or partially reacted materials, the percent yield of F-3,3-dimethyl-2-butanone based on the amount of 3,3-dimethyl-2-butanone injected was 12%. The characterizations of F-3,3-dimethyl-2-butanone, 3-difluoromethyl-F-3-methyl-2-butanone, and 3,3-bis(difluoromethyl)-F-2-butanone are given in Tables 13, 14, and 15, Appendix B, respectively.

V. Aerosol Fluorination of 2,2,4,4-Tetramethyl-3-pentanone

The aerosol fluorination of 2,2,4,4-tetramethyl-3-pentanone (pivalone, di-tert-butyl ketone) was conducted with the modified aerosol fluorination system. A pump speed corresponding to 2.9 mmol/hr was established and 1.0 ml (5.8 mmol) delivered over a two hour period. Details of the aerosol fluorination parameters are given in Table 14, Appendix A.

Products were transferred to the vacuum line and fractionated through -78°C , -131°C , and -196°C cold traps. The -78°C trap contents (0.346 g) were collected and separated on the SE-52 gas chromatographic column with the temperature program: 30°C , 5 min; $5^\circ\text{C}/\text{min}$ to 100°C ; 100°C , 1 min; $20^\circ\text{C}/\text{min}$ to 180°C . The major product was F-2,2,5-trimethyl-3-hexanone ($t_R = 9$ min) which constituted 71% (0.246 g, 0.53 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials, the percent yield of

F-2,2,5-trimethyl-3-hexanone based on the amount of 2,2,4,4-tetramethyl-3-pentanone injected was 9%. The characterization of F-2,2,5-trimethyl-3-hexanone is given in Table 16, Appendix B. Also isolated from the reaction was F-isobutane ($t_R = 2.5$ min), identified from its infrared spectrum.⁷⁰

CHAPTER III

RESULTS AND DISCUSSION

A. General Results

The efficacy of the aerosol direct fluorination process for the fluorination of ketones is somewhat surprising for a number of reasons. Low-temperature-gradient (LTG) fluorinations, useful for the fluorination of several types of functional group-containing molecules, have not produced fluorinated ketones under the usual conditions.³³ Due to the use of sodium fluoride as a nucleating species, the aerosol direct fluorination process is rich in fluoride ion and hence fluoride ion catalyzed oxidation of the ketone carbonyl might be expected to produce fluorooxy compounds.⁷⁸⁻⁸⁰ In addition, it might also be expected that the photochemical finishing stage of the process would result in photolytic cleavage of the ketone.^{64,81-83}

In reality none of the above problems were manifested in the results. The high concentration of fluoride ion may indeed be beneficial in that the acidity of the medium due to endogeneous hydrogen fluoride is reduced, thereby minimizing acid-catalyzed condensation reactions.⁸⁴ In addition, no losses directly attributable to photolytic cleavage were detected in any of the ketone fluorinations. For the acyclic ketones, aerosol direct fluorination produced the corresponding perfluoroketones as the major product; fragmentation was minimal in most cases.

Although the perfluoroketones constituted the majority of the products collected, a somewhat troublesome problem exists in the

aerosol direct fluorination of certain molecules. The aerosol system is dependent upon the generation of a particulate aerosol which is ideally crystalline, monodisperse (uniform size), and with little tendency to aggregate. In reality only a few compounds produce near perfect aerosols exhibiting all of the previous properties. Most compounds which produce excellent aerosols are highly symmetrical and pack well in a crystalline lattice, examples being neopentane, adamantane, cycloalkanes, cyclic ethers, and most highly branched, geometrically uniform molecules. Normal alkanes and especially their functional derivatives deviate in varying degrees from this ideal. If the conditions considered ideal are met, percent yields based on throughput and percent distributions will usually differ by only a few percent; as the molecules deviate from this ideal, the percent yields based on throughput begin to fall due to physical losses within the aerosol generator and reactor stages.²¹⁻²³ These losses can be significant and result in sometimes significant amounts of unfluorinated or complex mixtures of generally less than trifluorinated products collected at the close of the reaction when the system warms to ambient or is opened for cleaning between runs.

To minimize physical losses within the reactor, the quantities of material run are kept small to achieve more nearly ideal conditions. Throughputs of up to 10 mmol/hr are possible with some compounds, best results in general being obtained with throughputs of 2 to 5 mmol/hr on the present reactor's 1/2 inch cross section. Increased carrier flows can also significantly improve yields, but the present system's design sets a limit on how high a carrier flow can be employed due to

constrictions endemic to various portions of the system (e.g. the 3/8 inch FEP tubing in the photochemical stage). It is likely that scale-up of the system would allow much higher carrier flows and throughputs, while at the same time improving yields based on throughput.

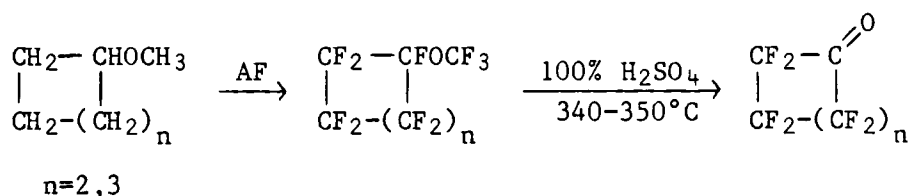
Whereas aerosol direct fluorination of acyclic ketones produced the perfluoroketones as the major product, the perfluorocycloketones were not produced by aerosol direct fluorination of the corresponding hydrocarbon. Although fragmentation is minimal with most of the acyclic ketones, almost total cleavage occurs in the aerosol direct fluorination of cyclopentanone. The major product collected (61% of the total by weight) was F-pentanoyl fluoride, which results from cleavage of the carbon-carbon bond alpha to the carbonyl group. In the case of cyclohexanone no such cleavage was apparent; all attempts at aerosol direct fluorination of cyclohexanone resulted in the production of non-volatile materials which would not transfer on the vacuum line.

F-Cyclopentanone and F-cyclohexanone are extremely hygroscopic materials and react readily with water to form the corresponding monohydrate.⁶⁶ This suggests the possibility that in the aerosol direct fluorinations of cyclopentanone and cyclohexanone any perfluorinated ketone formed may have been hydrolyzed to the non-volatile hydrate due to reaction with residual water inside the reactor. This would explain the complete absence of any perfluoroketone in the product mixture. It is interesting to note that in light of the amount of ring strain that would be relieved upon forming the hydrate, one would predict F-cyclopentanone to be more hygroscopic than F-cyclohexanone. Hence one would anticipate more problems with

cyclopentanone. However, it is cyclohexanone which yields only non-volatile products; aerosol direct fluorination of cyclopentanone produces F-pentanoyl fluoride. Cyclohexanone may be a special case however, as past aerosol direct fluorinations of certain six-membered ring compounds have been only partially successful.²²

Due to the failure of the aerosol direct fluorination process at producing the perfluorocycloketones directly from the hydrocarbons, alternate routes were sought. Perfluorocycloketones were synthesized via two separate two-step routes. Scheme I shows the synthesis of the perfluorocycloketones via the acid hydrolysis of the corresponding perfluorinated methyl cycloalkyl ethers, produced by the aerosol direct fluorination of the appropriate methyl ether.

Scheme I:

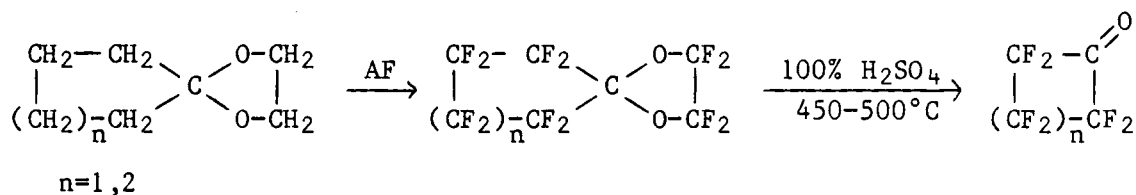


Both the perfluoroethers and the perfluoroketones are obtained in good yields. The perfluoroethers are very stable compounds. After 24 hours at 250°C in the presence of 100% sulfuric acid, F-methoxycyclopentane showed no evidence of reaction. Hydrolysis of the perfluoroethers at 350°C, however, gives excellent yields of the perfluoroketone with virtually no side products. Clayton, et al.⁶³ had previously reported the synthesis of F-cyclopentanone and F-cyclohexanone from the hydrolysis of the corresponding methyl or fluoromethyl

perfluorocycloalkyl ethers. The hydrolysis of a trifluoromethoxy group to a ketone was not reported, however.

Scheme II shows a second two-step route to perfluorocycloketones. The formation of a cyclic ethylene glycol ketal for the purpose of protecting a carbonyl group during subsequent reaction steps is a well known procedure.⁸⁵ An analogous procedure was thought capable of affording protection of the carbonyl group during aerosol direct fluorination. Aerosol direct fluorination of the ketals, formed by treatment of the ketone with ethylene glycol in an acidic solution, results in good yields of the corresponding perfluoroketals, which can then be hydrolyzed to the perfluoroketones in good yields.

Scheme II:



The direct fluorination reaction produces a molecule of hydrogen fluoride for every hydrogen substituted, and hence it might be expected that acid-catalyzed cleavage of the ketals would occur in the reactor. However, hydrogen fluoride solvolysis of the acid sensitive ketal group appears to be of little importance during the aerosol direct fluorination of the cyclopentanone and cyclohexanone ketals, and indeed this lack of solvolysis appears to be general as evidenced from the past successful aerosol direct fluorinations of 1,4-dioxane and 2,2-dimethyl-1,3-dioxolane.²⁰ As previously mentioned, the fact that the aerosol process is rich in fluoride ion may be beneficial in that the

acidity of the medium due to hydrogen fluoride is reduced, thereby minimizing acid-catalyzed reactions.

The perfluoroketals are extremely stable compounds. F-1,4-Diox-aspiro[4.5]decane fails to react after 26 hours at 350°C in the presence of 100% sulfuric acid. However, at 500°C the perfluoroketals are hydrolyzed to the perfluoroketones in good yields with virtually no side products.

Perfluoroketones are characterized by a very electron deficient carbonyl group, and this feature dominates the chemistry of the perfluoroketones. For example, F-acetone is not protonated even in the superacid $\text{FSO}_3\text{H-SbF}_5$ mixture.⁸⁶ The electron-attracting perfluoro-alkyl groups intensify the electrophilic properties of the carbonyl group which leads to changes in reactivity with respect to the characteristic ketone reactions and to new reactions not observed in the case of non-fluorinated ketones. Due to its ready availability, numerous studies have been carried out on F-acetone, thus confirming this altered reactivity.⁸⁷⁻⁸⁹ F-Acetone has such a high electrophilicity that it can react without prior activation of the carbonyl group, even with weak nucleophiles which react with non-fluorinated ketones only in the presence of catalysts.⁸⁷ For example, F-acetone reacts with cyclohexyl isocyanide without a catalyst to form a cyclohexyliminodioxolane, in contrast to the behavior of non-fluorinated ketones which react with isocyanides only in the presence of acids.⁹¹

In contrast to F-acetone, few studies have appeared in the literature relating to the reactions of the higher perfluoroketones due to their relative scarcity. Anello, et al. have studied several

reactions of F-cyclopentanone and F-cyclohexanone. Hydrates of the perfluoroketones were formed readily, reduction with sodium borohydride gave the corresponding secondary alcohols, and hydroxy acids were produced upon admixture of the perfluoroketones with malonic acid in pyridine.⁶⁶ In addition, F-cyclohexanone was found to undergo the Wittig reaction smoothly, heating of the ketone with carbethoxymethylenetriphenylphosphorane yielding ethyl perfluorocyclohexylidenyl acetate.⁶⁶ The reaction of F-cyclopentanone or F-cyclohexanone with potassium or cesium fluoride in polar solvents produces the perfluorinated alkoxides.^{66,92} Tatlow, et al.⁴⁰ have prepared decafluorocyclohexylidene imine from the reaction of F-cyclohexanone with liquid ammonia and phosphorous oxychloride in pyridine. F-cyclopentanone and F-cyclohexanone have been converted to the corresponding hydrates which were then mixed with Capran (polyamide, Allied Chemical) to form a flexible, transparent Capran film.⁶⁷ A number of reactions of F-cyclobutanone have been reported⁶² including the Diels-Alder reaction of F-cyclobutanone with butadiene.

Several studies have appeared in the literature pertaining to the reactions of the acyclic perfluoroketones. F-4-Heptanone reacts with methyl lithium and perfluoropropyl magnesium iodide to form 4-methylperfluoro-4-heptanol⁹³ and undergoes the Reformatsky reaction with ethyl bromoacetate and zinc to produce the corresponding β -hydroxy ester.⁹⁴ Reaction of F-4-heptanone with water forms the corresponding diol, and reaction with amines forms the corresponding amides.⁵¹ Attempts to prepare the 2,4-dinitrophenylhydrazone, semicarbazone, or oxime were unsuccessful.⁵² F-2-Pentanone, F-3-hexanone, and

F-4-heptanone have been reduced to the corresponding secondary alcohols with lithium aluminum hydride.⁵⁵ F-3-pentanone and F-4-heptanone underwent reaction with trialkyl phosphites to yield alkyl enol ethers of the perfluoroketones and dialkyl phosphorofluoridate.⁹⁵ Reactions of perfluoroalkyl perfluoroisopropyl ketones with primary amines have been shown to give the corresponding secondary amides and 2-hydrylperfluoropropane,⁹⁶ and with morpholine to give the corresponding tertiary amides and 2-hydrylperfluoropropane.⁹⁷ Condensation of F-2-butanone or F-2-hexanone with perfluoropropylene oxide, followed by pyrolysis of the condensation products, provides a route to the corresponding perfluoro(alkyl vinyl ether).⁹⁸

It is obvious from the above that the chemistry of the perfluoroketones is a virtually unexplored area; the unusual character of the carbonyl group in the perfluoroketones promises to have a wide variety of chemical reactivity not exhibited by the non-fluorinated ketones.

B. Synthesis of F-3-Pentanone

In all 3-pentanone reactions the major product collected was F-3-pentanone. For the three reactions listed in Table 1, Appendix A, the percent F-3-pentanone of all products collected by weight was 53%, 62%, and 71%; if no corrections are made for unreacted or partially reacted materials, the percent yields based on the throughput of 3-pentanone were 5%, 8%, and 12%, respectively.

An examination of the aerosol fluorination parameters shows that increased percent yields and percent distributions were obtained by running the reactor modules at a higher temperature, heating the coil

preceeding the photochemical stage, and employing an increased carrier flow. The higher temperatures and flows serve to reduce physical losses within the reactor, due to factors previously discussed. However, significant amounts of unreacted 3-pentanone were still found within the region of the first reactor module upon opening the system for cleaning. In fact, for all the aerosol direct fluorinations performed, significant amounts of unreacted starting materials were found inside the reactor upon opening for cleaning.

Giacometti, et al., in a study of the photolysis of F-3-pentanone, reported that at wavelengths of 264 to 313 nm F-3-pentanone was photolytically cleaved to produce carbon monoxide and F-n-butane (formed by recombination of CF_3CF_2 radicals) as the sole products.⁸¹ Since the cutoff for the FEP tubing of the photochemical stage is approximately 224 nm, it might be expected that this cleavage would present a serious problem in the aerosol direct fluorination of 3-pentanone. However, no evidence of photolytic cleavage was found in any of the reactions. The only major product found besides F-3-pentanone was F-n-propane; no significant amounts of F-n-butane were formed in the reactions. It would thus appear that conditions within the photochemical stage are such that no dissociation occurs upon exposure to the ultraviolet radiation (i.e., low temperature and low pressure).

