To the Graduate Council

I am submitting herewith a dissertation written by William Douglas Evans entitled "The Utility of Aerosol Direct Fluorination for the Prepraration of Functional Fluorocarbons." 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:

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Accepted for the council:

The Graduate School

THE UTILITY OF AEROSOL DIRECT FLUORINATION FOR THE PREPARATION OF FUNCTIONAL FLUOROCARBONS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

William Douglas Evans

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DEDICATION

To Ann, who waited impatiently for several years.

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I am deeply indebted to my research director, Dr. James L. Adcock, without whose guidance, patience and encouragement this dissertation would not have been possible. I also wish to thank Lily H. Grossman and Mark L. Robin for their assistance on the Aerosol Direct Fluorination system.

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ABSTRACT

The fluorination of compounds with survivable functionality permits the preparation of fluorinated compounds with preselected sites for further reactions. Perfluoroacyl fluorides and perfluoroalkyl chlorides have been successfully synthesized by the aerosol direct fluorination method in good yields and high purity.

Aerosol direct fluorination of the acid chloride analogs produced F-pivaloyl fluoride, F-butyryl fluoride, F-isobutyryl fluoride and chloro-F-acetyl fluoride. Aerosol fluorination of cyclopropyl carbonyl chloride gave F-isobutyryl fluoride and F-butyryl fluoride.

Aerosol fluorination of the primary alkyl chloride analogs produced F-neopentyl chloride, F-propyl chloride, F-butyl chloride, F-isobutyl chloride, F-isoamyl chloride, and 1-chloro-F-2-methylbutane. The aerosol fluorination of tert-butyl chloride gave complete 1,2-chloride rearrangement to produce F-isobutyl chloride. A similar chloride shift was observed upon fluorination of 1,2-dichloro-2-methylpropane to give 1,3-dichloro-F-2-methylpropane. These 1,2-chloride shifts occurred by rearrangement of primary radicals formed upon initial fluorination giving more stable tertiary radicals. In the aerosol fluorination of the secondary chlorides, isopropyl chloride, 2-chlorobutane, and 3-chloropentane, the production of analogous isomeric mixtures of primary and secondary F-alkyl chlorides gave evidence of a partial 1,2-chloride shift. This partial chloride rearrangement for secondary chlorides is similar to the

tertiary chlorides but does not occur completely due to the smaller difference in stabilities of primary and secondary radicals.

In the aerosol fluorination of secondary gem dichlorides, the observed 1,2-chloride shift results in the formation of chlorine-stabilized, tertiary-like radicals. 2,2-Dichloropropane gave 1,2-dichloro-F-propane and 1,3-dichloro-F-propane. 1,1-Dichlorocyclopentane gave a mixture of cis/trans-1,2-dichloro-F-cyclopentane and cis/trans-1,3-dichloro-F-cyclopentane. The primary gem dichloride, 1,1-dichloropropane, upon fluorination gave 1,1-dichloro-F-propane and 1,2-dichloro-F-propane. This partial 1,2-chloride shift would form a chlorine-stabilized, secondary-like radical. In the aerosol fluorination of 1,1-dichloroneopentane, a 1,2-chloride shift is blocked and only 1,1-dichloro-F-neopentane is produced. 1,1,1-Trichloroethane gave 1,1,2-trichloro-F-ethane via a 1,2-chloride shift.

Aerosol fluorination of neopentyl bromide produced F-isopentane and bromine. Data are presented which support carbocation rearrangements. The carbocations are presumed to arise from disproportionation of neopentyl bromine fluorides, $(CH_3)_3-C-CH_2BrF_x$.

The gas phase photolysis of mixtures of mono hydryl perfluorinated compounds, obtained from the fluorination of the analogous hydrocarbons, and one of the interhalogen compounds, BrCl or BrF, provided a simple route to F-alkyl bromides in good yields.

F-Neopentyl lithium was produced by reaction of F-neopentyl chloride with alkyl lithium. F-Neopentyl lithium reacted with

cyclohexene to give 7-fluoro-7-(nonafluoro-tert-butyl)-norcarane, with iodine to give F-neopentyl iodide, and with excess n-butyl lithium to give cis/trans-1,1,1-trifluoro-2,2-bis-(trifluoromethyl)-3-heptene.

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CHAPTER I

INTRODUCTION

A. BACKGROUND AND EARLY DIRECT FLUORINATIONS

The direct interaction of elementary fluorine with organic compounds has been studied since the isolation of the gas by Moissan in 1886. Progress was initially slow due to the difficulties encountered in the preparation of fluorine and to extreme reactivity of fluorine with organic compounds. Moissan and his students made numerous incompletely successful fluorination attempts from 1890 onwards. A notable failure by Moissan and Chavanne[1] in 1905 resulted in a disastrous explosion when they tried to react solid methane and liquid fluorine at -187°C.

The high reactivity of fluorine can be better understood by comparing the reaction mechanisms of chlorination and fluorination of an alkane. A radical chain mechanism is generally accepted for chlorination of an alkane.

(1-1) Initiation	$Cl_2 \xrightarrow[\text{heat } 300°C]{h\nu \text{ or}} 2\ Cl\cdot$	ΔH = + 58 Kcal/mol
(1-2) Propagation	$RH + Cl\cdot \longrightarrow R\cdot + HCl$	- 3
(1-3)	$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$	-23
(1-4) Termination	$R\cdot + Cl\cdot \longrightarrow RCl$	-80
(1-5)	$Cl\cdot + Cl\cdot \longrightarrow Cl\cdot$	-58
(1-6)	$R\cdot + R\cdot \longrightarrow R\text{-}R$	-83

The relatively modest energies for chain propagation steps are not sufficient to cause dissociation of molecular chlorine.

The proposed mechanism of flourination is somewhat similar.

(1-7)	Initiation	$F_2 \longrightarrow 2F\cdot$	ΔH = + 37 Kcal/mol
(1-8)		$F_2 + RH \longrightarrow R\cdot + HF + F\cdot$	+ 4
(1-9)	Propagation	$RH + F\cdot \longrightarrow R\cdot + HF$	- 34
(1-10)		$R\cdot + F_2 \longrightarrow RF + F.$	- 68
(1-11)	Termination	$R\cdot + F\cdot \longrightarrow RF$	-110
(1-12)		$F\cdot + F\cdot \longrightarrow F^2$	- 37
(1-13)		$R\cdot + R\cdot \longrightarrow RR$	- 83
(1-14)		$R\cdot \longrightarrow$ fragmentation	~ 80

An important difference is the alternate pathway (1-8) proposed by Miller for initiation.[2] This explains why little or no activation energy is needed for fluorination, especially at low temperatures. A similar step for chlorination initiation requires 54 Kcal/mol and therefore does not occur as readily.

Fluorination by molecular fluorine involves chain propagation steps which evolve the same or greater energy than the initiation steps. As a result, fluorination is a highly exothermic process which is not easily controlled.

An equally serious difficulty in the use of molecular fluorine is the high energy, 107 to 121 Kcal/mol, liberated on formation of the C-F bond. This energy exceeds the energy of the C-C bond and leads to fragmentation of the carbon skeleton.

Progress in direct fluorination occurred once the process was tamed by efficiently dissipating the heat evolved by diluting the fluorine with an inert gas or liquid. The first successful direct fluorination of an organic halogen compound was carried out by Ruff and Keim in 1931.[3] They passed a stream of CCl_4 vapor diluted with nitrogen and mixed with fluorine over a heated bed of cobaltic fluoride. The expected products $CFCl_3$, CF_2Cl_2, CF_3Cl, and CF_4 were obtained. In 1933, Bockemuller carried out direct fluorinations by passing fluorine diluted with nitrogen into dilute organic solutions of CF_2Cl_2.[4] In this manner he produced $C_6H_{11}F$ from cyclohexane, and $CFCl_2CFCl_2$, CCl_3CFCl_2, and $C_4F_2Cl_8$ from tetrachloroethylene. He also produced a mixture of 3- and 4- fluorobutanoic acids from either butanoic acid, butanoyl chloride, or butyric acetic anhydride. Isobutyric acid gave the β-fluoro acid, unlike the α-bromo isobutyric acid obtained by bromination.

In 1937, Miller, Calfee, and Bigelow sublimed C_2Cl_6 through copper gauze rolls into a current of fluorine diluted with nitrogen and made $CFCl_2CFCl_2$ in 20% yield.[5] In a similar manner, Calfee, Fukuhara, Young, and Bigelow working independently reported the fluorination of ethane.[6] They also fluorinated ethyl chloride and obtained the complex mixture of CF_4, CF_3Cl, CF_3CF_2Cl, CHF_2CH_2Cl, CH_3CHCl_2, and CHF_2CHCl_2.[7] The presence of the last two compounds indicated that substitution by both atomic chlorine and fluorine occurred as well as fragmentation. Hadley and Bigelow studied the

fluorination of methane under the same conditions and noted the free radical process in the formation of CF_4, CHF_3, C_2F_6, and C_3F_8.[8]

In 1940, Miller minimized excess heat accumulation by employing a fluorine flow countercurrent to liquid organic chloride compounds of more than one carbon atom.[9] In most cases, partial fluorination occurred smoothly. Complex mixtures resulted from the atomic substitution by both chlorine and fluorine. Fragmentation was not observed although dimerization was.

Other methods of lessening the severity of fluorination reactions involved the use of milder fluorinating agents, such as SbF_3 or CoF_3. These and other indirect methods of fluorination were developed during the war effort of the 1940's because they were easier to control and gave less fragmentation.

B. METHODS OF FLUORINATION

Swarts Reaction

Swarts began his studies on the preparation of fluorocarbon compounds by exchange reactions about 1890.[10] He was virtually the only researcher in the field until 1930 when Midgley and Henne used his methods for the application of fluoromethanes and ethanes as refrigerants.[11]

The Swarts reaction is essentially a nucleophilic displacement of halogen. For efficient reactions it is necessary to have an extremely strong Lewis acid present, such as pentavalent antimony. Frequently these reactions are carried out in HF solutions with $SbCl_5$ as a

catalyst. The reactivities of the substrates and the nature of the products obtained can be accounted for in terms of corresponding carbonium ion intermediates. The fluorinating power increases with greater Lewis acid strength. Hudlicky[12] presented the following order of strengths:

$SbF_3 < (SbF_3 + SbCl_3) < (SbF_3 + SbCl_5) < SbF_3Cl_2 < SbF_5$

Arsenic trifluoride is useful for selective replacement of one to three chlorines in saturated haloalkanes if $SbCl_5$ catalyst is present.[13] The order of the reactivity of groups to fluorination is similar to that of the antimony fluorides:[14]

$CCl_3 > CCl_2 > CHCl_2 >>> CHCL > CH_2Cl$.

However, monochloroalkanes give only tar.