The fact that the major fragmentation product found in the aerosol direct fluorination of 3-pentanone was F-n-propane is somewhat surprising. The photolysis of F-3-pentanone in the gas phase resulted in cleavage of the bonds alpha to the carbonyl group followed by

recombination of the CF_3CF_2 radicals to form carbon monoxide and F-n-butane as the sole products.⁸¹ The photolysis of F-3-pentanone in dichlorodifluoromethane has also led to cleavage of the alpha bond.⁹⁹ Since no significant amounts of either F-n-butane or F-ethane were formed, it is likely that photolytic cleavage was minimal and that F-propane was formed as a result of the combination of CF_3 and CF_3CF_2 radicals, formed by fragmentation of the carbon skeleton of 3-pentanone during the fluorination process.

Only one previous synthesis of F-3-pentanone appears in the literature. In a patented process (du Pont) F-3-pentanone was synthesized via the reaction of ethyl perfluorobutyrate with sodium ethoxide, followed by acidification and distillation from phosphorous pentoxide.⁵⁰ No characterization was given other than the boiling point (27°C).

F-3-Pentanone was identified from its infrared spectrum, electron-impact (70 eV) and chemical ionization (methane plasma) mass spectra, and ^{19}F nmr spectrum. The complete characterization is given in Table 1, Appendix B.

The carbonyl stretch of F-3-pentanone occurs at 1780 cm^{-1} compared to a value of 1710 cm^{-1} in 3-pentanone.¹⁰⁰ This shift of the carbonyl stretch to higher wavenumber upon perfluorination is general and results from the electron-withdrawing properties of the perfluoroalkyl groups. The electron-attracting perfluoroalkyl groups reduce the carbonyl dipole, raising the frequency of the carbonyl group.^{101,102} Strong absorption is also seen in the 1400 to 1000 cm^{-1} region, characteristic of C-F stretches.⁷⁰

The chemical ionization mass spectrum of F-3-pentanone exhibits a base peak at $m/e = 267$, corresponding to the molecular ion plus a hydrogen and confirming the molecular formula $C_5F_{10}O$. The peak at $m/e = 247$ corresponds to the molecular ion minus a fluorine. Observation of the $M+H$ ion is common in the chemical ionization mass spectrum when employing a methane plasma as is the observation of the parent minus fluorine peak.¹⁰³ Other major peaks seen in the chemical ionization mass spectrum are consistent with the structure of F-3-pentanone and include those at $m/e = 147$ and $m/e = 119$, corresponding to the fragments $C_3F_5O^+$ and $C_2F_5^+$, respectively, resulting from cleavage of the bond alpha to the carbonyl group.

The electron-impact mass spectrum of F-3-pentanone agrees well with that appearing in the literature.^{81,103} Large peaks are found at $m/e = 147$, 119, 100, and 69, corresponding to the $C_3F_5O^+$, $C_2F_5^+$, $C_2F_4^+$, and CF_3^+ fragments, respectively.

The ^{19}F nmr spectrum of F-3-pentanone consists of two singlets of relative intensity 3:2 at $\delta = -82.03$ and -121.38 ppm ($CFCl_3$ internal standard), corresponding to the CF_3 and CF_2 groups, respectively. The peaks occur in the region expected¹⁰⁴ and show only a very slight broadening ($J_{CF_2-CF_3} < 1$ Hz).

C. Synthesis of F-4-Heptanone

Aerosol direct fluorination of 4-heptanone produced F-4-heptanone as the major product, comprising 92% of the total products collected by weight; if no corrections are made for unreacted or partially reacted materials, the percent yield based on throughput of 4-heptanone was

18%. Small amounts of F-n-propane, resulting from cleavage of the bond alpha to the carbonyl group, were also produced as was evidenced by infrared assay of the product mixture. Hence, as was the case for 3-pentanone, photolytic cleavage in the photochemical stage appears to be negligible. The main source of losses are likely physical losses within the reactor; upon opening the reactor for cleaning, significant amounts of unreacted 4-heptanone were found.

F-4-Heptanone is one of the few perfluoroketones which has been well characterized and has been synthesized via several methods, all involving the reaction of a highly fluorinated species. The first reported synthesis of F-4-heptanone involved reaction of ethyl perfluorobutyrate, $C_3F_7COOC_2H_5$, with the Grignard reagent perfluoropropyl magnesium iodide, C_3F_7MgI , and resulted in a 20% yield of F-4-heptanone.⁵² The reaction of perfluoropropyl magnesium iodide with perfluorobutryl chloride, C_3F_7COCl , has also produced F-4-heptanone in a 31% yield.⁵⁵ Perfluoropropyl magnesium iodide is unstable at room temperature and hence is formed at low temperatures from perfluoropropyl iodide, C_3F_7I , and magnesium in the presence of the compound it is to be condensed with.⁵²

The reactions of ethyl perfluorobutyrate with sodium ethoxide,⁵⁰ sodium,⁵¹ or perfluoropropyl lithium, C_3F_7Li ,⁵³ have also produced F-4-heptanone in yields of 88%, 60%, and 28%, respectively. In addition, F-4-heptanone was produced in a 15% yield from the reaction of perfluoropropyl zinc iodide, C_3F_7ZnI , with perfluorobutryl chloride.⁵⁴

F-4-Heptanone was identified from its infrared spectrum, chemical ionization and electron-impact mass spectra, and ^{19}F nmr spectrum. The

complete characterization of F-4-heptanone is given in Table 2, Appendix B.

The infrared spectrum of F-4-heptanone was identical to that appearing in the literature.⁵² The spectrum exhibits a carbonyl stretch at 1785 cm^{-1} and strong absorption due to C-F stretching in the 1400 to 1000 cm^{-1} region.

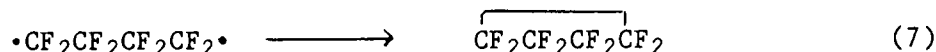
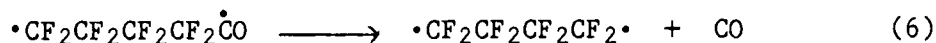
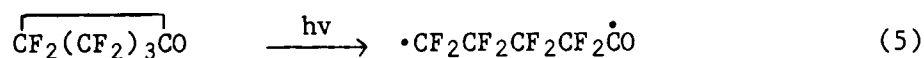
The chemical ionization mass spectrum of F-4-heptanone exhibits peaks at $m/e = 367$ and $m/e = 347$ corresponding to the molecular ion plus hydrogen and the molecular ion minus fluorine, respectively, confirming the molecular formula $\text{C}_7\text{F}_{14}\text{O}$. The electron-impact mass spectrum includes a peak at $m/e = 347$, corresponding to the molecular ion minus fluorine, as well as peaks corresponding to the fragments C_3F_7^+ ($m/e = 169$) and $\text{C}_4\text{F}_7\text{O}^+$ ($m/e = 197$), formed from cleavage of the bond alpha to the carbonyl group. The remaining peaks correspond to fragments consistent with the structure of F-4-heptanone, as seen in Table 2, Appendix B.

The ^{19}F nmr spectrum of F-4-heptanone consists of three peaks of relative intensity 3:2:2 at $\delta = -81.16$, -118.66 , and -126.31 ppm (CFCl_3 internal standard), respectively. The peak at $\delta = -81.16$ ppm is due to the CF_3 group, and the peaks at $\delta = -118.66$ and -126.31 ppm are assigned to the CF_2 groups alpha and beta to the carbonyl group, respectively. The CF_2 group alpha to the carbonyl group is more deshielded than the CF_2 group beta to the carbonyl function and hence appears further downfield.

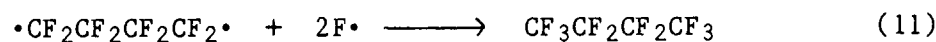
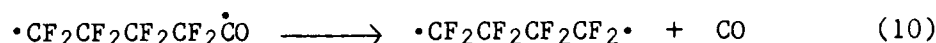
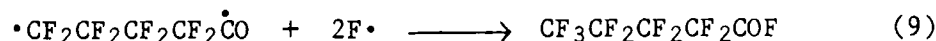
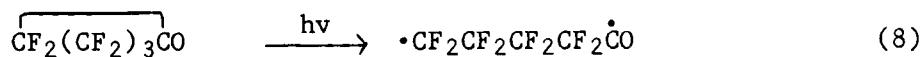
D. Aerosol Fluorination of Cyclopentanone

Aerosol direct fluorination of cyclopentanone produced F-pentanoyl fluoride, C_4F_7COF , and F-n-butane as the major products, constituting 61% and 11% of the total products collected by weight, respectively. No traces of F-cyclopentanone were found, and as previously mentioned it is believed that any F-cyclopentanone formed would have hydrolyzed due to reaction with residual water in the reactor.

Majer and Phillips⁶⁴ have reported that the gas phase photolysis of F-cyclopentanone produces only carbon monoxide and F-cyclobutane at 313 nm:



Since a relatively high concentration of fluorine atom radicals exists in the photochemical stage, it is possible that alpha cleavage of the perfluoroketone is followed by reaction with fluorine radicals to produce the observed products.



It is also possible that F-cyclopentanone is never formed, and the products formed result from cleavage of one or both of the bonds alpha to the carbonyl group during the fluorination process.

F-Pentanoyl fluoride has been synthesized by the action of nitrous oxide or nitric oxide on perfluoropentyl sulfonyl fluoride, $C_5F_{11}SO_2F$, which gave a 46% yield of the perfluoroacyl fluoride,¹⁰⁵ and is formed in trace amounts in the electrochemical fluorination of methyl-3-methoxypropionate.⁷¹

F-Pentanoyl fluoride was identified from its infrared spectrum, chemical ionization and electron-impact mass spectra, and ^{19}F nmr spectrum. The complete characterization is given in Table 3, Appendix B.

The infrared spectrum of F-pentanoyl fluoride exhibits a strong absorption at 1880 cm^{-1} , characteristic of the carbonyl stretch of acid fluorides,⁷⁰ and strong bands in the 1400 to 1000 cm^{-1} region characteristic of C-F stretches.

The chemical ionization mass spectrum of F-pentanoyl fluoride exhibits peaks at $m/e = 266$ and $m/e = 247$, corresponding to the molecular ion plus hydrogen and the molecular ion minus fluorine, respectively, confirming the molecular formula $C_5F_{10}O$. The electron-impact mass spectrum exhibits peaks at $m/e = 131, 119, 100, 69,$ and 47 , corresponding to the $C_3F_5^+$, $C_2F_5^+$, $C_2F_4^+$, CF_3^+ , and CFO^+ fragments, respectively.

The ^{19}F nmr spectrum of F-pentanoyl fluoride consists of five peaks of relative intensity 3:2:2:2:1 at $\delta = -81.59, -118.33, -123.98, -126.47,$ and $+24.85$ ppm ($CFCl_3$ internal standard), respectively. The

peak at $\delta = -81.59$ ppm is due to the CF_3 group, and the peaks at $\delta = -118.33$, -123.98 , and -126.47 ppm are due to the alpha, beta, and gamma CF_2 groups, respectively. The peak at $\delta = +24.85$ ppm indicates a very deshielded fluorine and is due to the fluorine attached to the carbonyl group; this peak occurs in the region expected for an acid fluoride.¹⁰⁴

E. Synthesis of F-3-Heptanone

Due to the low volatility of 3-heptanone, sufficient throughputs were not possible employing the basic aerosol fluorination system. Hence, the modified aerosol fluorination system, which employs a flash evaporator/sublimator fed by a syringe pump, was employed for the aerosol direct fluorination of 3-heptanone. This system offers several advantages over the basic system. No cold bath need be maintained as was needed at the hydrocarbon evaporator device of the basic system, and hence long reactions can be run with little supervision. In addition, lengthy and tedious throughput experiments are not required when using the modified system; only the boiling point of the material (or sublimation point in the case of solid reactants) need be ascertained and the flash evaporator/sublimator set at approximately 20°C above that point. A known volume of hydrocarbon is then delivered from the syringe pump and the density of the hydrocarbon allows calculation of the throughput. In the case of a solid reactant throughputs may be determined in the fashion employed for the case of the basic system. The ability to perform lengthy reactions with little maintenance using the modified aerosol fluorination system also has the advantage that a

single run can be performed with a large enough yield of products to allow characterization of the products after a single run; in the case of the basic system, relatively non-volatile materials giving room temperature throughputs of less than 2 mmol/hr required either runs of very long duration or multiple experiments before a sufficient amount of product could be accumulated for isolation. The basic system is still valuable, however, for the aerosol fluorination of volatile materials, which would boil out of the syringe set-up of the modified system.

The major product from the aerosol direct fluorination of 3-heptanone was F-3-heptanone; for optimum conditions (Table 5, Appendix A), F-3-heptanone constituted 59% of the total products collected by weight. Without correcting for unreacted or partially reacted materials, the percent yield based on the amount of 3-heptanone injected was 13%. The only other product formed in significant amounts was F-n-butane, which constituted 9% of the total products collected by weight. Fragmentation was thus minimal, the fragmentation products consisting mainly of F-n-butane and small amounts of F-ethane (infrared assay of -196°C cold trap contents), both resulting from cleavage of the bonds alpha to the carbonyl group.

F-3-Heptanone, which has not been synthesized previously, was identified from its infrared spectrum, chemical ionization and electron-impact spectra, and ^{19}F nmr spectrum. The complete characterization is given in Table 4, Appendix B.

The infrared spectrum of F-3-heptanone exhibits a carbonyl stretch at 1780 cm^{-1} and strong absorption due to C-F stretching in the $1400\text{ to }1000\text{ cm}^{-1}$ region.

The chemical ionization mass spectrum exhibits a strong peak at $m/e = 367$, corresponding to the molecular ion plus hydrogen and confirming the molecular formula $C_7F_{14}O$. The peak at $m/e = 383$ corresponds to the molecular ion plus CH_5 ; CH_5^+ is known to exist in the plasma discharge of methane and hence the occurrence of the $M+CH_5$ peak is also consistent with the structure of F-3-heptanone. The electron-impact mass spectrum exhibits peaks at $m/e = 219$, 147, and 119, corresponding to the $C_4F_9^+$, $C_3F_5O^+$, and $C_2F_5^+$ fragments, respectively, formed upon cleavage of the bonds alpha to the carbonyl group.

The ^{19}F nmr spectrum of F-3-heptanone consists of six complex multiplets of relative intensity 3:3:2:2:2:2 at $\delta = -79.82$, -81.99 , -118.01 , -121.67 , -124.79 , and -126.32 ppm ($CFCl_3$ internal standard), respectively. The CF_3 and CF_2 groups in F-3-pentanone appear at $\delta = -82.03$ ppm and $\delta = -121.38$ ppm, respectively, and by comparison the peaks at $\delta = -81.99$ and -121.67 ppm in the ^{19}F nmr spectrum of F-3-heptanone are assigned to the CF_3 and CF_2 groups of the perfluoroethyl segment of F-3-heptanone. In the ^{19}F nmr spectrum of F-4-heptanone the CF_3 , alpha CF_2 , and beta CF_2 groups appear at $\delta = -81.16$, -118.66 and -126.31 ppm, respectively, and by comparison the peaks at $\delta = -79.82$, -118.01 , -124.79 , and -126.32 ppm in the ^{19}F nmr spectrum of F-3-heptanone are assigned to the CF_3 , alpha CF_2 , beta CF_2 , and gamma CF_2 groups of the perfluoropentyl segment of F-3-heptanone. As one moves farther away from the carbonyl group, the CF_2 groups are less deshielded and hence appear further upfield.

F. Synthesis of F-2-Heptanone

The major products from the aerosol fluorination of 2-heptanone were F-2-heptanone and F-n-pentane which constituted 55% and 26% of the total products collected by weight, respectively. Without correcting for unreacted or partially reacted materials, the percent yield of F-2-heptanone based on the amount of 2-heptanone injected was 8%. As has been noted in the previous aerosol direct fluorinations, the major fragmentation product is usually that resulting from cleavage of the bonds alpha to the carbonyl group. As the ketone being fluorinated becomes more unsymmetrical, it is likely to form a poorer aerosol as previously discussed. Hence as the ketone becomes increasingly unsymmetric, one might expect a higher degree of fragmentation to occur in the aerosol direct fluorination process due to an increasingly poorer aerosol being formed. This seems to be borne out by the results of the aerosol direct fluorinations of 4-heptanone, 3-heptanone, and 2-heptanone. In the aerosol fluorination of 4-heptanone virtually no fragmentation products are found, 9% of the products in the fluorination of 3-heptanone are due to alpha cleavage, and 26% of the products in the fluorination of 2-heptanone are due to alpha cleavage.

Only a single previous synthesis of F-2-heptanone appears in the literature. F-2-Heptanone was prepared in a 95% yield from the action of antimony pentafluoride on ω -chloroperfluoro-1-heptene epoxide.⁴³ The chloroperfluoro-1-heptene epoxide is not readily available however, but is synthesized in an eight step reaction sequence starting with ω -hydriylperfluorononanoic acid.

F-2-heptanone was identified from its infrared spectrum, electron-impact and chemical ionization mass spectra, and ^{19}F nmr spectrum. The complete characterization is given in Table 5, Appendix B.

The infrared spectrum of F-2-heptanone exhibits a carbonyl stretch at 1790 cm^{-1} (identical to literature value⁴³) and strong absorptions in the 1400 to 1000 cm^{-1} region due to C-F stretches.

The chemical ionization mass spectrum exhibited a top mass peak at $m/e = 366$, corresponding to the molecular ion and confirming the molecular formula $\text{C}_7\text{F}_{14}\text{O}$. Peaks at $m/e = 131$, 97 , and 69 were also present, corresponding to the C_3F_5^+ , $\text{C}_2\text{F}_3\text{O}^+$, and CF_3^+ fragments, respectively. The electron-impact mass spectrum exhibited peaks at $m/e = 269$ and 97 , corresponding to the fragments $\text{C}_5\text{F}_{11}^+$ and $\text{C}_2\text{F}_3\text{O}^+$, respectively, resulting from cleavage of the bonds alpha to the carbonyl group. Other peaks consistent with the structure of F-2-heptanone were present at $m/e = 131$, 119 , 100 , and 69 , corresponding to the fragments C_3F_5^+ , C_2F_5^+ , C_2F_4^+ , and CF_3^+ , respectively.

The ^{19}F nmr spectrum of F-2-heptanone agreed with that appearing in the literature,⁴³ and consisted of five complex multiplets of relative intensity 3:3:2:4:2 at $\delta = -75.17$, -81.30 , -118.63 , -122.67 , and -126.67 ppm (CFCl_3 internal standard), respectively. The peaks at $\delta = -75.17$ and -81.30 ppm are due to the CF_3 groups attached to the carbonyl group and perfluoroalkyl group, respectively. The peaks at $\delta = -118.63$, -122.67 , and -126.67 ppm correspond to the alpha, beta plus gamma, and delta CF_2 groups, respectively. The beta and gamma CF_2 groups occupy similar environments and hence occur at approximately the same field, leading to a complex multiplet centered at $\delta = -122.67\text{ ppm}$.

G. Synthesis of F-2-Butanone

The major product from the aerosol fluorination of 2-butanone was F-2-butanone, which constituted 20% of the total products collected by weight; without correcting for unreacted or partially reacted materials, the percent yield of F-2-butanone based on the amount of 2-butanone injected was 9%. The remainder of products were unreacted or partially reacted materials, as ascertained by infrared assay of the complex mixture. The isolation of such a large amount of partially fluorinated materials may be due to 2-butanone forming a poor aerosol as would be the case if 2-butanone were to dissolve the NaF preaerosol. In such a case droplets large enough to settle out in the reactor could form, and the unfluorinated or partially fluorinated materials would be condensed within the reactor; upon warming of the reactor to ambient, during the time the reaction is stopped and the product trap removed, these materials would then collect in the product trap.

F-2-Butanone was first produced in poor yields via the direct fluorination of 2-butanone by Bigelow.³¹ F-2-butanone has also been synthesized via the action of antimony pentafluoride on 4-chloroperfluoro-1-butene epoxide⁴³ or F-2-butene epoxide¹⁰⁶ and by the reaction of F-2-(fluorosulfato)butane with cesium or potassium fluoride.⁶⁰

F-2-butanone was identified from its infrared spectrum, electron-impact and chemical ionization mass spectra, and ¹⁹F nmr spectrum. The complete characterization is given in Table 6, Appendix B.

The infrared spectrum agrees with that appearing in the literature,⁶⁰ and exhibits a carbonyl stretch at 1790 cm^{-1} and strong absorptions in the 1400 to 1000 cm^{-1} region due to C-F stretches.

The chemical ionization mass spectrum exhibits a top mass peak at $m/e = 217$, corresponding to the molecular ion plus hydrogen, and a peak at $m/e = 197$ corresponding to the molecular ion minus fluorine, confirming the molecular formula $\text{C}_4\text{F}_8\text{O}$. Additional peaks occur at $m/e = 147$, 97 , and 69 , corresponding to the fragments $\text{C}_3\text{F}_5\text{O}^+$, $\text{C}_2\text{F}_3\text{O}^+$, and CF_3^+ , respectively. The electron-impact spectrum exhibited peaks at $m/e = 147$, 119 , 97 , and 69 corresponding to the fragments $\text{C}_3\text{F}_5\text{O}^+$, C_2F_5^+ , $\text{C}_2\text{F}_3\text{O}^+$, and CF_3^+ , respectively, consistent with the structure of F-2-butanone.

The ^{19}F nmr spectrum of F-2-butanone consists of three peaks of relative intensity 3:3:2 at $\delta = -75.30$, -82.28 , and -122.11 ppm (CFCl_3 internal standard), respectively. The peak at $\delta = -75.30$ ppm corresponds to the CF_3 group attached to the carbonyl group, and is split into a triplet by coupling with the CF_2 group, which appears as a quartet at $\delta = -122.11$ ppm ($J = 8.8$ Hz). The peak at $\delta = -82.28$ ppm is assigned to the CF_3 group attached to the CF_2 group and appears as a singlet.

H. Synthesis of F-Acetone

The major product from the aerosol direct fluorination of acetone was F-acetone, which constituted 48% of the total products collected by weight. Without correcting for unreacted or partially reacted materials the percent yield of F-acetone based on the amount of acetone

injected was 4%. Also isolated from the reaction was 1-hydrylperfluoroacetone, which constituted 30% of the total products collected by weight. As discussed for the case of 2-butanone, the isolation of a significant amount of partially fluorinated materials may indicate partial dissolving of the NaF preaerosol by acetone.

The infrared spectrum of F-acetone was identical to that appearing in the literature.⁷³ F-Acetone is a well characterized material and is available commercially.

1-Hydrylperfluoroacetone, $\text{CF}_3\text{COCF}_2\text{H}$, exhibits a weak C-H stretch at 2970 cm^{-1} and a carbonyl stretch at 1790 cm^{-1} , in addition to strong absorption in the 1400 to 1000 cm^{-1} region due to C-F stretches. The electron-impact mass spectrum included peaks at $m/e = 148$ and 129 corresponding to the molecular ion and the molecular ion minus fluorine, respectively, in addition to peaks at $m/e = 119, 101, 97, 79, 69,$ and 51 corresponding to the fragments C_2F_5^+ , $\text{C}_2\text{F}_4\text{H}^+$, $\text{C}_2\text{F}_3\text{O}^+$, $\text{C}_2\text{F}_2\text{HO}^+$, CF_3^+ , and CF_2H^+ , respectively, consistent with the structure of 1-hydrylperfluoroacetone. The chemical ionization mass spectrum of 1-hydrylperfluoroacetone exhibited a base peak at $m/e = 150$, corresponding to the molecular ion plus two hydrogens. The ^{19}F nmr spectrum of 1-hydrylperfluoroacetone consists of a triplet at $\delta = -76.20\text{ ppm}$ ($J_{\text{CF}_3-\text{CF}_2} = 6.11\text{ Hz}$) and a doublet of quartets at $\delta = -129.51\text{ Hz}$ ($J_{\text{CF}_2-\text{H}} = 48.02\text{ Hz}$) corresponding to the CF_3 and CF_2 groups, respectively. The ^1H nmr consists of a triplet at $\delta = 6.15\text{ ppm}$.

I. Synthesis of F-Methoxycyclopentane

The aerosol direct fluorination of methoxycyclopentane produced F-methoxycyclopentane as the major product. The percent distribution of F-methoxycyclopentane was 57% of the total products collected by weight; without correcting for unreacted or partially reacted materials, the percent yield of F-methoxycyclopentane based on the amount of methoxycyclopentane injected was 22% (reaction 1, Table 9, Appendix A). A second run utilizing a higher hydrocarbon throughput resulted in a reduced percent yield (reaction 2, Table 9, Appendix A) and it is likely that the system was overloaded at this increased throughput.

F-Methoxycyclopentane has been synthesized in 83% yield via the photochemical reaction of trifluoromethyl hypofluorite, CF_3OF , with F-cyclopentene.⁷⁵

F-Methoxycyclopentane was identified from its infrared spectrum, chemical ionization and electron-impact mass spectra, and ^{19}F nmr spectrum. The complete characterization is given in Table 7, Appendix B.

The infrared spectrum of F-methoxycyclopentane exhibits strong absorptions in the 1400 to 1000 cm^{-1} region, characteristic of C-F stretches. The chemical ionization mass spectrum of F-methoxycyclopentane exhibits a top mass peak at $m/e = 317$ corresponding to the molecular ion plus hydrogen. The electron-impact mass spectrum of F-methoxycyclopentane exhibits a peak at $m/e = 297$ corresponding to the molecular ion minus fluorine, in addition to peaks at $m/e = 181$, 131 , 100 , and 69 corresponding to the fragments C_4F_7^+ , C_3F_5^+ , C_2F_4^+ , and

CF_3^+ , respectively, and agrees with the electron-impact mass spectrum appearing in the literature.⁷⁵

The ^{19}F nmr spectrum of F-methoxycyclopentane is in agreement with that appearing in the literature.⁷⁵ The CF_2 groups appear as two overlapping AB quartets; the first AB system is due to the CF_2 groups alpha to the trifluoromethoxy group and occurs at $\delta = -124.68$ and -135.68 ppm ($J = 259$ Hz), and the second AB quartet is due to the CF_2 groups beta to the trifluoromethoxy group and occurs with chemical shifts $\delta = -132.86$ and -137.96 ppm ($J = 255$ Hz). The coupling constants for the geminal fluorines are of the magnitude expected in a five-membered ring.¹⁰⁴ The trifluoromethoxy group gives rise to the absorption at $\delta = -55.42$ ppm. The peak at $\delta = -137.96$ ppm is due to the tertiary fluorine adjacent to the trifluoromethoxy group and is a complex multiplet. The coupling constants for the F-methoxycyclopentane system are given in Table 7, Appendix B.

J. Synthesis of F-1,4-Dioxaspiro[4.4]nonane

Aerosol fluorination of 1,4-dioxaspiro[4.4]nonane produced F-1,4-dioxaspiro[4.4]nonane as the major product. F-1,4-dioxaspiro[4.4]nonane constituted 74% of the total products collected by weight; without correcting for unreacted or partially reacted materials, the percent yield was 14%.

F-1,4-Dioxaspiro[4.4]nonane, which has not been synthesized previously, was characterized by its infrared spectrum, electron-impact and chemical ionization mass spectra, ^{19}F nmr spectrum, and by

elemental analysis. The complete characterization is given in Table 11, Appendix B.

The chemical ionization mass spectrum exhibits a base peak at $m/e = 325$ corresponding to the molecular ion minus fluorine, in addition to peaks at $m/e = 117$ and 97 corresponding to the fragments $C_5F_3^+$ and $C_2F_3O^+$, respectively. The electron-impact mass spectrum exhibits a molecular ion minus fluorine peak at $m/e = 325$ and also includes peaks at $m/e = 131$, 100 , and 69 corresponding to the fragments $C_3F_5^+$, $C_2F_4^+$, and CF_3^+ , respectively.

The ^{19}F nmr spectrum of F-1,4-dioxaspiro[4.4]nonane consists of three singlets of equal intensity at $\delta = -85.32$, -130.36 , and -131.69 ppm ($CFCl_3$ internal standard), corresponding to the ethylene ($\delta = -85.32$ ppm) and cyclopentyl ($\delta = -130.36$ and -131.69 ppm) fluorines, as shown in Table 11, Appendix B.

Elemental analysis also confirmed the molecular formula $C_7F_{12}O_2$, as seen from Table 11, Appendix B.

K. Synthesis of F-Cyclopentanone

F-Cyclopentanone was synthesized via two routes. In the first, F-methoxycyclopentane was converted to F-cyclopentanone in an 89% yield by treatment with 100% sulfuric acid and heating at $340^\circ C$ (61% conversion). At lower temperatures F-methoxycyclopentane shows no sign of reaction in the presence of 100% sulfuric acid, demonstrating its high thermal stability. The conversion of F-methoxycyclopentane to F-cyclopentanone is clean, virtually no side products being formed.

As an alternative, F-cyclopentanone can be produced from the acid hydrolysis of the perfluoroketal, F-1,4-dioxaspiro[4.4]nonane. At 450°C in the presence of 100% sulfuric acid, F-1,4-dioxaspiro[4.4]-nonane is converted to F-cyclopentanone in a 45% yield (23% conversion), with virtually no side products.

F-Cyclopentanone has been previously synthesized via several methods. In a patented process (du Pont), F-cyclopentanone has been produced in 70% yield via the rearrangement of perfluorocyclopentenyl epoxide over Lewis acid catalysts.^{37,38} Acid hydrolysis of methyl perfluorocyclopentyl ether, followed by distillation from phosphorous pentoxide gave F-cyclopentanone in a 47% yield.⁶³ Treatment of the 1,2-dichloroperfluorocyclopentene epoxide^{66,68} or 2,2-dichloroperfluorocyclopentanone^{66,67} with potassium fluoride in tetramethylene sulfone has also produced F-cyclopentanone. Holub and Bigelow reported the production of F-cyclopentanone in trace amounts in the direct fluorination of cyclopentanone.³¹

F-Cyclopentanone was identified from its infrared spectrum, electron-impact and chemical ionization mass spectra, and ¹⁹F nmr spectrum. The complete characterization is given in Table 8, Appendix B.

The infrared spectrum of F-cyclopentanone exhibits a carbonyl stretch at 1810 cm⁻¹, and strong absorptions in the 1400 to 1000 cm⁻¹ region due to C-F stretching.

The chemical ionization mass spectrum of F-cyclopentanone exhibits a peak at m/e = 209 corresponding to the molecular ion minus fluorine, and further confirmation of the molecular formula C₅F₈O is

obtained from the electron-impact mass spectrum which exhibits peaks at $m/e = 228$ and 209 , corresponding to the molecular ion and the molecular ion minus fluorine, respectively. The electron-impact mass spectrum was in agreement with that appearing in the literature.⁶³

The ^{19}F nmr spectrum of F-cyclopentanone consists of two multiplets of identical relative intensity at $\delta = -136.76$ and -126.52 ppm (CFCl_3 internal standard), corresponding to the CF_2 groups beta and alpha to the carbonyl function, respectively. The spectrum is consistent with that cited in the literature.⁶³

F-cyclopentanone is difficult to handle due to its extremely hygroscopic nature. Drastic measures to ensure a complete absence of moisture on the vacuum line are required in order to prevent its hydrolysis. Reaction of F-cyclopentanone with water produces a somewhat volatile hydrate with absorptions at 3625 and 2980 cm^{-1} in the infrared, which on further hydrolysis forms a non-volatile solid.