The Swarts process allows the synthesis of chloro-fluoro alkanes, ethers, and ketones from highly chlorinated reagents. As the number of attached fluorines increases, it becomes increasingly more difficult to remove chlorines. Thus many compounds can not be completely fluorinated. Another disadvantage is the difficulty in making highly chlorinated compounds which have more than four carbons. The Swarts method does not replace attached hydrogens. Industrial processes commonly use chromium oxides to synthesize small chain chloro-fluoro alkanes,[15] ketones,[15] and ethers.[16]

High Valency Metal Fluorides

The most important reagent of this group is CoF_3, although AgF_2, MnF_2, CeF_4, and PbF_4 have also been used.[17] This reaction is essentially an oxidation-reduction process. In the process developed by

Fowler and coworkers,[18] high valency CoF_3 is formed or regenerated by passing fluorine over a bed of CoF_2. Hydrocarbon vapor diluted with nitrogen is passed over a bed of CoF_3 in a batch process. There is less fragmentation than in a corresponding direct fluorination because the heat of reaction is only half that of the direct fluorination (ΔH = -50 Kcal/mol).[19] This method is good for general synthesis of saturated fluoroalkanes and fluorocycloalkanes. Both chlorines and hydrogens are substituted. However, other functional groups are also destroyed. A disadvantage is the high temperatures (300°C) or multiple passes necessary to achieve complete fluorination. Usually, not all highly deactivated chlorine or hydrogen atoms will be replaced below a temperature at which extensive degradation occurs.[20] Incomplete fluorination occurs with increasingly complex structures.

Catalytic Direct Fluorination

The catalytic metal packing process controls fluorination by quickly dissipating heat. The reactions occur in the vapor phase, in the interstices of packing, or on the surface of the packing. The early work of Bigelow[5-8] was expanded during the second world war by Cady and coworkers.[21] The process developed involved introducing organic vapors and fluorine diluted with nitrogen into a reactor filled with silver plated copper turnings. The greater efficiency of fluorination of the coated copper relative to the uncoated copper is thought to be due to formation of AgF_2. This process has become

obsolete since it gives the same results as the metal fluoride process and is not as easily scaled up or controlled as other processes.

Direct Fluorination of Liquids

The early solution fluorination reactions of Bockemuller[4] and Miller demonstrated the feasibility of partial fluorination. However, complete fluorination is more difficult as extensive polymerization and fragmentation occurs as well as reactions with the solvent. This method is now used for selective fluorination. Meritt[22] has reported selective cis addition of fluorine to a variety of alkenes in $CFCl_3$ at -78°C.

Jet Fluorination

In the jet fluorination process developed by Bigelow,[23,24,25] gas phase fluorination of organic compounds is controlled by good heat transfer in moving gas streams. This technique has been used in the preparation of many novel fluorine compounds. However, complex mixtures are often obtained. Also, highly branched or larger molecules give low yields.

Electrochemical Fluorination

Simons and coworkers,[26,27] who discovered the process, and later Nagase[28] found that electrochemical fluorinations could be carried out in liquid HF with a low voltage of 5-6 volts. The reactions are similar to the high valency metal fluorides in that hydrogens and halogens are replaced and all double bonds are saturated. Many organic compounds containing oxygen, nitrogen, or

sulfur atoms are highly soluble in HF and are also conducting. Acids, alcohols, and esters give perfluoroalkylacid fluorides and perfluoralkanes.[28] Ethers and nitrogen compounds give the corresponding perfluoroalkyl oxides and nitrides as well as fragment perfluoroalkanes. However, as the length of the hydrocarbon tail of functional compounds increases, the yields of fluorinated products decreases. This method is not very useful for nonsoluble alkanes, aromatics, and halogenated alkanes.

The Lamar and LTG Methods

The "Lamar" method developed by Lagow and Margrave[29-31] uses long reaction times and the high dilution of fluorine with helium. The helium acts as a heat sink in the removal of the heat evolved in the fluorination process. Perfluorination is obtained by gradually increasing the fluorine concentration during the long reaction times. A later development of this process by Lagow, Maraschin, and Adcock[32-36] coupled the high dilution and long reaction times with a low-temperature-gradient (LTG) reactor packed with copper turnings. In contrast to other methods, the LTG process produces good yields of highly branched fluorocarbons.[32,33] The LTG method is also useful for the fluorination of ethers,[34] esters,[35] acid fluorides,[35,36] acid anhydrides,[37] and cyclic amines.[38] However, it works well only for molecules with appreciable solid-state volatility and crystallinity. It is also a batch process generally suitable only for small scale synthesis.

C. THE AEROSOL DIRECT FLUORINATION SYSTEM

Development of the Aerosol Fluorination System

A critical analysis of the LTG direct fluorination process gave five sets of conditions which are believed to contribute to high yield reactions:[39]

1. Fluorination of molecules in the crystalline state.
2. Very high reactant surface area exposed to gaseous fluorine.
3. Low initial temperature.
4. High initial dilution of fluorine gas.
5. High efficiency of heat dissipation.

The crystalline matrix acts as an energy sink to dissipate reaction energies. The matrix also reduces the number of hydrocarbon radical recombinations. The high reactant surface area allows all molecules to be uniformly attacked by fluorine. Low temperatures reduce the vigor of the reactions by decreasing the overall kinetic energy. The low temperatures also reduce the number of radical chain initiations. High initial fluorine dilution also reduces the overall reaction rate. The high fluorine dilution also lowers the possibility of simultaneous attack by two fluorine molecules or radicals, which would lead to fragmentation. Efficient energy dissipation prevents fragmentation and combustion.[40]

However, in order to achieve perfluorination in a short time span, the above conditions must be modified. Initially, low temperatures and a low concentration of fluorine are necessary to prevent fragmentation. But as the degree of fluorination on a molecule

increases, the more difficult it becomes to replace the remaining hydrogens. Thus it becomes desirable to increase both the temperature and the fluorine concentration. The LTG technique is a batch process which changes both the applied temperature gradient and the fluorine concentration over a long time period, namely days. A flow process with increasing temperature and fluorine concentration gradients would imply a change in space and a much shorter reaction time. These fluorination enhancing conditions require that the reactant be mobile while it passes through progressively warmer regions which also have progressively higher fluorine concentrations. A mobile gaseous reactant could be used, but there is no convenient way to limit collisions between hydrocarbon radicals and thus limiting coupling reactions which give tars and oils. A liquid reagent stream does not allow for the uniform, rapid mixing of the very reactive gaseous fluorine. Thus uniform, controlled attack and substitution by fluorine does not occur at every C-H bond.

In order to maintain the efficiency of the LTG system, it is necessary to produce extremely small solid particulates which have gas-like mobility and remain crystalline. These particulates can then be suspended as an aerosol and transported using an inert carrier gas. These particulates possess extremely high surface areas which permit uniform attack by fluorine. The crystalline particulates also serve as an effective heat sink. Multiple collisions of the reactant particulates with carrier gas atoms would be very effective in dissipating heat. Helium would be an efficient carrier gas because of its

high thermal conductivity and its inertness. The excess energy would be continuously removed from the particulates by helium atoms to the cooled walls of the reactor.

Principles of aerosol production are well developed. The requirements for generators capable of producing aerosols are described by Fuchs and Sutugin,[41] Cadle,[42] and Goodrich.[43] A more recent paper by Sutugin describes a mixer-type generator which is useable for steady-state aerosol production in a flow reactor.[44] An essential difference in the aerosol generator developed by Adcock is its subambient operation.[39]

A description and an operating procedure of the aerosol fluorination system are given in the experimental methods chapter.

Early Reactions of the Aerosol Fluorination System

The aerosol fluorination system successfully produced the perfluorinated analogues of cyclohexane, neopentane, 1,4-dioxane, and 2,2-dimethyl-1,3-dioxolane.[39] These compounds are not easily fluorinated by most methods. F-Cyclohexane can be produced in moderate yields from hexachlorobenzene, benzene, and cyclohexane by the use of high valency fluorides or catalytic fluorination. The highly branched structure of neopentane is not amenable to fluorination without fragmentation. Only the LTG method produces F-neopentane in high yields.[33] Oxygen containing compounds such as 1,4-dioxane are generally only successfully fluorinated electrochemically. However, the carbon-carbon bond next to an oxygen in dioxane is easily cleaved.[29] This problem was circumvented by both the LTG[36] and

aerosol fluorination systems.[39] The very acid sensitive ketal, 2,2-dimethyl-1,3-dioxolane, was easily fluorinated without the HF solvolysis problems which plague other methods.[39]

The aerosol fluorination system has exhibited the ability to fluorinate a wide variety of compounds. Only the more limited Lamar/LTG systems have such capability. Since the aerosol fluorination system has shown that it can fluorinate most of the same compounds that the LTG system can, it should also be able to fluorinate compounds with carbonyl functionalities and possibly other functional groups. Thus, M. L. Robin began an investigation of the fluorination of ketones and ethers,[45] while this researcher began an investigation of the fluorination of carbonyl chlorides and alkyl chlorides.

D. STATEMENT OF THE PROBLEM

The Problem

The ability to retain a functional group on a hydrocarbon during fluorination is desirable in many aspects. It predetermines the site of functionality and produces the product in a single reaction. Simple, straight-chain perfluoroalkyl acids can be produced directly by electrochemical fluorination and indirectly by a variety of reactions analogous to their hydrocarbon counterparts. However, a more general method which can produce highly branched F-alkyl acid fluorides directly in good yields would be helpful.

Another method of preselecting a site for derivatizing fluorocarbons is by leaving a halogen in the desired position during the fluorination process. The fluorination of chloroalkanes by metathesis reactions using HF, F^-, or SbF_3 does not provide for prior selection of residual halogens although specific fluorocarbon halides may be obtained as products.[12,14,15] The feasibility of maintaining carbon-chlorine bonds during CoF_3 or electrochemical fluorination can be accomplished, although further chlorination, dimerization, and fragmentation also occurs.[20,27] A general method of fluorination which retains halogens in desired positions would be helpful.

The Investigation

The aerosol fluorination system offers a method for the direct preparation of F-alkyl acid fluorides and F-alkyl-chlorides. Thus the investigation consists of a study of the stability of a variety of functional groups, other than ketones[45] and amines, to the aerosol direct fluorination process. The investigation concentrates on acid chlorides and alkyl chlorides, although other functional groups such as chloro ethers, esters and alcohols are also briefly studied. The investigation attempts to clarify some of the confusion which exists concerning the basic fluorination reactions of alkyl halides. The investigation also consists of a brief study in derivatizing chloro-F-alkanes and hydryl-F-alkanes.

CHAPTER II

EXPERIMENTAL METHODS

A. AEROSOL FLUORINATION SYSTEM

The aerosol fluorination system discussed in Chapter I is shown in Figure 1. The system consists of:

(A) an oven to generate nucleating particles,

(B) a hydrocarbon evaporation system,

(C) an aerosol generator,

(D) the reactor modules,

(E) a photochemical stage,

(F) a product collection trap,

(G) and a cooling system.