L. Synthesis of F-Methoxycyclohexane

The aerosol fluorination of methoxycyclohexane produced F-methoxycyclohexane as the major product. The percent distribution of F-methoxycyclohexane was 90% of the total products collected by weight; without correcting for unreacted or partially reacted materials, the percent yield based on the amount of methoxycyclohexane injected was 32%.

The only previous synthesis of F-methoxycyclohexane appearing in the literature involved the photochemical reaction of trifluoromethyl hypofluorite, CF_3OF , with F-cyclohexene.⁷⁵

F-Methoxycyclohexane was identified from its infrared spectrum, chemical ionization and electron-impact mass spectrum, and ^{19}F nmr spectrum. The complete characterization is given in Table 9, Appendix B.

The chemical ionization mass spectrum of F-methoxycyclohexane exhibits peaks at $m/e = 161, 131, 100,$ and 69 corresponding to the fragments $\text{C}_4\text{F}_5\text{OH}_2^+$, C_3F_5^+ , C_2F_4^+ , and CF_3^+ respectively. The electron-impact mass spectrum exhibits a peak at $m/e = 281$ corresponding to the molecular ion minus the OCF_3 group, in addition to peaks at $m/e = 259, 231, 131$ and 69 corresponding to the fragments $\text{C}_6\text{F}_9\text{O}^+$, C_5F_9^+ , C_3F_5^+ , and CF_3^+ , respectively.

The ^{19}F nmr spectrum of F-methoxycyclohexane agrees with that appearing in the literature,⁷⁵ and consists of peaks at $\delta = -53.83$ and -142.77 ppm (CFCl_3 internal standard) corresponding to the CF_3 group and the tertiary fluorine, respectively, and three overlapping AB quartets between $\delta = -118$ ppm and $\delta = -137$ ppm. Chemical shifts and coupling constants are given in Table 9, Appendix B.

M. Synthesis of F-1,4-Dioxaspiro[4.5]decane

Aerosol direct fluorination of 1,4-dioxaspiro[4.5]decane produced F-1,4-dioxaspiro[4.5]decane as the major product. The percent distribution of F-1,4-dioxaspiro[4.5]decane was 76% of the total products collected by weight; without correcting for unreacted or partially reacted materials, the percent yield based on the amount of 1,4-dioxaspiro[4.5]decane injected was 12%.

F-1,4-Dioxaspiro[4.5]decane, which has not been previously synthesized, was characterized by its infrared spectrum, chemical ionization and electron-impact mass spectrum, ^{19}F nmr spectrum, and by elemental analysis. The complete characterization is given in Table 12, Appendix B.

The chemical ionization mass spectrum of F-1,4-dioxaspiro[4.5]-decane exhibits a top mass peak at $m/e = 414$ corresponding to the molecular ion plus HF, and peaks at $m/e = 182, 172, 151, 131, 117, 100, 97,$ and 95 corresponding to the fragments $\text{C}_3\text{F}_6\text{O}_2^+, \text{C}_8\text{F}_4^+, \text{C}_3\text{F}_6\text{H}^+, \text{C}_3\text{F}_5^+, \text{C}_5\text{F}_3^+, \text{C}_2\text{F}_4^+, \text{C}_2\text{F}_3\text{O}^+,$ and $\text{C}_3\text{F}_3\text{H}_2^+$, respectively. The electron-impact mass spectrum exhibits a top mass peak at $m/e = 375$ corresponding to the molecular ion minus fluorine, confirming the molecular formula $\text{C}_8\text{F}_{14}\text{O}_2$. Further confirmation of the molecular formula was obtained from elemental analysis (Table 12, Appendix B).

The ^{19}F nmr spectrum of F-1,4-dioxaspiro[4.5]decane consists of a singlet at $\delta = -83.22$ ppm and a broad peak at $\delta = -132.02$ ppm with relative intensity 4:10 corresponding to the ethylenic CF_2 groups and the ring CF_2 groups, respectively.

Elemental analysis also confirmed the molecular formula as $\text{C}_8\text{F}_{14}\text{O}_2$, as shown in Table 12, Appendix B.

N. Synthesis of F-Cyclohexanone

F-Cyclohexanone was synthesized via two routes. In the first, F-methoxycyclohexane was converted to F-cyclohexanone in an 82% yield (28% conversion) by treatment with 100% sulfuric acid and heating at

350°C. The conversion of F-methoxycyclohexane to F-cyclohexanone is clean, virtually no side products being formed.

As an alternative F-cyclohexanone can be produced from the acid hydrolysis of the perfluoroketal, F-1,4-dioxaspiro[4.5]decane. At 500°C in the presence of 100% sulfuric acid, F-1,4-dioxaspiro[4.5]-decane is converted to F-cyclohexanone in a 100% yield (36% conversion), with virtually no side products.

F-Cyclohexanone has been previously synthesized via a number of methods. Rearrangement of perfluorocyclohexene epoxide over Lewis acid catalysts produces F-cyclohexanone,^{37,39} as does treatment of the epoxide with potassium fluoride in sulfolane.⁴⁰ Acid hydrolysis of methyl or fluoromethyl perfluorocyclohexyl ether, followed by distillation from phosphorous pentoxide, also produced F-cyclohexanone.⁶³ Treatment of 1,2-dichloroperfluorocyclohexene epoxide^{66,68} or 2,2-dichloroperfluorocyclohexanone^{66,67} with potassium fluoride also leads to the formation of F-cyclohexanone.

F-Cyclohexanone was identified from its infrared spectrum, electron-impact mass spectrum, and ¹⁹F nmr spectrum. The complete characterization is given in Table 10, Appendix B.

The infrared spectrum of F-cyclohexanone exhibits a carbonyl stretch at 1795 cm⁻¹ and strong absorption in the 1400 to 1000 region due to C-F stretches.

The electron-impact mass spectrum of F-cyclohexanone exhibits a peak at m/e = 278 corresponding to the molecular ion, and also includes peaks at m/e = 181, 131, 100, and 69 corresponding to the fragments C₄F₇⁺, C₃F₅⁺, C₂F₄⁺, and CF₃⁺, respectively.

The ^{19}F nmr spectrum of F-cyclohexanone agreed with that cited in the literature,⁶³ and consists of a singlet and a broad peak of relative intensity 4:6 at $\delta = -125.15$ ppm and $\delta = -133.23$ ppm (CFCl_3 internal standard), respectively. The peak at $\delta = -125.15$ ppm corresponds to the CF_2 groups alpha to the carbonyl group and the broad peak at $\delta = -133.23$ ppm is due to the remaining CF_2 groups.

F-Cyclohexanone is difficult to handle due to its extremely hygroscopic nature. Reaction of F-cyclohexanone with water produces a hydrate with absorptions at 3600 and 2960 cm^{-1} in the infrared, which on further hydrolysis forms a non-volatile solid.

0. Synthesis of F-3,3-Dimethyl-2-butanone

The aerosol direct fluorination of 3,3-dimethyl-2-butanone produced F-3,3-dimethyl-2-butanone, 3-difluoromethyl-F-3-methyl-2-butanone, and 3,3-bis(difluoromethyl)-F-2-butanone as the major products, constituting 23%, 25%, and 13% of the total products collected by weight, respectively. The isolation of significant quantities of the mono- and di-hydril products reflects the sterically crowded nature of the tert-butyl group; replacement of the final hydrogen is somewhat difficult due to the very crowded nature of the fluorinated tert-butyl group.

The products, which have not been previously synthesized, were characterized by their infrared spectra, electron-impact and chemical ionization mass spectra, and ^{19}F nmr spectra.

The characterization of F-3,3-dimethyl-2-butanone is given in Table 13, Appendix B. The infrared spectrum exhibits a carbonyl

stretch at 1770 cm^{-1} and strong absorptions in the $1400\text{--}1000\text{ cm}^{-1}$ region due to C-F stretches. The chemical ionization mass spectrum exhibits large peaks at $m/e = 317$ and 297 corresponding to the molecular ion plus hydrogen and the molecular ion minus fluorine, respectively, and a base peak at $m/e = 97$, corresponding to the $\text{C}_2\text{F}_3\text{O}^+$ fragment, formed via cleavage of the bond alpha to the carbonyl group. The electron-impact mass spectrum exhibits a top mass peak at $m/e = 247$, corresponding to the molecular ion minus a CF_3 group, and a consistent fragmentation pattern. The ^{19}F nmr spectrum of F-3,3-dimethyl-2-butanone consists of a dectet of relative intensity 3 at $\delta = -73.88$ ppm due to the CF_3 group attached directly to the carbonyl function and a quartet of relative intensity 9 at $\delta = -62.12$ ppm due to the remaining CF_3 groups.

The characterization of 3-difluoromethyl-F-3-methyl-2-butanone is given in Table 14, Appendix B. The infrared spectrum exhibits a weak C-H stretch at 3015 cm^{-1} and a carbonyl stretch at 1760 cm^{-1} . The chemical ionization mass spectrum exhibits a top mass peak at $m/e = 300$ corresponding to the molecular ion plus two hydrogens and the electron-impact mass spectrum includes large peaks at $m/e = 97$ and 51 corresponding to the $\text{C}_2\text{F}_3\text{O}^+$ and CF_2H^+ fragments, respectively. The ^{19}F nmr spectrum consists of three complex multiplets at $\delta = -62.05$, -73.85 , and -126.69 ppm corresponding to the CF_3 groups on the tert-butyl segment, the CF_3 group attached to the carbonyl function, and the CF_2H group, respectively; the peak at $\delta = -126.69$ is a doublet of multiplets, ($J_{\text{CF}_2\text{-H}} = 51.5\text{ Hz}$). The ^1H nmr spectrum consists of a triplet at $\delta = +6.63$ ppm.

The characterization of 3,3-bis(difluoromethyl)-F-2-butanone is given in Table 15, Appendix B. The infrared spectrum exhibits a weak C-H stretch at 3010 cm^{-1} and a carbonyl stretch at 1755 cm^{-1} . The chemical ionization mass spectrum exhibits a base peak at $m/e = 282$ corresponding to the molecular ion plus two hydrogens, in addition to large peaks at $m/e = 212$, 97, and 69 corresponding to the fragments $\text{C}_5\text{F}_7\text{OH}_3^+$, $\text{C}_2\text{F}_3\text{O}^+$, and CF_3 , respectively. The electron-impact mass spectrum exhibits large peaks at $m/e = 212$, 142, 69, and 51 corresponding to the fragments $\text{C}_5\text{F}_7\text{OH}_3^+$, $\text{C}_4\text{F}_4\text{OH}_2^+$, CF_3^+ , and CF_2H^+ , respectively. The ^{19}F nmr spectrum consists of three complex multiplets of relative intensity 3:3:4 at $\delta = -74.61$, -62.99 , and -125.18 ppm corresponding to the CF_3 group attached to the carbonyl function, the remaining CF_3 group, and the CF_2H groups, respectively. The peak at $\delta = -125.18$ ppm is a doublet of multiplets ($J_{\text{CF}_2-\text{H}} = 52.7\text{ Hz}$). The ^1H nmr spectrum consists of a triplet at $\delta = +6.59$ ppm.

P. Aerosol Fluorination of 2,2,4,4-Tetramethyl-3-pentanone:

A Skeletal Rearrangement

Aerosol direct fluorination of 2,2,4,4-tetramethyl-3-pentanone produced F-2,2,5-trimethyl-3-hexanone as the major product. This result is the first example of a skeletal rearrangement during aerosol direct fluorination of ketones, and the mechanism of this novel rearrangement is currently under investigation. The characterization of F-2,2,5-trimethyl-3-hexanone, which has not been previously synthesized, is given in Table 16, Appendix B.

The infrared spectrum of F-2,2,5-trimethyl-3-hexanone exhibits a carbonyl stretch at 1770 cm^{-1} and strong absorptions in the 1400 to 1000 cm^{-1} region due to C-F stretches.

The chemical ionization mass spectrum exhibits peaks at $m/e = 483$, 467 , and 447 , corresponding to the molecular ion plus CH_5 , the molecular ion plus hydrogen, and the molecular ion minus fluorine, respectively. In addition, the base peak occurs at $m/e = 219$, corresponding to the C_4F_9^+ fragment resulting from the cleavage of the bonds alpha to the carbonyl group. The electron-impact mass spectrum exhibits a peak at $m/e = 447$ due to the molecular ion minus fluorine, and also includes peaks at $m/e = 247$, 219 , and 69 due to the fragments $\text{C}_5\text{F}_9\text{O}^+$, C_4F_9^+ , and CF_3^+ , respectively.

The ^{19}F nmr spectrum consists of four multiplets of relative intensity 9:6:2:1 at $\delta = -61.61$, -71.82 , -109.32 , and -184.26 ppm (CFCl_3 internal standard), corresponding to the tert-butyl CF_3 groups, the remaining CF_3 groups, the CF_2 group, and the tertiary fluorine, respectively. The coupling constants are given in Table 16, Appendix B. The signal at $\delta = -61.61$ ppm due to the tert-butyl CF_3 groups is a triplet of multiplets due to coupling with the CF_2 and the remaining CF_3 groups. The signal at $\delta = -71.82$ ppm is a triplet of doublets due to coupling with the CF_2 group and the tertiary fluorine. The CF_2 group appears as a hexadectet of doublets at $\delta = -109.32$ ppm due to coupling with the CF_3 groups and the tertiary fluorine. The hexadectet arises from the fact that the coupling constants of the CF_2 group with the two different CF_3 groups are identical. The tertiary fluorine appears as a multiplet at $\delta = -184.26$ ppm.

Q. Miscellaneous Aerosol Fluorinations

Adamantane. Due to the success of the flash evaporator unit in allowing the aerosol direct fluorination of high boiling liquids, it was of interest to ascertain whether or not solids could be successfully perfluorinated employing the flash evaporator/sublimator unit. Adamantane has a relatively high room temperature volatility in addition to forming an excellent aerosol and was thus chosen as a model compound for testing the solid handling capabilities of the modified aerosol fluorination system. The major product formed in the aerosol direct fluorination of adamantane was F-adamantane, produced in a 28% yield.¹⁰⁷ The characterization of F-adamantane is given in Table 17, Appendix B. Whereas previous fluorinations of adamantane and substituted adamantanes have led to incomplete fluorination or significant degrees of ring-opening,^{108,109} aerosol fluorination of adamantane produced no ring-opened species. F-Adamantane is of interest as a synthetic blood substitute¹¹⁰⁻¹¹² and the only other method of preparation other than the aerosol direct fluorination process appears in a recent patent application wherein adamantane in methylcyclohexane was contacted with a cobalt trifluoride bed at 275°C to produce 1-hydrylpentadecafluoroadamantane and F-adamantane (no yields given).¹¹³

Tetramethyl orthocarbonate. Aerosol direct fluorination of tetramethyl orthocarbonate produced F-trimethyl orthoformate and F-tetramethyl orthocarbonate as the major products.¹¹⁴ The characterizations of F-trimethyl orthoformate and F-tetramethyl

orthocarbonate, which have not been previously synthesized, are given in Tables 18 and 19, Appendix B, respectively. The synthesis of F-tetramethyl orthocarbonate represents the first synthesis of a perfluorinated orthocarbonate.

CHAPTER IV

SUMMARY

A series of perfluoroketones were synthesized in a one step process via the aerosol direct fluorination of the corresponding acyclic hydrocarbon ketone; in the case of the cyclic ketones, a two step process involving aerosol direct fluorination of the appropriate methyl cycloalkyl ether or cycloalkyl ethylene glycol ketal, followed by acid hydrolysis of the perfluorinated ether or ketal, provides a route to the corresponding perfluorocycloketones. The perfluoroketones, several of which have not been previously synthesized, were characterized by infrared spectrophotometry, electron-impact and chemical ionization mass spectroscopy, and ^{19}F nuclear magnetic resonance spectroscopy. Modification of the basic aerosol fluorination system extended the usefulness of the process, allowing the fluorination of both solid and high boiling liquid hydrocarbons.

Extension of the aerosol direct fluorination process to the production of perfluoroketones represents an important advance in direct fluorination technology. In fact, the aerosol direct fluorination method is the only method presently available capable of producing perfluoroketones directly from the relatively inexpensive, readily available hydrocarbon analogs. All other methods for the production of perfluoroketones involve relatively expensive, highly fluorinated materials, or in some cases highly chlorinated materials, and hence the ability to produce perfluoroketones directly from inexpensive hydrocarbon starting materials is very advantageous. Although the yields of

the perfluoroketones are somewhat lower than one would hope for, it is believed that this is due mainly to the small scale of the present system and that scale-up would significantly reduce losses. These losses are primarily reactant losses within the reactor stages. The fact that the aerosol direct fluorination method is a flow process suggests its feasibility as a general method for the commercial production of perfluoroketones.

The chemistry of many perfluorinated ketones, while predicted to be of great interest, is relatively unexplored due to their nonavailability. As a result of this research, the availability of gram quantities of these perfluoroketones will now allow their chemical and physical properties to be examined.

The first successful aerosol direct fluorination of a solid has also been achieved, producing F-adamantane directly from the hydrocarbon analog. F-adamantane has been previously synthesized only with great difficulty and the fluorination of substituted adamantanes as well as adamantane itself are characterized by either incomplete fluorination or significant ring-opening. The aerosol direct fluorination process results in complete fluorination and no significant ring-opening in the case of adamantane, and raises the possibility of producing other perfluorinated adamantane systems possibly useful as synthetic blood substitutes.

LIST OF REFERENCES

LIST OF REFERENCES

1. H. Moissan, Ann. Chim. Phys., 24, 224 (1891).
2. 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.
3. W. Bockemuller, Annalen, 506, 20 (1933).
4. J. D. Calfee and L. A. Bigelow, J. Am. Chem. Soc., 59, 2072 (1937).
5. N. Fukuhara and L. A. Bigelow, J. Am. Chem. Soc., 63, 788 (1941).
6. G. H. Cady, A. V. Grosse, E. J. Barber, L. L. Burger, and Z. D. Sheldon, Ind. Eng. Chem., 39, 290 (1947).
7. W. K. R. Musgrave and F. Smith, J. Chem. Soc., 3021 (1949).
8. W. K. R. Musgrave and F. Smith, J. Chem. Soc., 3026 (1949).
9. R. N. Haszeldine and F. Smith, J. Chem. Soc., 2689 (1950).
10. R. N. Haszeldine and F. Smith, J. Chem. Soc., 2787 (1950).
11. E. A. Tyczkowski and L. A. Bigelow, J. Am. Chem. Soc., 77, 3007 (1955).
12. 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.
13. N. J. Maraschin and R. J. Lagow, J. Am. Chem. Soc., 94, 8601 (1972).
14. N. J. Maraschin and R. J. Lagow, Inorg. Chem., 12, 1459 (1973).
15. J. L. Adcock and R. J. Lagow, J. Org. Chem., 38, 3617 (1973).
16. J. L. Adcock and R. J. Lagow, J. Am. Chem. Soc., 96, 7588 (1974).
17. J. L. Adcock, R. A. Beh, and R. J. Lagow, J. Org. Chem., 40, 3271 (1975).
18. J. L. Adcock and R. J. Lagow, unpublished results.
19. J. L. Adcock, B. D. Catsikis, J. W. Thompson, and R. J. Lagow, J. Fluorine Chem., 7, 197 (1976).
20. J. L. Adcock, K. Horita, and E. B. Renk, J. Am. Chem. Soc., 103, 6937 (1981).

21. J. L. Adcock and E. B. Renk, "Low Temperature Fluorination of Aerosol and Condensed Phase Sol Suspensions of Hydrocarbons Utilizing Elemental Fluorine," Office of Naval Research, Contract Technical Report No. 1.
22. J. L. Adcock and E. B. Renk, "Low Temperature Fluorination of Aerosol and Condensed Phase Sol Suspensions of Hydrocarbons Utilizing Elemental Fluorine," Office of Naval Research, Contract Technical Report No. 2.
23. J. L. Adcock, K. Horita, and E. B. Renk, "Low Temperature Fluorination of Aerosol and Condensed Phase Sol Suspensions of Hydrocarbons Utilizing Elemental Fluorine," Office of Naval Research, Contract Technical Report No. 3.
24. J. L. Adcock and E. B. Renk, U.S. Patent 4,330,465 (1982).
25. R. D. Chambers, "Fluorine in Organic Chemistry," Wiley Interscience, New York, 1973, p. 16.
26. J. H. Simons, U.S. Patent 2,500,000 (1950).
27. J. H. Simons, Trans. Electrochem. Soc., 95, 47 (1949).
28. J. H. Simons, in "Fluorine Chemistry," Vol. 1, J. H. Simons, Ed., Academic, New York, 1950, p. 414.
29. J. Burdon 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.
30. R. D. Fowler, W. B. Burford, J. M. Hamilton, R. G. Sweet, C. E. Weber, J. S. Kasper, and I. Litant in "Preparation, Properties, and Technology of Fluorine and Organofluorine Compounds," C. Slessor and S. R. Schram, Eds., McGraw-Hill, New York, 1951, p. 349.
31. F. F. Holub and L. A. Bigelow, J. Am. Chem. Soc., 72, 4879 (1950).
32. R. D. Bagnall, P. L. Coe, and J. C. Tatlow, J. Chem. Soc., Perkin Trans., 2277 (1972).
33. J. L. Adcock, unpublished results.
34. Farbwerke Hoechst A.-G., French Patent 1,343,392 (1963).
35. F. W. Swamer (to E. I. du Pont de Nemours and Co.), French Patent 1,372,549 (1964).
36. A. Antonini, R. Putters, and G. Wettruff (to Rhone-Progil), German Patent 2,221,844 (1972).

37. E. P. Moore and A. S. Milian (to E. I. duPont de Nemours and Co.) U.S. Patent 3,321,515 (1967).
38. E. I. du Pont de Nemours and Co., French Patent 1,416,013 (1965).
39. E. P. Moore and A. S. Milian (to E. I. duPont de Nemours and Co.) British Patent 1,019,788 (1966).
40. P. L. Coe, J. H. Sleight, and J. C. Tatlow, J. Fluorine Chem., 15, 339 (1980).
41. A. Y. Zapevalov, T. A. Filyakova, and I. P. Kolenko, Isz. Akad. Nauk SSSR, Ser. Khim., 12, 2812 (1979).
42. D. E. Morin (to Minnesota Mining and Manufacturing Co.) U.S. Patent 3,213,134 (1965).
43. A. Y. Zapevalov, I. P. Kolenko, V. S. Plashkin, and P. G. Neifeld, Zh. Org. Khim., 14, 259 (1978).
44. S. A. Postovoi, E. I. Mysov, Yu. V. Zeifman, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 7, 1586 (1982).
45. R. D. Smith, F. S. Fawcett, and D. D. Coffmann, J. Am. Chem. Soc., 84, 4285 (1962).
46. F. S. Fawcett and R. D. Smith (to E. I. duPont de Nemours and Co.) U.S. Patent 3,185,734 (1965).
47. F. S. Fawcett (to E. I. du Pont de Nemours and Co.) U.S. Patent 3,113,967 (1963).
48. Y. M. Vilencik, G. I. Lekontseva, and L. S. Semerikova, Zh. Vses. Khim. o-Va., 26, 210 (1981).
49. R. D. Chambers, C. A. Heaton, and W. K. R. Musgrave, J. Chem. Soc. C, 1933 (1968).
50. D. W. Wiley (to E. I. du Pont de Nemours and Co.) U.S. Patent 3,091,643 (1963).
51. M. Hauptschein and R. A. Braun, J. Am. Chem. Soc., 77, 4930 (1957).
52. A. L. Henne and W. C. Francis, J. Am. Chem. Soc., 75, 992 (1953).
53. O. R. Pierce, E. T. McBee, and G. F. Judd, J. Am. Chem. Soc., 76, 474 (1954).
54. W. T. Miller, Jr., E. Bergman, and A. H. Fainberg, J. Am. Chem. Soc., 79, 4159 (1957).

55. R. N. Haszeldine, J. Chem. Soc., 1748 (1953).
56. R. N. Haszeldine, J. Chem. Soc., 1273 (1953).
57. T. J. Brice, J. D. LaZerte, L. J. Hals, and W. H. Pearlson, J. Am. Chem. Soc., 75, 2698 (1953).
58. R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 3005 (1955).
59. E. T. McBee and R. M. Robb (to Purdue Research Foundation) U.S. Patent 2,567,569 (1951).
60. J. J. Delfino and J. M. Shreeve, Inorg. Chem., 5, 308 (1966).
61. Pennsalt Chemicals Corp., British Patent 926,411 (1963).
62. D. C. England, J. Am. Chem. Soc., 83, 2205 (1961).
63. A. B. Clayton, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 7370 (1965).
64. J. R. Majer and D. Phillips, J. Chem. Soc. B, 201 (1969).
65. J. A. Oliver, R. Stephens, and J. C. Tatlow, J. Fluorine Chem., 6, 19 (1975).
66. L. G. Anello, A. K. Price, and R. F. Sweeney, J. Org. Chem., 33, 2692 (1968).
67. L. G. Anello and R. F. Sweeney (to Allied Chemical) U.S. Patent 3,379,765 (1968).
68. A. K. Price and R. F. Sweeney (to Allied Chemical) U.S. Patent 3,350,457 (1967).
69. W. Espenscheid, E. Matijevic, and M. Kerker, J. Phys. Chem., 68, 2831 (1964).
70. D. G. Weiblen, in "Fluorine Chemistry," Vol. 2, J. H. Simons, Ed., Academic Press, New York, 1954, pp. 449-503.
71. V. V. Berenblit, V. A. Nikitin, V. P. Sass, L. N. Senyushov, Yu. K. Starobin, and Yu. V. Tsyganov, Zh. Org. Khim., 15, 284 (1979).
72. E. L. Pace, A. C. Plaush, and H. V. Samuelson, Spectrochim. Acta, 22, 993 (1966).
73. "Sadtlter Standard Spectra, Infrared Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 6840K.
74. A. I. Vogel, J. Chem. Soc., 1809 (1948).

75. M. S. Toy and R. S. Stringham, J. Fluorine Chem., 5, 481 (1975).
76. R. A. Daignault and E. L. Eliel, Org. Syn., 47, 37 (1967).
77. P. Mastagli, P. Lambert, and C. Hirigoyen, Compt. Rend., 251, 2191 (1960).
78. O. Ruff, A. Pitochelli, and M. Lustig, J. Am. Chem. Soc., 88, 4531 (1966).
79. O. Ruff, A. Pitochelli, and M. Lustig, J. Am. Chem. Soc., 89, 2481 (1967).
80. F. A. Hohorst and J. M. Shreeve, Inorg. Synth., 11, 143 (1968).
81. G. Giacometti, H. Okabe, S. J. Price, and E. W. R. Steacie, Can. J. Chem., 38, 104 (1960).
82. G. H. Miller, G. O. Pritchard, and E. W. R. Steacie, Z. Physik. Chem., 15, 262 (1958).
83. A. S. Gordon, Can. J. Chem., 44, 529 (1966).
84. F. A. Carey and R. D. Sundberg, "Advanced Organic Chemistry," Part B, Plenum Press, New York, 1977, p. 34.
85. N. L. Allinger, M. P. Cava, D. C. De Jongh, C. R. Johnson, N. A. Lebel, and C. A. Stevens, "Organic Chemistry," Worth, New York, 1971, p. 477.
86. G. A. Olah and C. U. Pittman, J. Am. Chem. Soc., 88, 3310 (1966).
87. N. P. Gambaryan, E. M. Rokhlin, Y. V. Zeifman, C. Ching-Yun, and I. L. Knunyants, Angew. Chem. Internat. Edit., 5, 947 (1966).
88. H. P. Braendlin and E. T. McBee, in "Advances in Fluorine Chemistry," Vol. 3, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Eds., Butterworths, London, 1963, p. 1.
89. C. G. Krespan and W. J. Middleton, in "Fluorine Chemistry Reviews," Vol. 1, P. Tarrant, Ed., Dekker, New York, 1967, p. 145.
90. N. P. Gambaryan, E. M. Rokhlin, Yu. V. Zeifman, L. A. Simonyan, and I. L. Knunyants, Doklady Akad. Nauk SSSR, 166, 864 (1966).
91. I. Ugi, Angew. Chem. Internat. Edit., 1, 8 (1962).
92. F. W. Evans, M. H. Litt, A. M. Weidler-Kubaneck, and F. P. Avonda, J. Org. Chem., 33, 1837 (1968).
93. E. T. McBee, C. W. Roberts, and S. G. Curtis, J. Am. Chem. Soc., 77, 6387 (1955).

94. E. T. McBee, O. R. Pierce, and D. L. Christman, J. Am. Chem. Soc., 77, 5181 (1955).
95. D. W. Wiley and H. E. Simmons, J. Org. Chem., 29, 1876 (1964).
96. G. F. Ovchinnikov, Yu. Ya. Sud'enkov, and I. P. Kolenko, Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva, 19, 105 (1974).
97. Yu. Ya. Sud'enkov and T. P. Poltanova, Izv. Akad. Nauk SSSR, Ser. Khim., 2, 477 (1977).
98. T. B. Zapevalova, A. Ya. Zapevalova, V. P. Sass, I. P. Kolenko, V. S. Plashkin, and S. V. Sokolov, Zh. Org. Khim., 14, 487 (1978).
99. P. J. Krusic, K. S. Chen, P. Meakin, and J. K. Kochi, J. Phys. Chem., 78, 2036 (1974).
100. "The Sadtler Standard Spectra, Infrared Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 28516K.
101. L. J. Bellamy and R. L. Williams, J. Chem. Soc., 4294 (1957).
102. V. P. Zhukov and V. A. Gubanov, J. Mol. Structure, 41, 281 (1977).
103. J. R. Majer in "Advances in Fluorine Chemistry," Vol. 2, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Eds., Butterworths, London, 1961, p. 55.
104. C. H. Dungan and J. R. Van Wazer, "Compilation of Reported ^{19}F nmr Chemical shifts," Wiley, New York, 1970.
105. W. A. Severson and T. J. Brice (to Minnesota Mining and Manufacturing Co.) U.S. Patent 2,765,326 (1956).
106. I. P. Kolenko, T. I. Filyakova, A. Ya. Zapevalov, and E. P. Lurie, Izv. Akad. Nauk. SSSR, Ser. Khim., 11, 2509 (1979).
107. J. L. Adcock and M. L. Robin, J. Org. Chem., in press.
108. R. E. Moore and G. L. Driscoll, J. Org. Chem., 43, 4978 (1978).
109. G. Robertson, E. K. S. Liu, and R. J. Lagow, J. Org. Chem., 43, 4981 (1978).
110. R. E. Moore, L. C. Clark, Jr., and M. L. Miller, Int. Congr. Ser. Excerpts Med. 1979 (486) (Proc. Int. Symp. Perfluorochem. Blood Substitutes, 4th, 1978), p. 68.
111. Green Cross Corp., Japanese Patent 72,110 (1980).

112. L. C. Clark, Jr. and R. E. Moore, Prog. Clin. Biol. Res., 55 (Red Cell), 595 (1981).
113. R. E. Moore (to Suntech. Inc.) British Patent Application 6B, 2,079,273 (1982).
114. J. L. Adcock and M. L. Robin, to be published.