When a bed of sodium fluoride in a nickel combustion boat (Fisher) is heated to 850°C in the oven (Hoskins Electric Furnace, Model FD-303A), highly dispersed NaF particles are sublimed into a main helium carrier gas. These particles have an average radius of 17.5Å and serve as condensation nuclei for hydrocarbon condensation.[46] The oven temperature is monitored by a temperature gauge (Thermo Elec. Mfg. Co.) connected to a thermocouple wire (Alpha 5766 Type J, iron constantan) placed in an Inconel thermocouple probe which is inserted into the oven.

Before entering the aerosol generator, the main helium stream carrying the NaF particles is chilled to near -196°C by passing through a liquid nitrogen cooled heat exchanger.

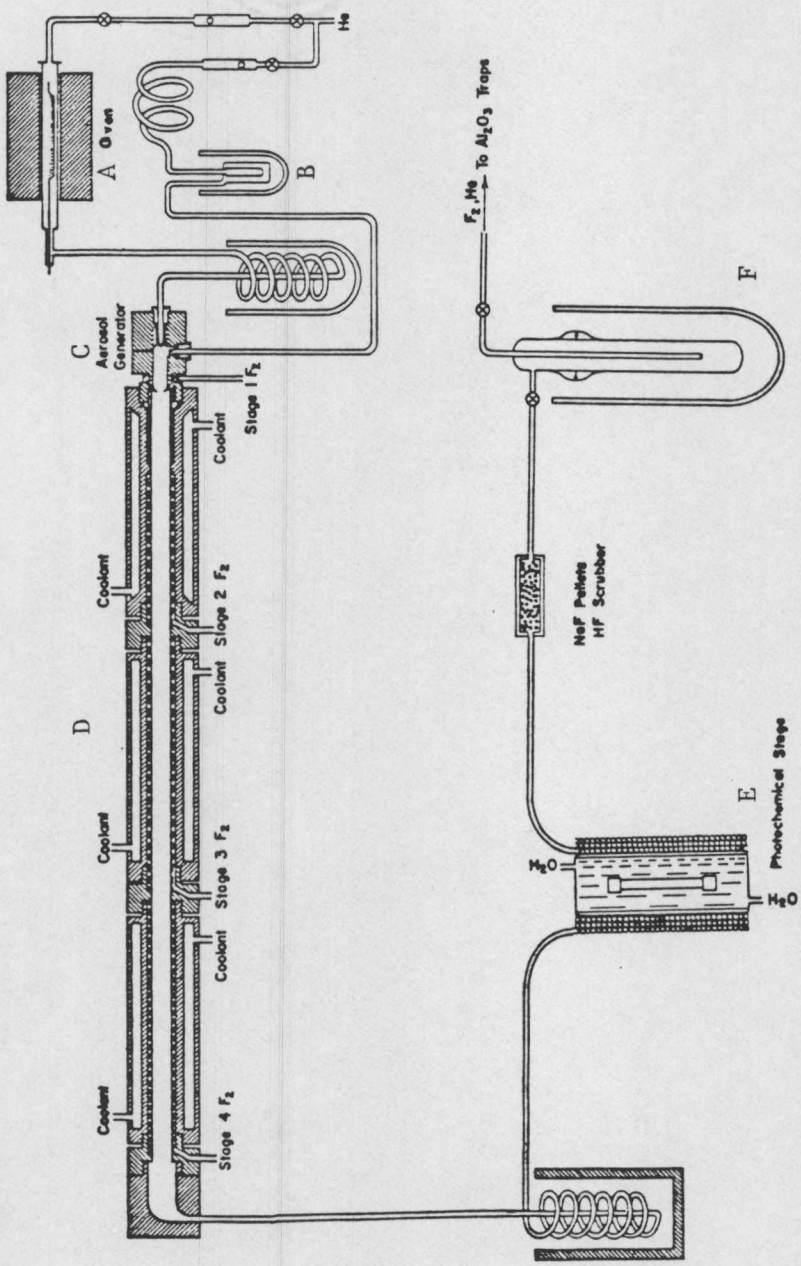


Figure 1. Aerosol fluorination system.

(A) Oven
(B) Hydrocarbon evaporator
(C) Aerosol generator
(D) Reactor modules
(E) Photochemical stage
(F) Product collection trap

A hydrocarbon stream is produced in an evaporator device shown in Figure 2a. The hydrocarbon evaporates at a predetermined rate when a carefully controlled helium stream is bubbled through the liquid by means of a dispersion tube. The hydrocarbon vapor then passes through flexible Teflon tubing into the heated inlet of the aerosol generator. A smaller device shown in Figure 2b is used for high boiling liquids or for small volume samples. The outlet of this "mini" evaporator is inserted directly into the heated aerosol generator. A 12 inch, 20 gauge syringe needle bubbles helium through 5 mL or less of sample. The entire mini evaporator can be heated such that high boiling liquids can be evaporated directly into the aerosol generator.

The aerosol generator is shown in Figure 3. The chilled main helium carrier gas containing the NaF particles enters the generator through a Teflon insert at the back of the generator. The Teflon insert serves as an insulator between the liquid nitrogen chilled Helium carrier and the heated brass body of the aerosol generator. The hydrocarbon stream is introduced into the aerosol generator at a right angle to the chilled carrier gas through simple male Ultratorr fittings screwed into the brass body. The hydrocarbon vapor condenses into aggregates around the chilled NaF particles forming an aerosol. An additional gas inlet opposite the hydrocarbon inlet is available to balance the helium flows if necessary. In order to make sure that hydrocarbon condenses only around the NaF particles, the entire aerosol generator is heated. Coils of nichrome wire between layers of asbestos paper surrounding the brass body are heated by an external

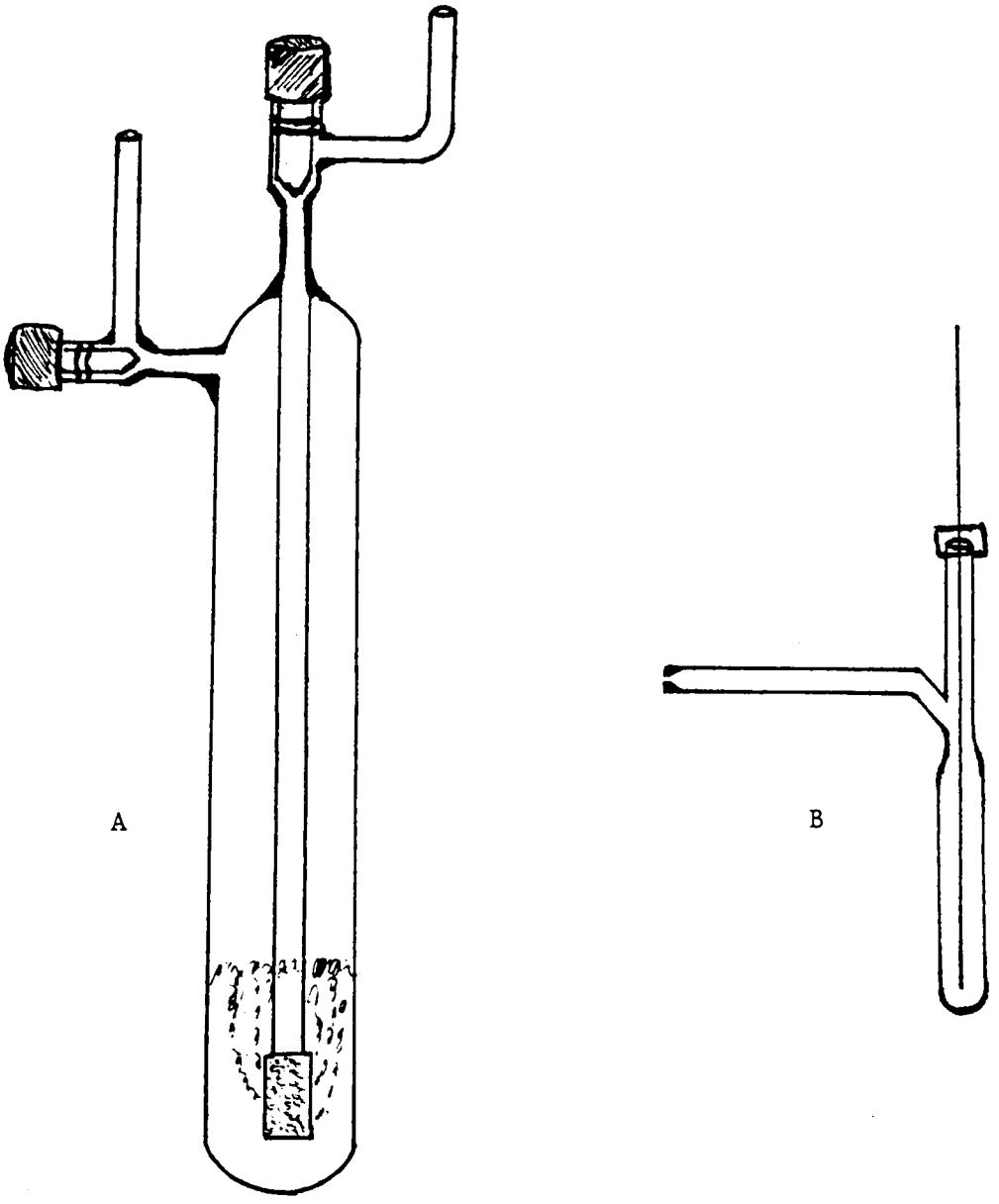


Figure 2. Hydrocarbon evaporators

(A) Large volume hydrocarbon evaporator
(B) Mini evaporator for small volumes and high boiling liquids