APPENDICES

APPENDIX A

AEROSOL FLUORINATION PARAMETERS

TABLE A-1
AEROSOL FLUORINATION OF 3-PENTANONE

Parameters	Reaction		
	1	2	3
Fluorine flows (cc/min)			
Module 1	20	20	20
Module 2	20	20	20
Module 3	0	0	0
Helium diluent flows (cc/min)			
Module 1	20	20	20
Module 2	20	20	20
Module 3	0	0	0
Reactor temperatures (°C) ^a			
Module 1	-30	-40	-20
Module 2	-30	-30	-10
Module 3	RT	RT	RT
End coil	RT	RT	100
Main carrier He (cc/min)	400	400	600
Hydrocarbon throughput (mmole/hr)	2.2	2.2	2.2
Reaction time (hr)	4	4	4
Overall F ₂ :hydrocarbon ratio	67:1	67:1	67:1
Product ^b distribution, % collected	53	62	71
Product yield, grams	0.113	0.198	0.271
Product yield, % theoretical	5	8	12

^aRT = room temperature.

^bF-3-Pentanone.

TABLE A-2
AEROSOL FLUORINATION OF 4-HEPTANONE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	20
Module 2	30
Module 3	0
Helium diluent flows (cc/min)	
Module 1	20
Module 2	20
Module 3	0
Reactor temperatures (°C) ^a	
Module 1	-45
Module 2	-30
Module 3	RT
End coil	RT
Main carrier He (cc/min)	750
Hydrocarbon throughput (mmole/hr)	2.5
Reaction time (hr)	4
Overall F ₂ :hydrocarbon ratio	49:1
Product ^b distribution, % collected	92
Product yield, grams	0.675
Product yield, % theoretical	18

^aRT = room temperature.

^bF-3-Heptanone.

TABLE A-3
AEROSOL FLUORINATION OF CYCLOPENTANONE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	10
Module 2	15
Module 3	20
Helium diluent flows (cc/min)	
Module 1	30
Module 2	30
Module 3	30
Reactor temperatures (°C) ^a	
Module 1	-40
Module 2	-30
Module 3	RT
End coil	100
Main carrier He (cc/min)	750
Hydrocarbon throughput (mmole/hr)	2.3
Reaction time (hr)	3
Overall F ₂ :hydrocarbon ratio	48:1
Product ^b distribution, % collected	61
Product yield, grams	0.378
Product yield, % theoretical	21

^aRT = room temperature.

^bF-Pentanoyl fluoride.

TABLE A-4
AEROSOL FLUORINATION OF CYCLOHEXANONE

Parameters	Reaction			
	1	2	3	4
Fluorine flows (cc/min)				
Module 1	15	10	5	20
Module 2	20	20	10	45
Module 3	0	0	15	0
Helium diluent (cc/min)				
Module 1	30	20	20	50
Module 2	30	20	20	50
Module 3	0	0	20	0
Reactor temperatures (°C) ^a				
Module 1	-20	-30	-50	-40
Module 2	-10	-20	-30	-20
Module 3	RT	RT	RT	RT
End coil	RT	RT	RT	RT
Main carrier He (cc/min)	550	450	400	1000
Hydrocarbon throughput (mmole/hr)	1.9	1.9	1.9	1.9
Overall F ₂ :hydrocarbon ratio	45:1	39:1	39:1	83:1
Product distribution, % collected	-	-	-	-
Product yield, % theoretical	-	-	-	-

^aRT = room temperature.

TABLE A-5
AEROSOL FLUORINATION OF 3-HEPTANONE

Parameters	Reaction			
	1	2	3	4
Fluorine flows (cc/min)				
Module 1	20	20	20	20
Module 2	20	20	20	20
Module 3	30	30	30	40
Helium diluent (cc/min)				
Module 1	150	150	150	150
Module 2	150	150	150	150
Module 3	150	150	150	150
Reactor temperatures (°C) ^a				
Module 1	-40	-40	-30	-40
Module 2	-30	-30	-20	-30
Module 3	0	0	0	RT
End coil	RT	100	100	100
Main carrier He (cc/min)	900	500	1000	500
Evaporator/sublimator temp (°C)	180	180	180	180
Evaporator/sublimator flows (cc/min)				
Primary	50	450	950	450
Secondary	33	50	50	50
Tertiary	0	0	0	0
Hydrocarbon throughput (mmole/hr)	2.6	1.9	1.9	3.5
Reaction time (hr)	3	3.7	2.5	6
Overall F ₂ :hydrocarbon ratio	66:1	90:1	90:1	56:1
Product ^b distribution, % collected	35	70	9	59
Product yield, grams	0.077	0.162	0.024	0.975
Product yield, % theoretical	3	6	1	13

^aRT = room temperature.

^bF-3-Heptanone.

TABLE A-6
AEROSOL FLUORINATION OF 2-HEPTANONE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	40
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-30
Module 2	-20
Module 3	RT
End coil	RT
Main carrier helium (cc/min)	600
Evaporator/sublimator temp (°C)	175
Evaporator/sublimator flows (cc/min)	
Primary	500
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmol/hr)	3.8
Reaction time (hr)	3.2
Overall F ₂ :hydrocarbon ratio	51:1
Product ^b distribution, % collected	55
Product yield (grams)	0.348
Product yield, % theoretical	8

^aRT = room temperature.

^bF-2-Heptanone.

TABLE A-7
AEROSOL FLUORINATION OF 2-BUTANONE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	10
Module 2	10
Module 3	20
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-30
Module 2	-20
Module 3	RT
End coil	RT
Main carrier helium (cc/min)	600
Evaporator/sublimator temp (°C)	100
Evaporator/sublimator flows (cc/min)	
Primary	500
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmol/hr)	3.9
Reaction time (hr)	4.0
Overall F ₂ :hydrocarbon ratio	25:1
Product ^b distribution, % collected	20
Product yield (grams)	0.311
Product yield, % theoretical	9

^aRT = room temperature.

^bF-2-Butanone.

TABLE A-8
AEROSOL FLUORINATION OF ACETONE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	10
Module 2	10
Module 3	20
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-40
Module 2	-30
Module 3	RT
End coil	RT
Main carrier helium (cc/min)	600
Evaporator/sublimator temp (°C)	80
Evaporator/sublimator flows (cc/min)	
Primary	500
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmol/hr)	5.1
Reaction time (hr)	4.0
Overall F ₂ :hydrocarbon ratio	19:1
Product ^b distribution, % collected	48
Product yield (grams)	0.148
Product yield, % theoretical	4

^aRT = room temperature.

^bF-Acetone.

TABLE A-9
AEROSOL FLUORINATION OF METHOXYCYCLOPENTANE

Parameters	Reaction	
	1	2
Fluorine flows (cc/min)		
Module 1	15	15
Module 2	20	20
Module 3	30	30
Helium diluent (cc/min)		
Module 1	150	150
Module 2	150	150
Module 3	150	150
Reactor temperatures (°C) ^a		
Module 1	-20	-20
Module 2	-10	-10
Module 3	RT	RT
End coil	RT	RT
Main carrier He (cc/min)	500	700
Evaporator/sublimator temp (°C)	150	150
Evaporator/sublimator flows (cc/min)		
Primary	400	650
Secondary	50	50
Tertiary	0	0
Hydrocarbon throughput (mmole/hr)	3.7	4.3
Reaction time (hr)	5.5	8
Overall F ₂ :hydrocarbon ratio	43:1	37:1
Product ^b distribution, % collected	57	38
Product yield, grams	1.381	1.363
Product yield, % theoretical	21	13

^aRT = room temperature.

^bF-Methoxycyclopentane.

TABLE A-10
AEROSOL FLUORINATION OF METHOXYCYCLOHEXANE

Parameters	Reaction 1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	40
Helium diluent flows (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-30
Module 2	-20
Module 3	RT
End coil	RT
Main carrier He (cc/min)	800
Evaporator/sublimator temp (°C)	150
Evaporator/sublimator flows (cc/min)	
Primary	750
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmole/hr)	3.8
Reaction time (hr)	6.7
Overall F ₂ :hydrocarbon ratio	51:1
Product ^b distribution, % collected	90
Product yield, grams	2.991
Product yield, % theoretical	32

^aRT = room temperature.

^bF-Methoxycyclohexane.

TABLE A-11

AEROSOL FLUORINATION OF 1,4-DIOXASPIRO[4.4]NONANE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	10
Module 2	20
Module 3	30
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-20
Module 2	-10
Module 3	RT
End coil	RT
Main carrier helium (cc/min)	700
Evaporator/sublimator temp (°C)	175
Evaporator/sublimator flows (cc/min)	
Primary	600
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmole/hr)	4.2
Reaction time (hr)	6
Overall F ₂ :hydrocarbon ratio	35:1
Product ^b distribution, % collected	74
Product yield, grams	1.222
Product yield, % theoretical	14

^aRT = room temperature.^bF-1,4-Dioxaspiro[4.4]nonane.

TABLE A-12

AEROSOL FLUORINATION OF 1,4-DIOXASPIRO[4.5]DECANE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	40
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-20
Module 2	-10
Module 3	RT
End coil	100
Main carrier helium (cc/min)	750
Evaporator/sublimator temp (°C)	225
Evaporator/sublimator flows (cc/min)	
Primary	650
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmole/hr)	4.3
Reaction time (hr)	5
Overall F ₂ :hydrocarbon ratio	45:1
Product ^b distribution, % collected	76
Product yield, grams	0.973
Product yield, % theoretical	11

^aRT = room temperature.^bF-1,4-Dioxaspiro[4.5]decane.

TABLE A-13

AEROSOL FLUORINATION OF 3,3-DIMETHYL-2-BUTANONE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	10
Module 2	20
Module 3	30
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-40
Module 2	-30
Module 3	RT
End coil	RT
Main carrier helium (cc/min)	600
Evaporator/sublimator temp (°C)	125
Evaporator/sublimator flows (cc/min)	
Primary	500
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmol/hr)	2.8
Reaction time (hr)	2.25
Overall F ₂ :hydrocarbon ratio	52:1
Product ^b distribution, % collected	23
Product yield (grams)	0.238
Product yield, % theoretical	12

^aRT = room temperature.^bF-3,3-Dimethyl-2-butanone.

TABLE A-14

AEROSOL FLUORINATION OF 2,2,4,4-TETRAMETHYL-3-PENTANONE

Parameters	Reaction
	1
Fluorine flows (cc/min)	
Module 1	20
Module 2	20
Module 3	40
Helium diluent (cc/min)	
Module 1	150
Module 2	150
Module 3	150
Reactor temperatures (°C) ^a	
Module 1	-30
Module 2	-20
Module 3	RT
End coil	RT
Main carrier helium (cc/min)	600
Evaporator/sublimator temp (°C)	200
Evaporator/sublimator flows (cc/min)	
Primary	500
Secondary	50
Tertiary	0
Hydrocarbon throughput (mmol/hr)	2.9
Reaction time (hr)	2
Overall F ₂ :hydrocarbon ratio	67:1
Product ^b distribution, % collected	71
Product yield (grams)	0.246
Product yield, % theoretical	9

^aRT = room temperature.^bF-2,2,5-Trimethyl-3-hexanone.

APPENDIX B
CHARACTERIZATION OF COMPOUNDS

TABLE B-1
CHARACTERIZATION OF F-3-PENTANONE

Infrared (cm^{-1}):

3620(w), 1780(m), 1320(s), 1230(vs), 1175(vs), 1110(s), 1025(m),
880(m), 830(m), 750(m), 710(s), 600(m).

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

CI(CH_4):

267(100) $\text{C}_5\text{F}_{10}\text{OH}$, M+H; 247(31) $\text{C}_5\text{F}_9\text{O}$, M-F; 197(1) $\text{C}_4\text{F}_7\text{O}$;
147(31) $\text{C}_3\text{F}_5\text{O}$; 119(14) C_2F_5 ; 101(2) $\text{C}_2\text{F}_4\text{H}$; 100(1) C_2F_5 ; 97(1) $\text{C}_2\text{F}_3\text{O}$;
69(4) CF_3 .

EI(70 eV):

148(1) $^{13}\text{CC}_2\text{F}_5\text{O}$; 147(40) $\text{C}_3\text{F}_5\text{O}$; 122(1) $\text{C}_3\text{F}_4\text{O}$; 120(2) $^{13}\text{CCF}_5$;
119(100) C_2F_5 ; 100(12) C_2F_4 ; 93(1) C_3F_3 ; 81(1) C_2F_3 ; 78(1) $\text{C}_2\text{F}_2\text{O}$;
69(32) CF_3 ; 50(2) CF_2 ; 31(3) CF .

^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; δ (mult.);integral]:

$\delta_{\text{CF}_3} = -82.03$ ppm (s); 3
 $\delta_{\text{CF}_2} = -121.38$ ppm (s); 2
J < 1 Hz

TABLE B-2
CHARACTERIZATION OF F-4-HEPTANONE

Infrared (cm^{-1}):

1785(m), 1395(m), 1240(s), 1200(m), 1160(m), 1140(m), 1080(m),
1015(m), 845(m), 780(w).

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

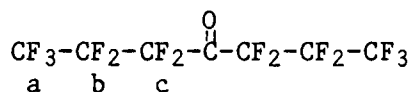
CI(CH_4):

414(9) $\text{C}_{11}\text{F}_{14}\text{O}$; 381(4) $\text{C}_8\text{F}_{14}\text{OH}_3$; 368(3) $^{13}\text{CC}_6\text{F}_{14}\text{OH}$, $\text{C}_7\text{F}_{14}\text{OH}_2$;
367(39) $\text{C}_7\text{F}_{14}\text{OH}$, M+H; 348(8) $^{13}\text{CC}_6\text{F}_{13}\text{O}$; 347(100) $\text{C}_7\text{F}_{13}\text{O}$, M-F;
297(1) $\text{C}_6\text{F}_{11}\text{O}$; 279(6) $\text{C}_6\text{F}_{10}\text{OH}$; 197(1) $\text{C}_4\text{F}_7\text{O}$; 169(5) C_3F_7 ; 119(3) C_2F_5 ;
117(1) C_5F_2 ; 100(1) C_2F_4 ; 69(2) CF_3 .

EI(70 eV):

347(1) $\text{C}_7\text{F}_{13}\text{O}$, M-F; 197(15) $\text{C}_4\text{F}_7\text{O}$; 181(1) C_4F_7 ; 170(3) $^{13}\text{CC}_2\text{F}_7$;
169(100) C_3F_7 ; 150(3) C_3F_6 ; 131(4) C_3F_5 ; 119(15) C_2F_5 ; 109(5) $\text{C}_3\text{F}_3\text{O}$;
100(16) C_2F_4 ; 93(2) C_3F_3 ; 81(2) C_2F_3 ; 70(1) $^{13}\text{CF}_3$; 69(81) CF_3 ;
50(2) CF_2 ; 31(3) CF .

^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; δ (mult.);integral]:



$$\delta_a = -81.16 \text{ ppm (m); 3}$$

$$\delta_b = -126.31 \text{ ppm (m); 2}$$

$$\delta_c = -118.66 \text{ ppm (m); 2}$$

TABLE B-3

CHARACTERIZATION OF F-PENTANOYL FLUORIDEInfrared (cm^{-1}):

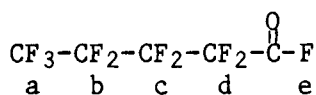
1880(s), 1350(w), 1275(m), 1265(s), 1240(vs), 1215(s), 1140(s),
1110(s), 1020(s), 945(m), 930(m), 905(m), 875(m), 840(w), 825(w),
815(m), 740(m), 710(m).

Mass Spectra [$m/e(\text{int.})$ formula]:CI(CH_4):

418(11) $\text{C}_{10}\text{F}_{14}\text{O}_2$; 281(11) $\text{C}_5\text{F}_9\text{O}_3\text{H}_2$; 266(1) $\text{C}_5\text{F}_{10}\text{O}$, M; 247(7) $\text{C}_5\text{F}_9\text{O}$,
M-F; 220(4) $^{13}\text{CC}_3\text{F}_9$; 219(100) C_4F_9 ; 197(7) $\text{C}_4\text{F}_7\text{O}$; 169(1) C_3F_7 ;
131(13) C_3F_5 ; 119(1) C_2F_5 ; 103(6)???: 101(9) $\text{C}_2\text{F}_4\text{H}$; 100(4) C_2F_4 ;
69(3) CF_3 .

EI(70 eV):

219(4) C_4F_9 ; 169(19) C_3F_7 ; 131(17) C_3F_5 ; 119(22) C_2F_5 ; 100(10) C_2F_4 ;
97(3) $\text{C}_2\text{F}_3\text{O}$; 93(2) C_3F_3 ; 85(4) CF_3O ; 81(1) C_2F_3 ; 78(6) $\text{C}_2\text{F}_2\text{O}$;
70(1) $^{13}\text{CF}_3$; 69(100) CF_3 ; 50(2) CF_2 ; 47(7) CFO ; 31(4) CF .

 ^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.})$; integral]:

$$\phi_a = -81.59 \text{ ppm (t}\cdot\text{t)}; 3$$

$$\phi_b = -126.47 \text{ ppm (m)}; 2$$

$$\phi_c = -123.98 \text{ ppm (m)}; 2$$

$$\phi_d = -118.33 \text{ ppm (q}\cdot\text{q)}; 2$$

$$\phi_e = +24.85 \text{ ppm (p)}; 1$$

$$J_{ac} = 9.76 \text{ Hz}$$

$$J_{ab} = 2.14 \text{ Hz}$$

$$J_{bc} = 3.05 \text{ Hz}$$

$$J_{bd} = 9.76 \text{ Hz}$$

$$J_{ad} = 1.83 \text{ Hz}$$

$$J_{ce} = J_{de} = 7.33 \text{ Hz}$$

TABLE B-4
CHARACTERIZATION OF F-3-HEPTANONE

Infrared (cm^{-1}):

1780(m), 1350(m), 1330(m), 1295(m), 1245(s), 1190(m), 1165(m),
1140(m), 1110(w), 1050(w), 1020(w), 900(w), 840(w), 805(w),
745(w), 720(w), 705(w).

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

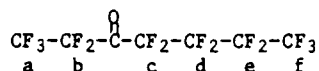
CI(CH_4):

414(25) $\text{C}_{11}\text{F}_{14}\text{O}$; 383(12) $\text{C}_8\text{F}_{14}\text{OH}_5$; 368(7) $^{13}\text{CC}_6\text{F}_{14}\text{OH}$, $\text{C}_7\text{F}_{14}\text{OH}_2$;
367(86) $\text{C}_7\text{F}_{14}\text{OH}$, M^+H ; 348(7) $^{13}\text{CC}_6\text{F}_{13}\text{O}$, $\text{C}_7\text{F}_{13}\text{OH}$; 347(97) $\text{C}_7\text{F}_{13}\text{O}$, M^+F ;
247(18) $\text{C}_5\text{F}_9\text{O}$; 219(65) C_4F_9 ; 197(8) $\text{C}_4\text{F}_7\text{O}$; 169(8) C_3F_7 ; 151(7) $\text{C}_3\text{F}_6\text{H}$;
147(28) $\text{C}_3\text{F}_5\text{O}$; 131(28) C_3F_5 ; 119(62) C_2F_5 ; 117(10) C_5F_3 ; 109(7) $\text{C}_3\text{F}_3\text{O}$;
101(11) $\text{C}_2\text{F}_4\text{H}$; 100(36) C_2F_4 ; 97(12) $\text{C}_2\text{F}_3\text{O}$; 95(7) C_5FO ; 93(7) C_3F_3 ;
77(34)???, 73(10)??? 70(1) $^{13}\text{CF}_3$; 69(100) CF_3 .

EI(70 eV):

220(3) $^{13}\text{CC}_3\text{F}_9$; 219(58) C_4F_9 ; 169(3) C_3F_7 ; 147(26) $\text{C}_3\text{F}_5\text{O}$; 131(28) C_3F_5 ;
120(2) $^{13}\text{CCF}_5$; 119(100) C_2F_5 ; 100(18) C_2F_4 ; 70(1) $^{13}\text{CF}_3$; 69(72) CF_3 ;
31(2) CF .

^{19}F NMR [$\delta_{\text{CFCF}_3} = 0.0$ ppm; $\delta(\text{mult.})$; integral]:



$\delta_a = -81.99$ ppm ; 3

$\delta_b = -121.67$ ppm (m); 2 Couplings are small and
multiplets are complex.

$\delta_c = -118.01$ ppm (m); 2

$\delta_d = -124.79$ ppm (m); 2

$\delta_e = -126.32$ ppm (m); 2

$\delta_f = -79.82$ ppm (m); 3

TABLE B-5
CHARACTERIZATION OF F-2-HEPTANONE

Infrared (cm^{-1}):

1790(m), 1360(m), 1300(m), 1245(vs), 1215(s), 1185(s), 1145(s),
1020(m), 975(w), 830(w), 805(m), 740(w), 720(m), 645(m).

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

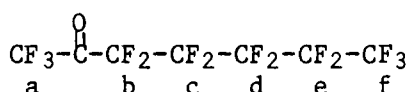
CI(CH_4):

366(35) $\text{C}_7\text{F}_{14}\text{O}$, M; 230(4) $\text{C}_5\text{F}_8\text{OH}_2$; 180(2) $\text{C}_4\text{F}_6\text{OH}_2$; 168(2) $\text{C}_3\text{F}_6\text{OH}_2$;
131(7) C_3F_5 ; 118(6) $\text{C}_2\text{F}_4\text{OH}_2$; 109(1) $\text{C}_3\text{F}_3\text{O}$; 100(6) C_2F_4 ; 98(2) C_5F_5 ,
 $^{13}\text{CCF}_3\text{O}$; 97(74) $\text{C}_2\text{F}_3\text{O}$; 93(2) C_3F_3 ; 87(6) C_3FO_2 ; 78(1) $\text{C}_2\text{F}_2\text{O}$;
70(1) $^{13}\text{CF}_3$; 69(100) CF_3 .

EI(70 eV):

269(4) C_5F_{11} ; 231(1) C_5F_9 ; 181(5) C_4F_7 ; 169(4) C_3F_7 ; 147(2) $\text{C}_3\text{F}_5\text{O}$;
131(17) C_3F_5 ; 119(19) C_2F_5 ; 109(2) $\text{C}_3\text{F}_3\text{O}$; 100(8) C_2F_4 ; 97(48) $\text{C}_2\text{F}_3\text{O}$;
93(2) C_3F_3 ; 78(2) $\text{C}_2\text{F}_2\text{O}$; 70(1) $^{13}\text{CF}_3$; 69(100) CF_3 .

^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; δ (mult.);integral]:



$\delta_a = -75.17$ ppm (m); 3

$\delta_b = -118.63$ ppm (m); 2

$\delta_{c,d} = -122.67$ ppm (m); 4 Multiplets are complex.

$\delta_e = -126.67$ ppm (m); 2

$\delta_f = -81.30$ ppm (m); 3

TABLE B-6
CHARACTERIZATION OF F-2-BUTANONE

Infrared (cm^{-1}):

1790(m), 1330(w), 1305(m), 1240(vs), 1200(s), 1070(w), 1025(m),
900(m), 875(m), 710(m).

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

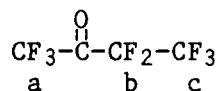
CI(CH_4):

217(66) $\text{C}_4\text{F}_8\text{OH}$, M+H; 197(46) $\text{C}_4\text{F}_7\text{O}$, M-F; 147(14) $\text{C}_3\text{F}_5\text{O}$; 119(14) C_2F_5 ;
97(81) $\text{C}_2\text{F}_3\text{O}$; 87(21) $\text{C}_4\text{F}_2\text{H}$; 85(21) CF_3O ; 83(5) C_4FO ; 71(6)??;
69(100) CF_3 .

EI(70 eV):

147(6) $\text{C}_3\text{F}_5\text{O}$; 119(29) C_2F_5 ; 100(7) C_2F_4 ; 97(50) $\text{C}_2\text{F}_3\text{O}$; 78(3) $\text{C}_2\text{F}_2\text{O}$;
70(1) $^{13}\text{CF}_3$; 69(100) CF_3 ; 50(4) CF_2 ; 32(65) CFH , O_2 (?).

^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.})$; integral]:



$\phi_a = -75.30$ ppm (t); 3

$\phi_b = -122.11$ ppm (q); 2

$\phi_c = -82.28$ ppm (s); 3

$J_{ab} = 8.79$ Hz

$J_{ac}, J_{bc} < 1$ Hz

TABLE B-7

CHARACTERIZATION OF F-METHOXYCYCLOPENTANEInfrared (cm^{-1}):

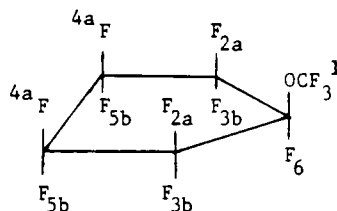
1320(s), 1280(vs), 1235(vs), 1220(s), 1190(s), 1150(s), 1040(w),
995(s), 985(s), 890(w), 850(w), 730(w), 660(w).

Mass Spectra [$m/e(\text{int.})$ formula]:CI(CH_4):

317(2) $\text{C}_6\text{F}_{12}\text{OH}$, M^+H ; 282(3) $\text{C}_6\text{F}_{11}\text{H}$; 232(4) $\text{C}_5\text{F}_9\text{H}$; 183(35) $\text{C}_4\text{F}_7\text{H}_2$;
175(33) $\text{C}_5\text{F}_6\text{H}$; 173(24) $\text{C}_8\text{F}_4\text{H}$; 171(23) $\text{C}_5\text{F}_5\text{O}$; 155(6) C_5F_5 ; 153(31) C_8F_3 ;
132(100) $\text{C}_3\text{F}_5\text{H}$; 116(9) $\text{C}_2\text{F}_4\text{O}$; 101(28) $\text{C}_2\text{F}_4\text{H}$; 100(16) C_2F_4 ;
96(21) C_5FOH ; 94(8) $\text{C}_3\text{F}_3\text{H}$; 74(10) C_3F_2 ; 69(9) CF_3 .

EI(70 eV):

297(1) $\text{C}_6\text{F}_{11}\text{O}$, $M-F$; 231(8) C_5F_9 ; 181(13) C_4F_7 ; 131(51) C_3F_5 ;
100(16) C_2F_4 ; 93(4) C_3F_3 ; 81(3) C_2F_3 ; 69(100) CF_3 .

 ^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm]

Chemical shift, $\phi(\text{ppm})$	Int.	Coupling constants, Hz	Assignment
-55.42	3	$J_{16} = 10.0$ $J_{12} = 6.0$ $J_{13} = 3.9$	1
-124.68	4	$J_{2a,3b} = 259.4$	2a
-135.68			3b
-129.34	4	$J_{4a,5b} = 254.8$	4a
-132.86			5b
-137.96	1	Complex multiplet	6

TABLE B-8
CHARACTERIZATION OF F-CYCLOPENTANONE

Infrared (cm^{-1})

1810(m), 1345(m), 1300(m), 1230(m), 1200(vs), 1145(m), 1115(m),
1010(s), 965(s), 725(m).

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

CI(CH_4):

209(1) $\text{C}_5\text{F}_7\text{O}$, M-F; 182(32) $\text{C}_4\text{F}_7\text{H}$; 132(100) $\text{C}_3\text{F}_5\text{H}$; 101(70) $\text{C}_2\text{F}_4\text{H}$.

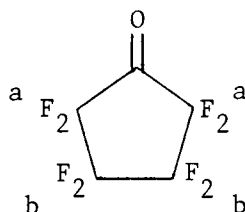
EI(70 eV):

228(1) $\text{C}_5\text{F}_8\text{O}$, M; 209(1) $\text{C}_5\text{F}_7\text{O}$, M-F; 200(2) C_4F_8 ; 181(2) C_4F_7 ;

132(2) $^{13}\text{CC}_2\text{F}_5$; 131(78) C_3F_5 ; 109(9) $\text{C}_3\text{F}_3\text{O}$; 101(2) $^{13}\text{CCF}_4$;

100(100) C_2F_4 ; 93(8) C_3F_3 ; 81(5) C_2F_3 ; 69(11) CF_3 ; 50(4) CF_2 ; 31(6) CF .

^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.})$; integral]:



$\phi_a = -126.52$ ppm (m); 1

$\phi_b = -136.76$ ppm (m); 1

TABLE B-9
CHARACTERIZATION OF F-METHOXYCYCLOHEXANE

Infrared (cm^{-1}):

1300(s), 1270(vs), 1255(vs), 1230(s), 1195(vs), 1150(s), 1055(w),
995(s), 980(vs), 880(w), 850(w), 730(w), 680(w), 660(w), 630(m),
610(m).

Mass Spectra [$m/e(\text{int.})$ formula]:

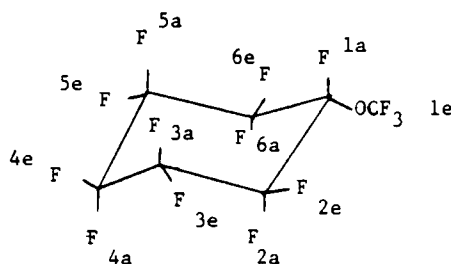
CI(CH_4):

161(23) $\text{C}_4\text{F}_5\text{OH}_2$; 131(100) C_3F_5 ; 119(7) C_2F_5 ; 113(9) $\text{C}_3\text{F}_4\text{H}$;
100(17) C_2F_4 ; 93(8) C_3F_3 ; 69(65) CF_3 .

EI(70 eV):

281(4) C_6F_{11} ; 259(1) $\text{C}_6\text{F}_9\text{O}$; 231(7) C_5F_9 ; 181(7) C_4F_7 ; 131(52) C_3F_5 ;
100(6) C_2F_4 ; 69(100) CF_3 .

^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm]



Chemical shift, δ (ppm)	Int.	Coupling constants, Hz	Assignment
-53.83	3		1e
-142.77	1		1a
-119.98	4	$J_{2a,2e} = J_{6a,6e} = 282$	2a,6a
-131.22			2e,6e
-122.30	4	$J_{3a,3e} = J_{5a,5e} = 299$	3a,5a
-133.54			3e,5e
-123.81	2	$J_{4a,4e} = 271$	4a
-134.63			4e

TABLE B-10
CHARACTERIZATION OF F-CYCLOHEXANONE

Infrared (cm^{-1}):

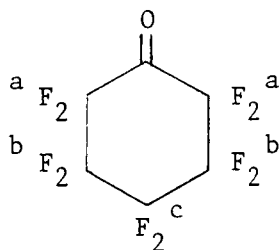
1795(m), 1300(s), 1255(s), 1220(w), 1185(vs), 1080(m), 990(s),
960(vs), 805(w), 615(w).

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

EI(70 eV):

278(2) $\text{C}_6\text{F}_{10}\text{O}$, M; 231(1) C_5F_9 ; 181(12) C_4F_7 ; 132(3) $^{13}\text{CC}_2\text{F}_5$;
131(100) C_3F_5 ; 112(2) C_3F_4 ; 109(3) $\text{C}_3\text{F}_3\text{O}$; 100(23) C_2F_4 ; 93(5) C_3F_3 ;
81(3) C_2F_3 ; 69(10) CF_3 ; 31(1) CF .