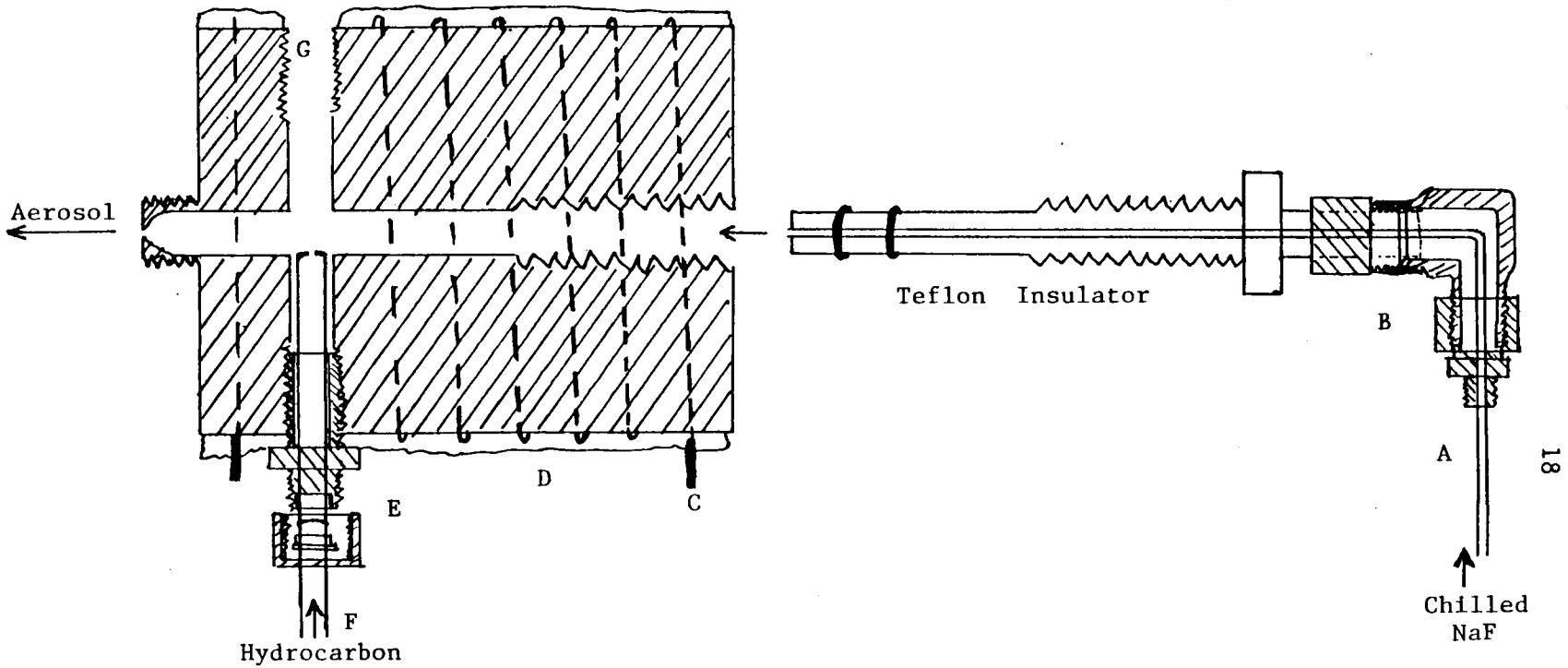


Figure 3. Aerosol generator.

(A) 1/8 inch Teflon tubing from -196°C heat exchanger.
(B) 3/8 inch union elbow with attached Teflon insulator.
(C) Nichrome wire heating coil.
(D) Porcelain and asbestos insulation.
(E) 1/4 inch ultratorr-swagelock fitting.
(F) Heated hydrocarbon inlet tube.
(G) Secondary gas inlet.

voltage source. The asbestos layers are coated with a synthetic porcelain (Sauereisen No. 33, Sauereisen Cements Co.) which provides good thermal and moisture insulation.

The chilled aerosol is then directly channeled into the reactor where it is mixed with elemental fluorine diluted with helium. The reactor as shown in Figure 4 consists of 3 modules. The first reactor module consists of an outer cooling unit and two inner inserts, stage 1 and stage 2. The second and third modules have one cooling unit and one insert each, stage 3 and stage 4 respectively. Both the outer units and the inserts are made of Monel. The inserts provide the means of fluorine introduction through small holes drilled along their inner surfaces. This allows the fluorine concentration to be greatest at the far end of the insert where it enters. This provides a fluorine concentration gradient which increases down the length of the reactor.

Fluorine flows are monitored with a Hastings mass flowmeter (Model LF 20-X) and Hastings mass flow transducers (Model LF 20-X, Types F-100M and F-20M). Fluorine flows are controlled by Whitey forged-bonnet monel valves. The fluorine is diluted and mixed with helium in a gas manifold before delivery to the reactor. The helium flows are monitored by Matheson #600 and #603 rotameters.

The outer units of the reactor modules may be independently cooled by the circulation of chilled freon. The cooling system is shown schematically in Figure 5. A freon reservoir cooled to approximately -50°C or lower by either liquid nitrogen or dry ice/methanol

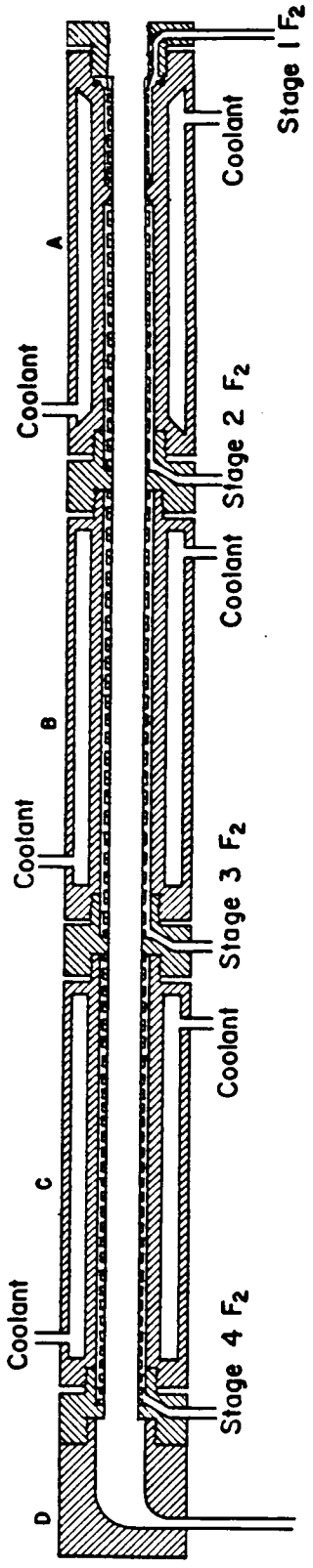


Figure 4. Reactor modules.

(A) Module 1 with stage 1 and stage 2 inserts.
(B) Module 2 with stage 3 insert.
(C) Module 3 with stage 4 insert.
(D) Endcap.

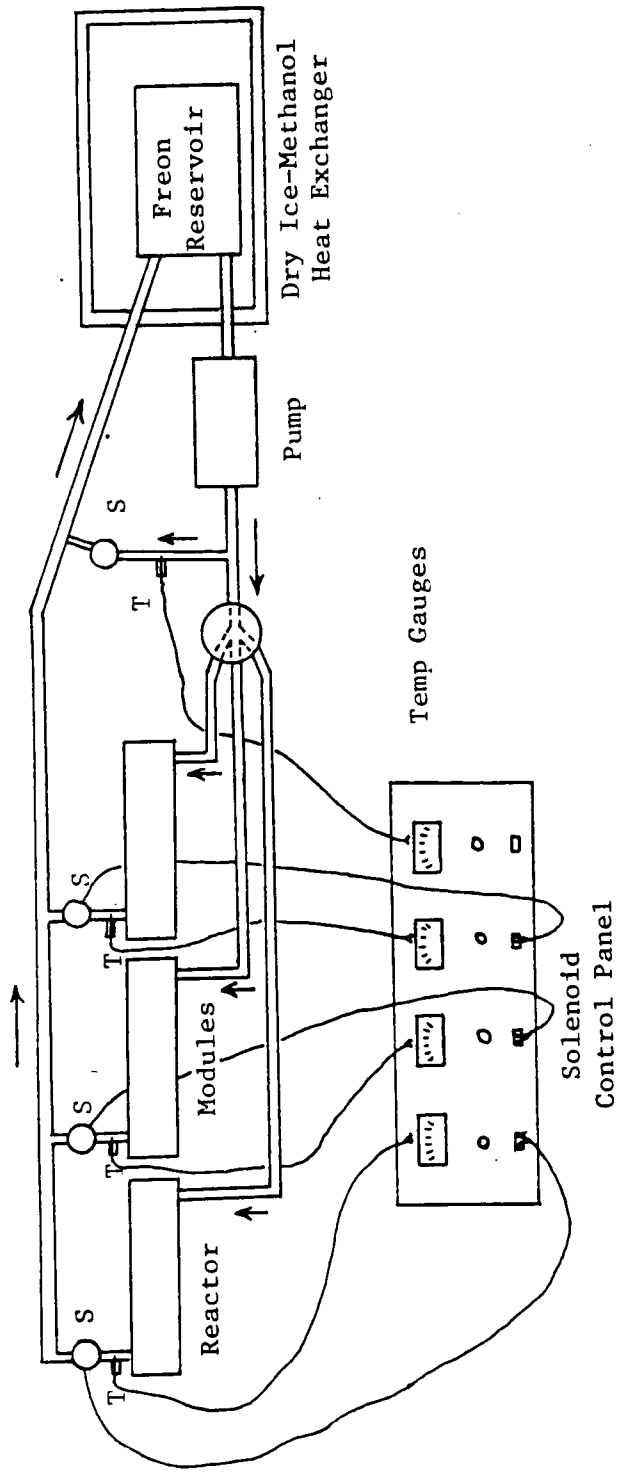


Figure 5. Reactor cooling system.

(S) Solenoids.
(T) Thermocouples.

serves as a heat exchanger. The freon coolent (Genetron 11, $CFCl_3$, Allied Chemical) is drawn from the bottom of the reservoir and pumped on demand to the individual modules by a magnetic drive pump (Eastern/Iwaki, MD-15T). The temperature of the modules is monitored by temperature gauges (GE type D053) connected to thermocouple wires inserted into the coolent outlets. The coolent flows are controlled by solenoid valves (ASCO) on the outlet side of the modules. The associated electronics allow the solenoids to remain open until preset temperatures are reached.

Although the reactor as shown in Figure 4 has three modules, additional modules can be added before the end cap. Thus the reactor can be as long as desired. Following the end cap, a copper coil provides additional length for fluorination to occur. This coil can be cooled, heated, or left at room temperature, depending on the volatility of the fluorinated products.