^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; δ (mult.);integral]:



$\delta_a = -125.15$ ppm (s) ; 4

$\delta_{b,c} = -133.23$ ppm (broad); 6

TABLE B-11

CHARACTERIZATION OF F-1,4-DIOXASPIRO[4.4]NONANE

Infrared (cm^{-1}):

1405(w), 1310(vs), 1270(s), 1245(vs), 1210(vs), 1160(vs), 975(vs),
810(m), 725(w), 655(w), 595(w), 520(m).

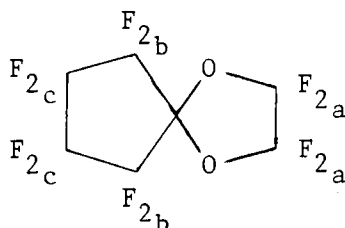
Mass Spectra [m/e(int.)formula]:

CI(CH_4):

326(8) $^{13}\text{CC}_6\text{F}_{11}\text{O}_2$; 325(100) $\text{C}_7\text{F}_{11}\text{O}_2$, M-F; 313(3) $\text{C}_6\text{F}_{11}\text{O}_2$; 131(6) C_3F_5 ;
117(98) C_5F_3 ; 97(19) $\text{C}_2\text{F}_3\text{O}$.

EI(70 eV):

325(4) $\text{C}_7\text{F}_{11}\text{O}_2$, M-F; 225(5) $\text{C}_5\text{F}_7\text{O}_2$; 194(48) $\text{C}_4\text{F}_6\text{O}_2$; 181(5) C_4F_7 ;
163(8) $\text{C}_3\text{F}_5\text{O}_2$; 162(6) C_4F_6 ; 132(3) $^{13}\text{CC}_2\text{F}_5$; 131(100) C_3F_5 ;
119(10) C_2F_5 ; 109(7) $\text{C}_3\text{F}_3\text{O}$; 100(60) C_2F_4 ; 97(16) $\text{C}_2\text{F}_3\text{O}$; 93(7) C_3F_3 ;
69(19) CF_3 .

 ^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.})$; integral]: $\phi_a = -85.32$ ppm (s); 4 $\phi_b = -130.36$ ppm (s); 4 $\phi_c = -131.69$ ppm (s); 4

Elemental Analysis:
Calc. For $\text{C}_7\text{F}_{12}\text{O}_2$: %C = 24.44; %F = 66.26; %H = 0.00Found: %C = 24.22; %F = 66.25; %H = 0.00

TABLE B-12

CHARACTERIZATION OF F-1,4-DIOXASPIRO[4.5]DECANEInfrared (cm^{-1}):

1400(w), 1310(m), 1280(s), 1250(vs), 1220(s), 1190(vs), 1165(vs),
1050(w), 980(vs), 970(vs), 820(m), 730(m), 625(w), 595(w).

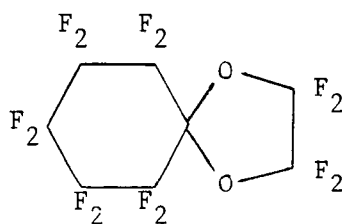
Mass Spectra [m/e(int.)formula]:

CI(CH_4):

414(11) $\text{C}_8\text{F}_{15}\text{O}_2\text{H}$; 348(4) $\text{C}_7\text{F}_{13}\text{OH}$; 182(12) $\text{C}_3\text{F}_6\text{O}_2$; 172(24) C_8F_4 ;
151(18) $\text{C}_3\text{F}_6\text{H}$; 143(13) C_4F_5 ; 131(100) C_3F_5 ; 117(66) C_5F_3 ;
113(8) $\text{C}_2\text{F}_3\text{O}_2$; 100(19) C_2F_4 ; 99(8) C_4FO_2 ; 97(71) $\text{C}_2\text{F}_3\text{O}$; 95(42) $\text{C}_3\text{F}_3\text{H}_2$,
 C_5FO ; 93(7) C_3F_3 ; 75(5) C_2FO_2 ; 69(6) CF_3 .

EI(70 eV):

375(1) $\text{C}_8\text{F}_{13}\text{O}_2$, M-F; 259(3) $\text{C}_6\text{F}_9\text{O}$; 244(4) $\text{C}_5\text{F}_8\text{O}_2$; 231(2) C_5F_9 ;
194(5) $\text{C}_4\text{F}_6\text{O}_2$; 181(8) C_4F_7 ; 163(4) $\text{C}_3\text{F}_5\text{O}_2$; 143(2) C_4F_5 ; 132(3) $^{13}\text{CC}_2\text{F}_5$;
131(100) C_3F_5 ; 109(5) $\text{C}_3\text{F}_3\text{O}$; 100(20) C_2F_4 ; 97(13) $\text{C}_2\text{F}_3\text{O}$; 69(31) CF_3 .

 ^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; $\delta(\text{mult.})$; integral]:

$\delta = -83.22$ ppm (s) ; 4

$\delta = -132.02$ ppm (s, broad); 10

Elemental Analysis:

Calc. For $\text{C}_8\text{F}_{14}\text{O}_2$: %C = 24.38; %F = 67.49; %H = 0.00

Found: %C = 23.85; %F = 66.78; %H = 0.00

TABLE B-13

CHARACTERIZATION OF F-3,3-DIMETHYL-2-BUTANONE

Infrared (cm^{-1}):

1770(m), 1275(vs), 1230(s), 1200(s), 1055(w), 985(m), 870(m),
730(m), 720(m), 690(w).

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

CI(CH_4):

317(59) $\text{C}_6\text{F}_{12}\text{OH}$, M+H; 297(84) $\text{C}_6\text{F}_{11}\text{O}$, M-F; 129(16) $\text{C}_3\text{F}_4\text{OH}$;
113(11) $\text{C}_3\text{F}_4\text{H}$; 98(2) $^{13}\text{CCF}_3\text{O}$; 97(100) $\text{C}_2\text{F}_3\text{O}$; 69(58) CF_3 .

EI(70 eV):

247(6) $\text{C}_5\text{F}_9\text{O}$, M- CF_3 ; 181(16) C_4F_7 ; 159(8) $\text{C}_4\text{F}_5\text{O}$; 131(5) C_3F_5 ;
97(21) $\text{C}_2\text{F}_3\text{O}$; 93(5) C_3F_3 ; 70(1) $^{13}\text{CF}_3$; 69(100) CF_3 .

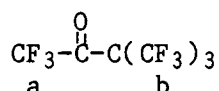
 ^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.})$; integral]: $\phi_a = -73.88$ ppm (d); 3 $\phi_b = -62.12$ ppm (q); 9 $J_{ab} = 6.1$ Hz

TABLE B-14

CHARACTERIZATION OF 3-DIFLUOROMETHYL-F-3-METHYL-2-BUTANONE

Infrared (cm^{-1}):

3015(w), 1760(m), 1390(m), 1370(m), 1275(vs), 1235(vs), 1190(s),
1135(m), 1120(m), 1065(m), 1020(w), 980(s), 910(w), 870(s),
765(m), 750(m), 730(s), 705(m), 655(m).

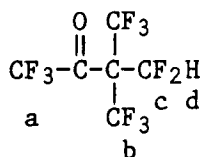
Mass Spectra [m/e(int.)formula]:

$$\text{Cl}(\text{CH}_4):$$

300(8)C₆F₁₁OH₃, M+2H; 230(16)C₅F₈OH₂; 164(100)C₄F₆H₂;
160(6)C₄F₅OH; 97(15)C₂F₃O; 69(5)CF₃.

EI(70 eV):

231(28)C₅F₉; 164(33)C₄F₆H₂; 160(61)C₄F₅OH; 97(50)C₂F₃O;
69(100)CF₃; 51(38)CF₂H.

¹⁹F NMR [δ_{CFC1_3} = 0.0 ppm; δ (mult.);integral]:
$$\phi_a = -73.85 \text{ ppm (m)}; 3$$

$\delta_{\text{H}} = -62.05$ ppm (m); 6 Complex multiplets.

$$\delta_c = -126.69 \text{ ppm (m)}; 2$$
 ^1H NMR [$\delta_{\text{TMS}} = 0.0$ ppm; δ (mult.)]:
$$\delta = +6.63 \text{ ppm (t)} \quad J_{\text{CF}_2\text{-H}} = 51.5 \text{ Hz}$$

TABLE B-15

CHARACTERIZATION OF 3,3-BIS(DIFLUOROMETHYL)-F-2-BUTANONEInfrared (cm^{-1}):

3010(w), 1755(m), 1365(w), 1275(m), 1250(vs), 1225(vs), 1190(s),
1160(m), 1130(m), 1060(m), 1020(m), 900(w), 870(w), 730(s).

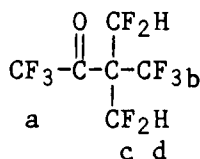
Mass Spectra [$m/e(\text{int.})$ formula]:

CI(CH_4):

282(100) $\text{C}_6\text{F}_{10}\text{OH}_4$, $M+2\text{H}$; 212(36) $\text{C}_5\text{F}_7\text{OH}_3$; 164(11) $\text{C}_4\text{F}_6\text{H}_2$;
142(16) $\text{C}_4\text{F}_4\text{OH}_2$; 97(65) $\text{C}_2\text{F}_3\text{O}$; 69(43) CF_3 .

EI(70 eV):

212(64) $\text{C}_5\text{F}_7\text{OH}_3$; 164(9) $\text{C}_4\text{F}_6\text{H}_2$; 146(41) $\text{C}_6\text{F}_3\text{OH}$; 142(100) $\text{C}_4\text{F}_4\text{OH}_2$;
97(35) $\text{C}_2\text{F}_3\text{O}$; 91(15) $\text{C}_3\text{F}_2\text{OH}$; 69(85) CF_3 ; 51(43) CF_2H .

 ^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.})$; integral]:

$\phi_a = -74.61$ ppm (m); 3

$\phi_b = -62.99$ ppm (m); 3 Complex multiplets.

$\phi_c = -125.18$ ppm (m); 4

 ^1H NMR [$\delta_{\text{TMS}} = 0.0$ ppm; δ (mult.)]:

$\delta = +6.59$ ppm (t) $J_{\text{CF}_2-\text{H}} = 52.7$ Hz

TABLE B-16

CHARACTERIZATION OF F-2,2,5-TRIMETHYL-3-HEXANONEInfrared (cm^{-1}):

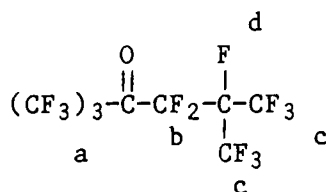
1770(m), 1270(vs), 1205(m), 1150(m), 1140(m), 1045(m), 980(s),
730(s), 710(m), 680(m).

Mass Spectra [$m/e(\text{int.})$ formula]:CI(CH_4):

483(2) $\text{C}_{10}\text{F}_{18}\text{OH}_5$, M+ CH_5 ; 467(12) $\text{C}_9\text{F}_{18}\text{OH}$, M+H; 447(54) $\text{C}_9\text{F}_{17}\text{O}$, M-F;
247(55) $\text{C}_5\text{F}_9\text{O}$; 220(4) $^{13}\text{CC}_3\text{F}_9$; 219(100) C_4F_9 ; 201(84) C_4F_8 ;
181(98) C_4F_7 ; 119(31) C_2F_5 ; 117(34) $\text{C}_2\text{F}_4\text{O}$; 69(75) CF_3 .

EI(70 eV):

447(1) $\text{C}_9\text{F}_{17}\text{O}$, M-F; 247(37) $\text{C}_5\text{F}_9\text{O}$; 219(43) C_4F_9 ; 200(10) C_4F_8 ;
181(20) C_4F_7 ; 159(24) $\text{C}_4\text{F}_5\text{O}$; 131(22) C_3F_5 ; 100(9) C_2F_4 ; 69(100) CF_3 .

 ^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; $\delta(\text{mult.})$; integral]:

$$\delta_a = -61.61 \text{ ppm (t}\cdot\text{m)}; 9$$

$$\delta_b = -109.32 \text{ ppm (m}\cdot\text{d)}; 2$$

$$\delta_c = -71.82 \text{ ppm (t}\cdot\text{d)}; 6$$

$$\delta_d = -184.26 \text{ ppm (m)}; 1$$

$$J_{ab} = J_{bc} = 10.26 \text{ Hz}$$

$$J_{ac} = 0.88 \text{ Hz}$$

$$J_{ad} = 0 \text{ Hz}$$

$$J_{bd} = 4.40 \text{ Hz}$$

$$J_{cd} = 6.10 \text{ Hz}$$

TABLE B-17
CHARACTERIZATION OF F-ADAMANTANE

Infrared (cm^{-1}):			
1295(s), 1280(vs), 960(s), 645(w), 595(w).			
Mass Spectra [m/e(int.)formula]:			
EI(70 eV):			
424(1) $\text{C}_{10}\text{F}_{16}$, M; 406(2) $^{13}\text{CC}_9\text{F}_{15}$; 405(15) $\text{C}_{10}\text{F}_{15}$, M-F; 255(7) C_7F_9 ; 206(7) $^{13}\text{CC}_5\text{F}_7$; <u>205(100)C_6F_7</u> ; 155(9) C_5F_5 ; 131(42) C_3F_5 ; 93(7) C_3F_3 ; 69(24) CF_3 .			
^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.}); \text{integral}$]:			
$\phi_{\text{CF}_2} = -121.20$ ppm (p); 12		$J_{\text{CF}_2-\text{CF}} \approx 6$ Hz	
$\phi_{\text{CF}} = -223.53$ ppm (m); 4			
Elemental Analysis:	%C	%F	%H
Calc. for $\text{C}_{10}\text{F}_{16}$	28.32	71.68	0.00
Found	28.60	71.88	0.00

TABLE B-18

CHARACTERIZATION OF F-TRIMETHYL ORTHOFORMATE

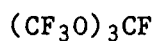
Infrared (cm^{-1}):

1320(s), 1300(vs), 1230(vs), 1175(m), 1120(vs), 1105(vs), 910(m),
730(m).

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

EI(70 eV):

204(21) $\text{C}_3\text{F}_8\text{O}$; 69(100) CF_3 ; 47(2) CFO .

 ^{19}F NMR [$\phi_{\text{CFCl}_3} = 0.0$ ppm; $\phi(\text{mult.})$; integral]:
 $\phi_{\text{CF}_2} = -57.14$ ppm (d) ; 9

 $\phi_{\text{CF}} = -58.85$ ppm (dec); 1

 $J_{\text{CF}_3-\text{CF}} = 9.76$ Hz

TABLE B-19

CHARACTERIZATION OF F-TETRAMETHYL ORTHOCARBONATE

Infrared (cm^{-1}):

1320(vs), 1260(vs), 1225(s), 1215(vs), 1100(vs), 920(m), 885(w),
730(m).

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

EI(70 eV):

267(40) $\text{C}_4\text{F}_9\text{O}_3$; 113(11) $\text{C}_2\text{F}_3\text{O}_2$; 69(100) CF_3 .

^{19}F NMR [$\delta_{\text{CFCl}_3} = 0.0$ ppm; δ (mult.);integral]:

$(\text{CF}_3\text{O})_4\text{C}$

$\delta = -56.67$ ppm (s)

VITA

Mark Lester Robin was born in Detroit, Michigan on December 21, 1954. After graduating from Edwin Denby High School in Detroit, Michigan, he attended Wayne State University in Detroit, Michigan, where he received his Bachelor of Science degree in chemistry in 1978. He entered the Graduate School of The University of Tennessee at Knoxville in September of 1978. In August of 1977 he married Debra Katherine Orlowski of Detroit.