The photochemical stage shown in Figure 6 consists of a Hanovia, 550 watt, medium pressure mercury ultraviolet lamp in a water cooled, quartz immersion well. This is surrounded by 4 meters of coiled 3/8 inch by 0.015 inch wall FEP Teflon tubing, a water coolant space, and a pyrex filter surrounded by 6 meters of the same coiled FEP Teflon tubing. Partially fluorinated products and fluorine from the reactor first pass through the outer FEP Tubing coil (A). The pyrex filter (B) limits irradiation to wavelengths greater than 280 nm. The reactants flowing into the second coil (C) are irradiated down to the transmission cut off of FEP Teflon at 224 nm. The photochemical

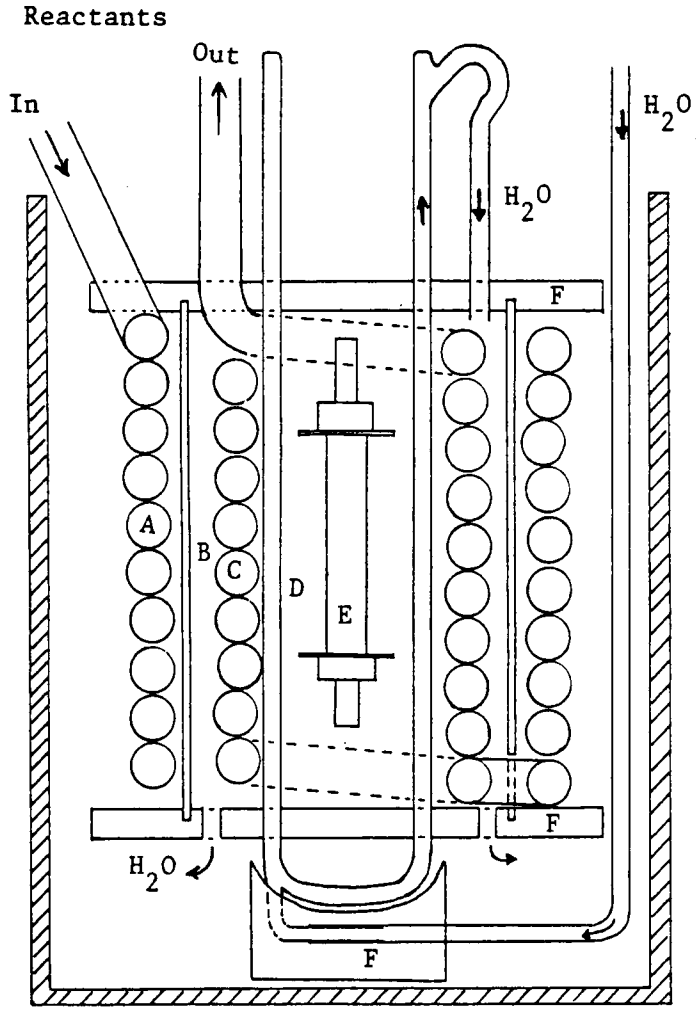


Figure 6. Photochemical stage.

(A) Outer FEP Teflon coil.
(B) Pyrex filter.
(C) Inner FEP Teflon Coil.
(D) Immersion well.
(E) Hanovia U. V. lamp, 550 watt.
(F) Teflon supports.

stage is cooled by water flowing through the immersion well and around the inner and outer coils.

A NaF trap is placed between the photochemical stage and the product collection trap to remove unwanted HF. This trap consists of an 8 inch by 1 inch diameter brass cylinder filled with anhydrous NaF pellets. Flexible Teflon tubing with male Ultratorr fittings are used for easy, strain-free connection of the product collection trap. Unreacted fluorine is trapped by alumina (ALCOA) in two large brass cylinders connected in tandem.

B. CHARACTERIZATION

Crude product from the aerosol reactor was collected in a liquid nitrogen cooled trap after removal of HF. The trap and liquid nitrogen dewar were removed and then connected to a vacuum line where the helium was removed through another liquid nitrogen cooled trap. Products were then transferred upon warming of the product trap. The vacuum line and the product trap are of glass construction with Kontes "HiVac", Teflon stopcocks. The vacuum line consists of a set of fractionation traps in series, a set of smaller collection traps in parallel, assorted inlets, and a Welch "Duo-Seal" vacuum pump (model number 1402B). Products were fractionated on the vacuum line to remove SiF_4 and any remaining HF. Infrared (IR) assay (PE 257) determined the importance of each fraction. Individual fractions or combinations thereof were separated by gas chromatography (Bendix, Model 2300, subambient multicontroller). Either of two columns were

used; 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 hrs) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb p, conditioned at 250°C (12 hrs). Following gas chromatographic separation all products of "significance" were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry, PE1330; electron impact (70eV) and chemical ionization (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A Computer); and ^{1}H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. Elemental analyses where necessary are performed by Schwartzkopf Microanalytical Labortatories, Woodside, N.Y. Characterizations of compounds are tabulated in Appendix B.

C. AEROSOL FLUORINATION REACTIONS

Typical Reaction Procedures

Before a reaction was started, the hydrocarbon throughputs were determined. From appropriate vapor pressure data, hydrocarbon reservoir temperatures were established. Temperatures which produced 10 to 40 mm partial vapor pressure were found to produce suitable throughputs. Throughputs were determined by trapping and weighing the hydrocarbon for a certain time period before it entered the aerosol generator. Once a temperature was selected, a plot of hydrocarbon throughput versus the helium carrier flow through the evaporator was

established. The plots for several acid chlorides are shown in Figure 7. The throughput plots for several alkyl chlorides at different temperatures are shown in Figures 8 to 12. Figure 13 gives the throughput plots of three alkyl bromides. Figure 14 demonstrates how temperature changes can affect the throughputs. The throughputs of the two esters change dramatically with only a 10°C difference in room temperature.

Before a new compound was fluorinated, the reactor modules and aerosol generator were cleaned, the NaF trap was renewed, and fresh NaF was added to the nickel boat in the oven. The NaF in both the oven and the HF trap needed to be renewed after 4 runs. The oven was heated with a low helium flow until it reached operating temperatures of 800-850°C. As this required about 2 hours, throughputs were often determined then.

Once the oven reached operating temperatures and a desired throughput was known, all appropriate helium flows were turned on to approximately half the reaction values. At this time cooling of the reactor system commenced. Before the desired temperatures were reached, fluorine was introduced into the reactor modules. This passivated the reactor surfaces if they had been exposed to the atmosphere. Also any organic material remaining in the reactor was fluorinated and removed without contaminating that run. Final fluorine flow settings were then set according to the desired degree of fluorination. A setting of 1 mL/min delivers 2.44 mmol/h of fluorine. If perfluorination was desired, 2 to 3 fluorine molecules

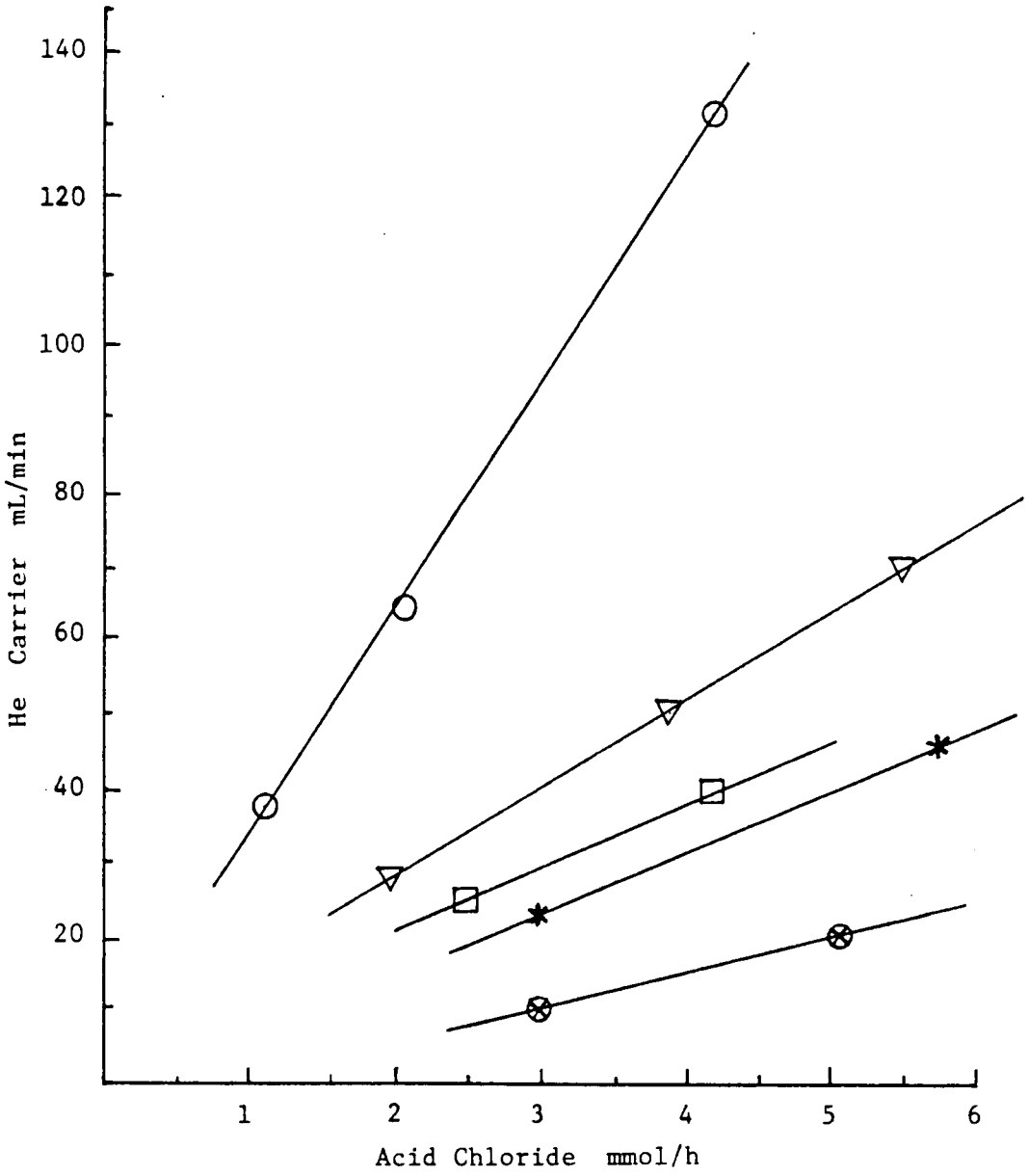


Figure 7. Throughputs for acid chlorides

pivaloyl chloride (0°C)

cyclopropyl carbonyl chloride (22°C)

butyryl chloride (22°C)

iso-butyryl chloride (22°C)

chloroacetyl chloride (22°C)

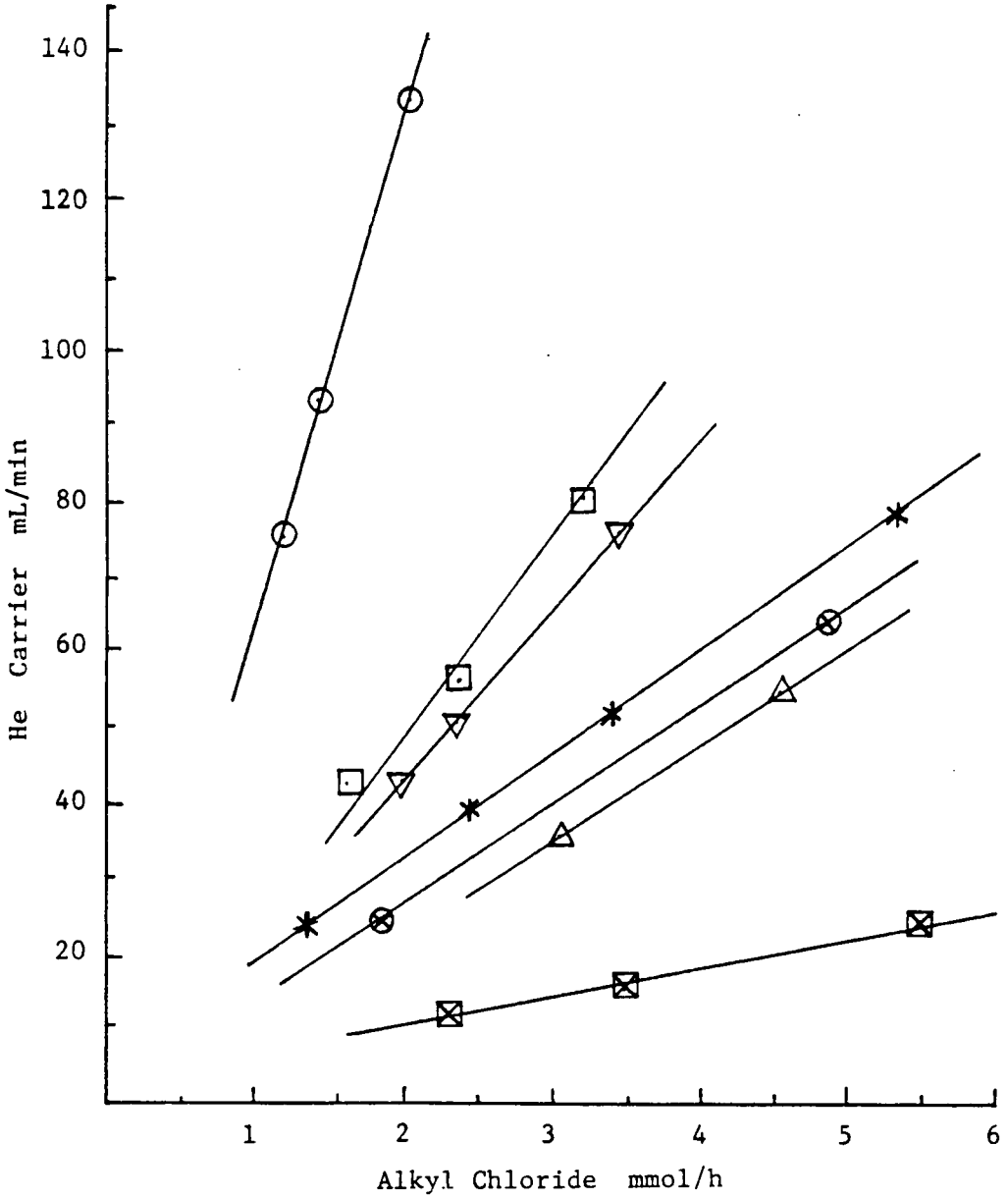


Figure 8. Throughputs for alkyl chlorides at -7°C.

cyclopentyl chloride

tert-amyl chloride

neopentyl chloride

butyl chloride

iso-butyl chloride

sec-butyl chloride

tert-butyl chloride

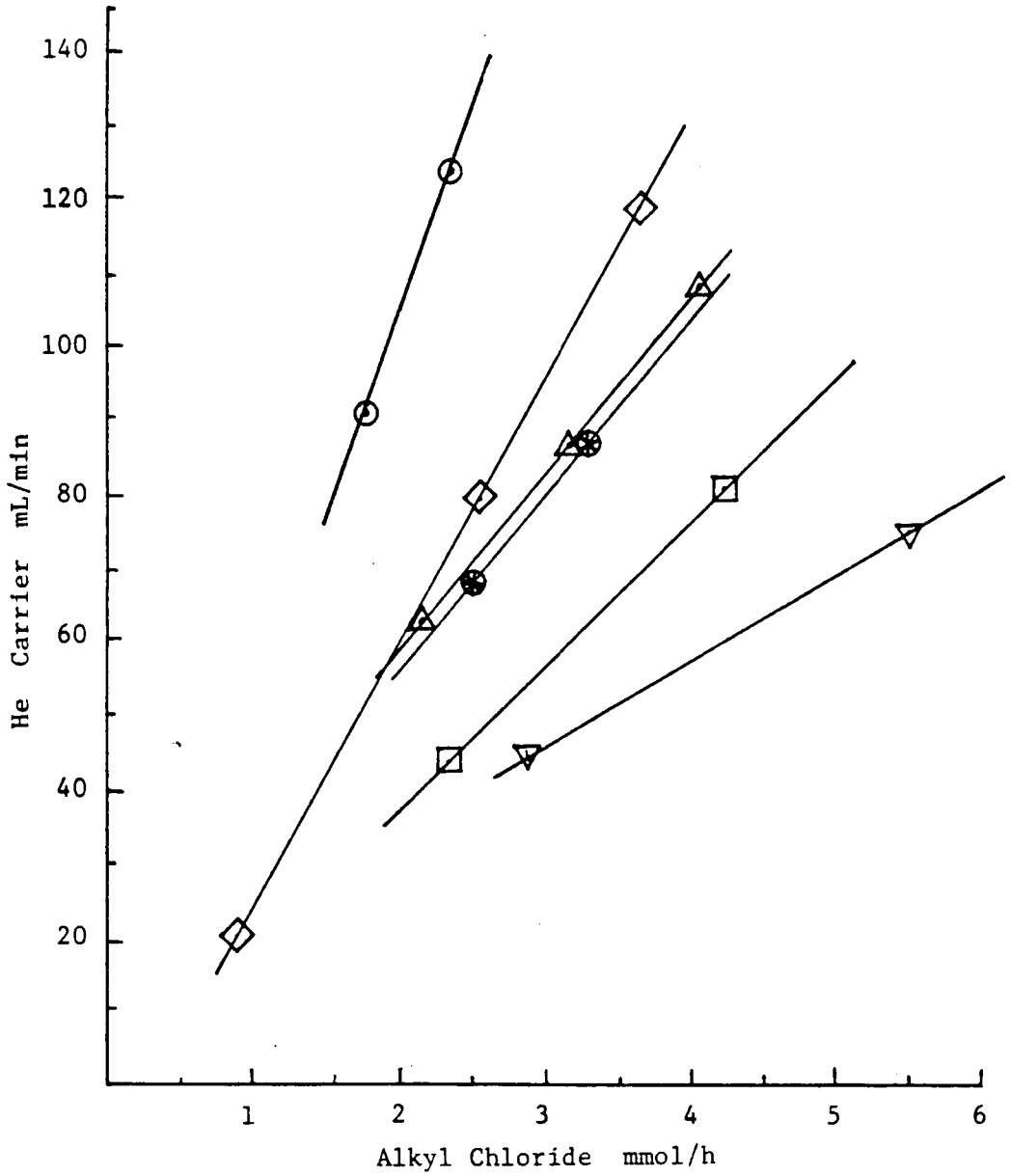


Figure 9. Throughputs for chloropentanes at 0°C.

cyclopentyl chloride

3-chloropentane

1-chloro-3-methylbutane

1-chloro-2-methylbutane

2-chloro-2-methylbutane

neopentyl chloride

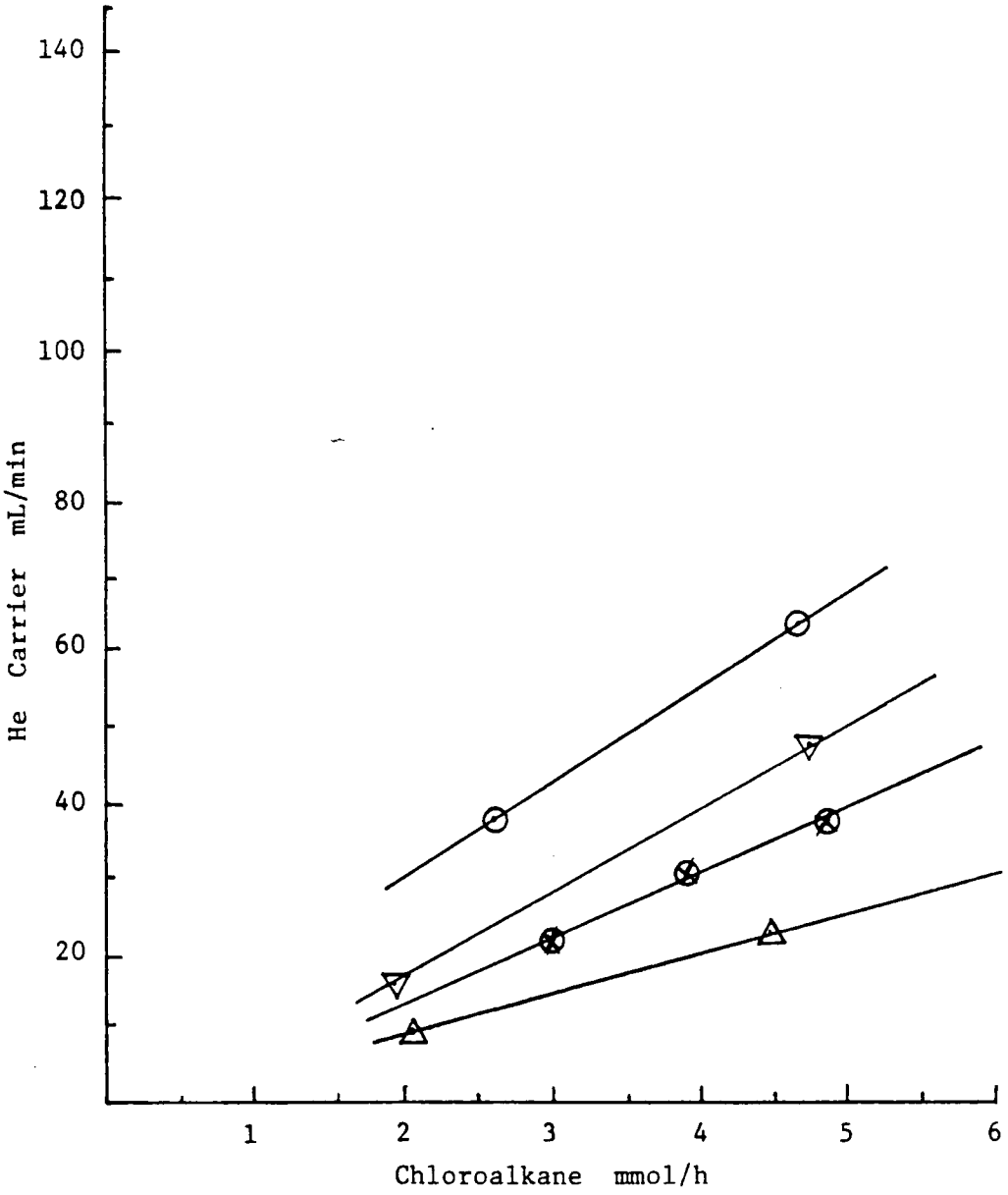


Figure 10. Throughputs for chloroalkanes at 0°C

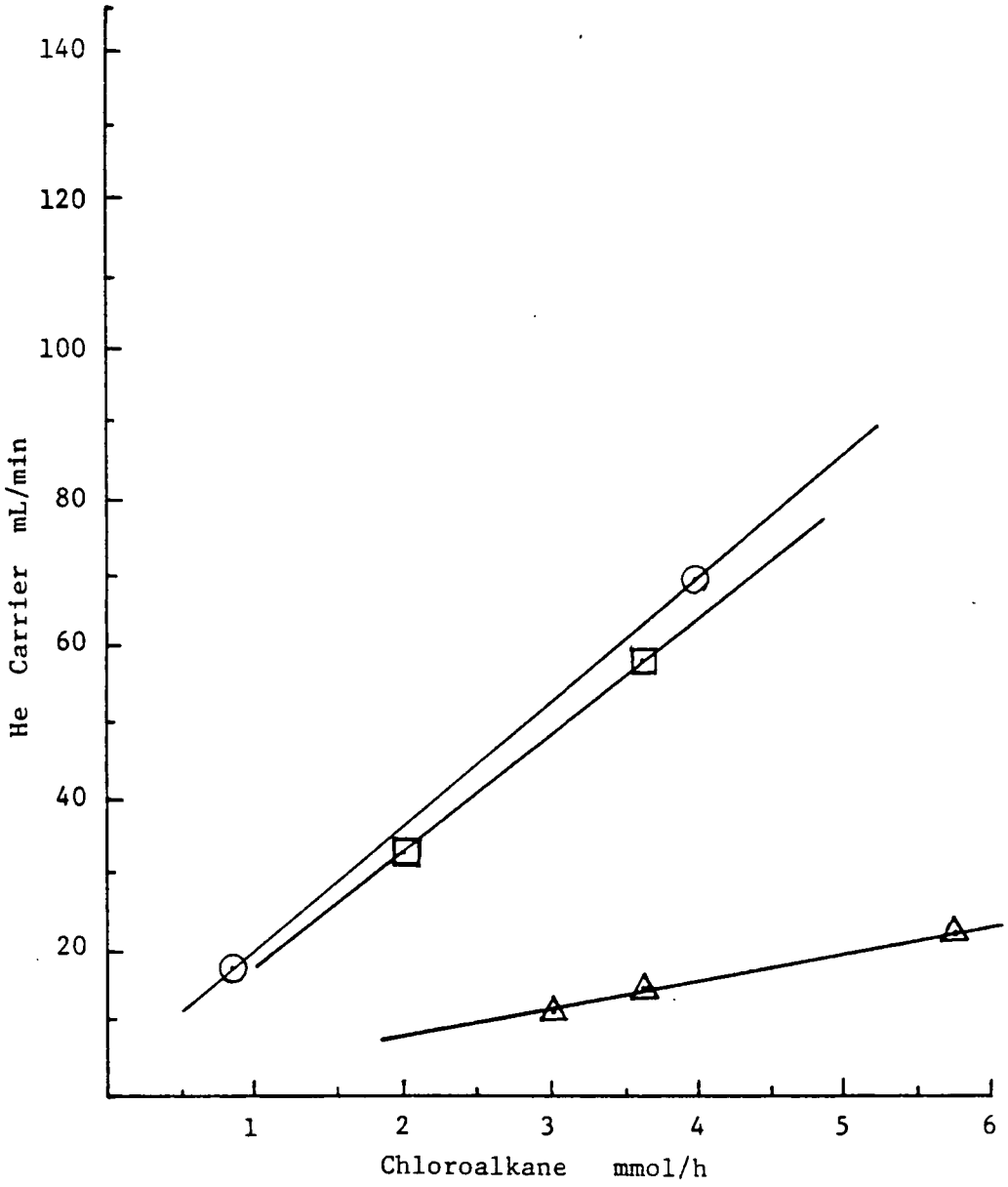


Figure 11. Throughputs of chloroalkanes at 22°C

tetrachloroethane

1,2-dichloro-2-methylpropane

1-chloro-3-methylbutane

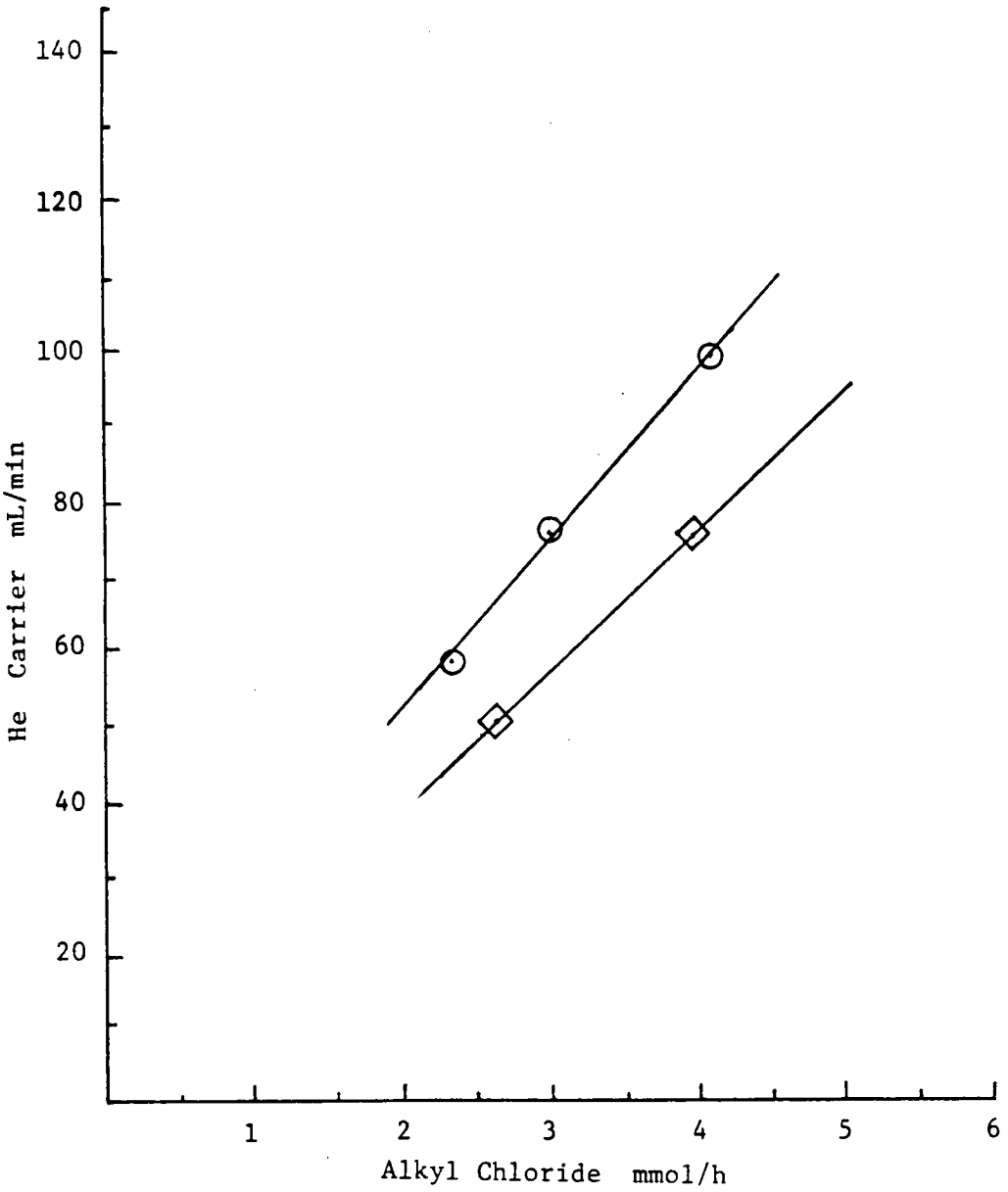


Figure 12. Throughputs for alkyl chlorides at -45°C

propyl chloride

iso-propyl chloride

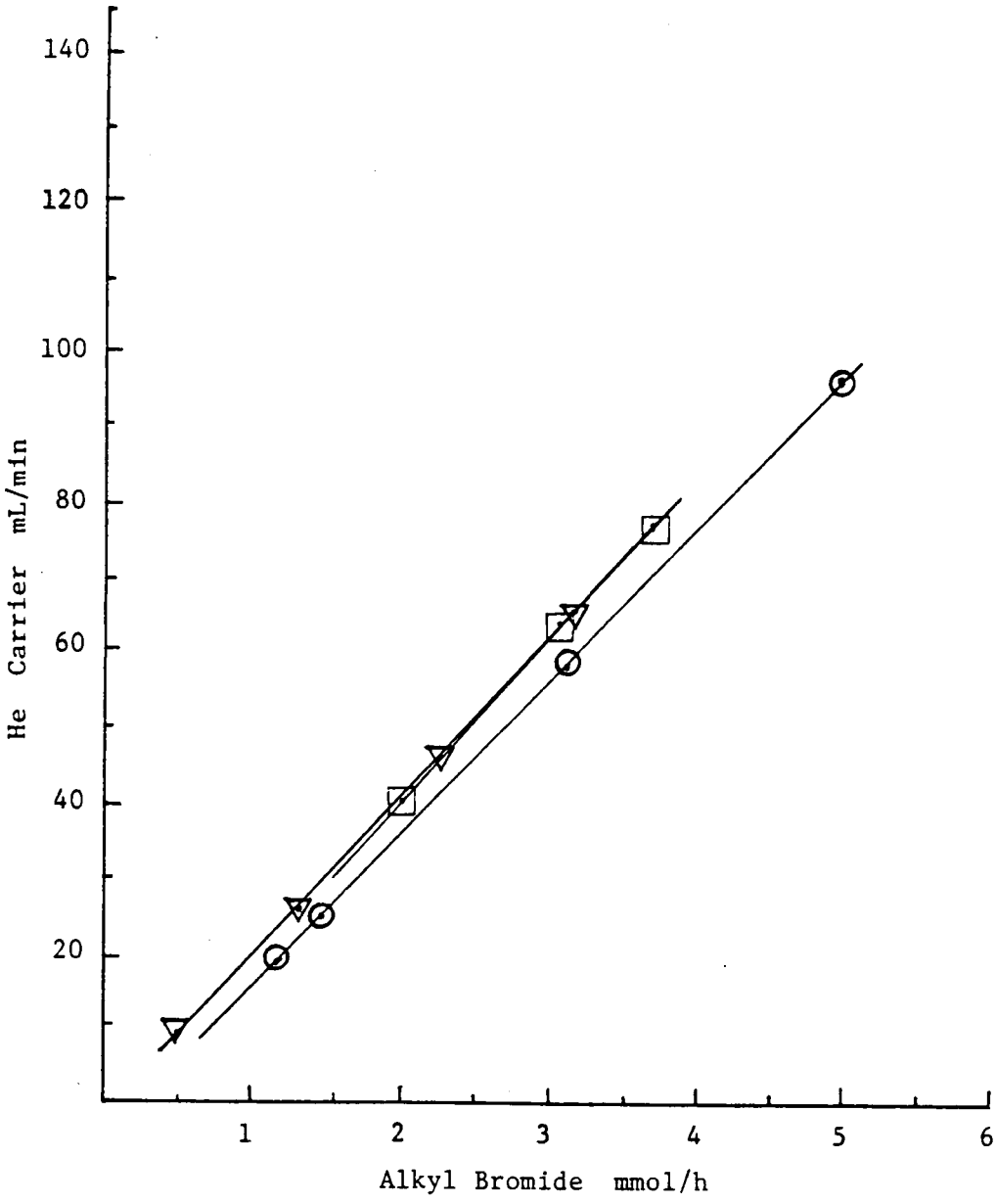


Figure 13. Throughputs for alkyl bromides at -7°C.

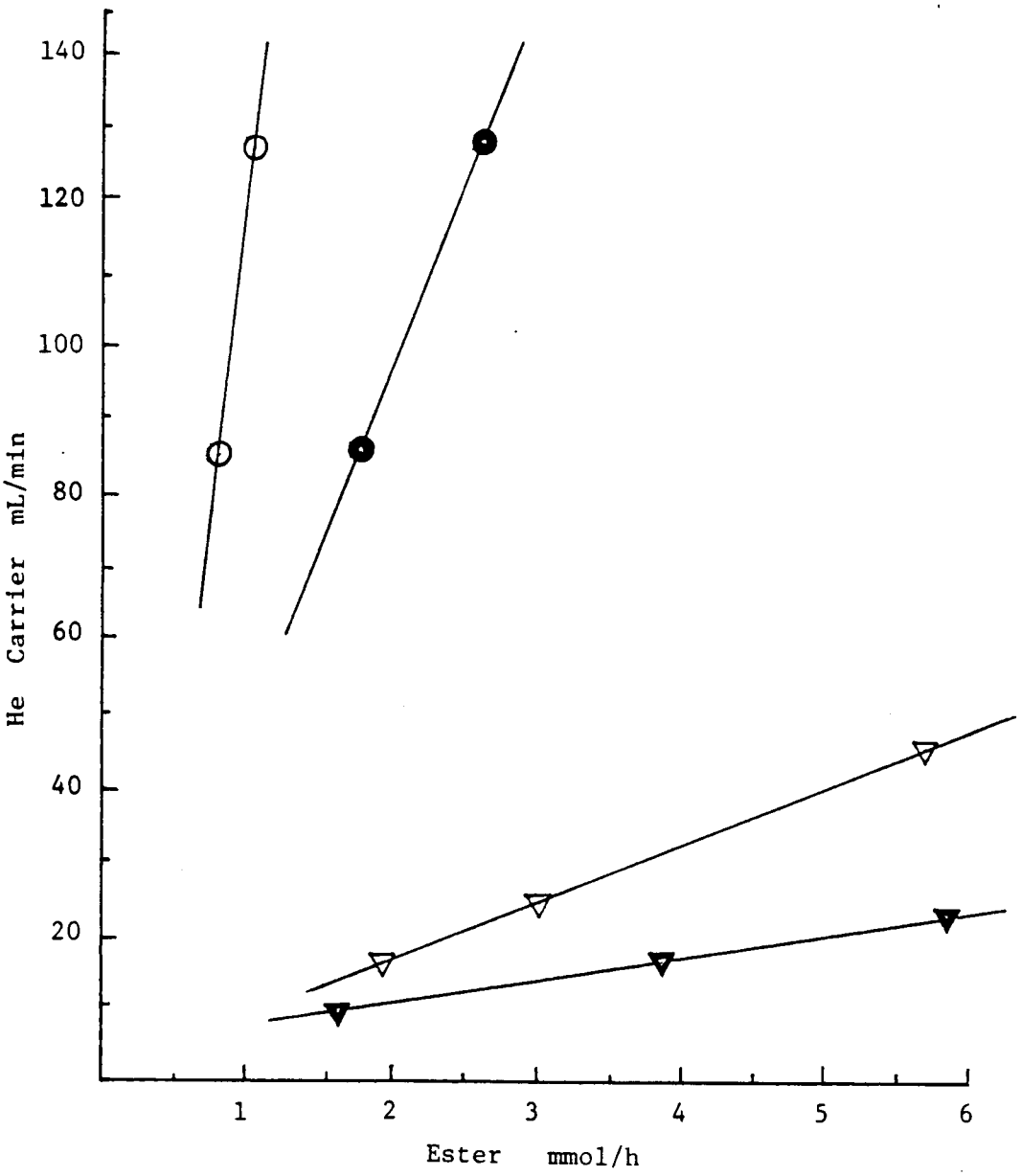


Figure 14. Throughputs for esters at room temperature.

ethyl 3-chloropropanoate at 22°C

ethyl 3-chloropropanoate at 32°C

iso-propyl propanoate at 22°C

iso-propyl propanoate at 32°C

were introduced for every hydrogen present. This usually gave 3 to 4% fluorine concentration in the last stage.

If the photochemical stage was used, the U. V. lamp and its cooling water were turned on 10 minutes before the hydrocarbon flow was started. Hydrocarbon was introduced as long as desired. This was usually about four hours.

Any drop in the flows indicated the system was partially blocked. This usually occurred in the NaF trap if it was not renewed frequently. Fluorine and hydrocarbon flows could be stopped temporarily while the trap was renewed. A blockage elsewhere is more serious and requires complete shut down.

Shutting down the system is in the reverse order of start up with the exception of the oven which is turned off with the hydrocarbon flow. A low helium flow is maintained as the reactor warms up in order to flush out fluorine and any other materials.

Typical aerosol fluorination reactions for individual compounds are given in the following experimental sections. Details of the aerosol fluorination parameters are tabulated in Appendix A. Compounds are characterized in Appendix B. All reactions are photochemically finished unless otherwise stated.

Pivaloyl Chloride:

Trimethylacetyl chloride (Aldrich) (pivaloyl chloride or 2,2-dimethylpropanoyl chloride) has a vapor pressure at 0°C such that a helium flow of 60 mL/min through the sparge tube of the

hydrocarbon evaporator produces a throughput of 0.24 g/h (2.0 mmol/h). A 3 hour photochemically finished run produced 0.79 g of crude product after fractionation on the vacuum line. Separation of this material by gas chromatography on the SE-52 column (0°C/5 min; 25°C/min to 100°C/5 min; 25°C/min to 200°C/15 min) gave 2% F-isobutane (I) at 3 min, 40% F-pivaloyl fluoride (II) at 4 min, 2% 3-hydryl-F-pivaloyl fluoride (III) at 7 min, and 15% 3-chloro-F-pivaloyl fluoride (IV) at 9 min. The major product, 0.316 g of F-pivaloyl fluoride (II), was collected in 19.7% yield based on the theoretical throughput for a 3 h run. Characterizations of (I), (II) and (III) are given in Table B-1, while (IV) is characterized in Table B-2. The aerosol fluorination parameters for this reaction are given as run 6a in Table A-1.

Another reaction (run 7) with a higher main-carrier helium flow and higher fluorine flows gave 1.05 g of crude product, of which 73% was F-pivaloyl fluoride (II) in 48% yield.

Butyryl Chloride

Butyryl chloride was prepared by dropping $SOCl_2$ (Fischer) into ice-cold butyric acid (Eastman), refluxing at 70°C, and fractionally distilling the solution. Butyryl chloride has a vapor pressure at 23°C such that a helium flow of 30 mL/min produces a throughput of 0.27 g/h (3.0 mmol/h). A 3 hour run produced 1.41g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (0°C/5 min; 10°C/min to 40°C/4 min; 25°C/min to 180°C/10 min) gave 80% F-butyryl fluoride (V) at 11 min, in 58% yield of the theoretical

throughput. It is characterized in Table B-1. The aerosol fluorination parameters are given in Table A-2.

Iso-Butyryl Chloride

Iso-butyryl chloride (Aldrich) has a vapor pressure at 23°C such that a helium flow of 30 mL/min produces a throughput of 0.426 g/h (4.0 mmol/h). A 3 hour run produced 1.48 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (0°C/5 min; 10°C/min to 40°C/4 min; 25°C/min to 180°C/10 min) gave 8.8% F-iso-butyryl fluoride (VI) at 10 min, 7.4% F-iso-butyryl chloride (VII) at 15 min, 18% 3-hydryl-F-2-methylpropanoyl fluoride (VIII) at 16 min, 18% 2-hydryl-F-2-methylpropanoyl fluoride (IX) at 7.5 min, 15% $(CF_2H)_2$ CFCOF (X) at 21 min, and 5% $(CF_3)(CF_2H)CHCOF$ (XI) at 22 min. The calculated yield of (VI) was 5%.

A second 3-h run with a lower throughput of 0.32 g/h (3.0 mmol/h) and higher fluorine flows gave 1.37 g of crude product after fractionation. GC separation of this material gave 75% F-iso-butyryl fluoride (VI), 5% (VIII) and traces of (IX), (X) and (XI). The calculated yield of F-iso-butyryl fluoride (VI) was 53%. The aerosol fluorination parameters for both runs are given in Table A-3. Characterizations of these products are given: (VI), (VII), (IX) Table B-1, (VIII) Table B-3, (X), (XI) Table B-4.

Cyclopropyl Carbonyl Chloride

Cyclopropyl carbonyl chloride was prepared from cyclopropyl carboxylic acid and $SOCl_2$ by the method of Dadson and Minta.[47]

Cyclopropyl carbonyl chloride has a vapor pressure at 22°C such that a helium flow of 23 mL/min produces a throughput of 0.19 g/h (1.8 mmol/h). A 2.5 hour run produced 0.5833 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (0°C/5 min; 10°C/min to 60°C/0 min; 25°C/min to 180°C/10 min) gave 13% F-isobutyryl fluoride (VI) at 7.5 min, 20% F-butyryl fluoride (V) at 8.5 min and unidentified compounds at 10 min (7%), 11 min (21%), 15 min (7%) and 16 min (29%). The calculated yields of the two open chain F-butyl fluorides were 13% (VI) and 8% (V) based on the theoretical throughput. The aerosol fluorination parameters for this reaction are given as run 3 in Table A-4.

Chloroacetyl Chloride

Choroacetyl chloride was prepared by the addition of $SOCl_2$ to chloroacetic acid (Eastman). Chloroacetyl chloride has a vapor pressure at 28°C such that a helium flow of 10 mL/min gives a throughput of 0.34 g/h (3 mmol/h). A 3 hour run produced 0.80 g of crude products after fractionation on the vacuum line. Purification of the products on the QF-1 column (5°C/5 min; 10°C/min to 75°C/4 min; 25°C/min to 180°C/10 min) gave 26% F-acetyl fluoride (XII) at 4 min and 51% chloro-F-acetyl fluoride (XIII) at 10 min. The calculated yields of (XII) and (XIII) were 20% and 34%, respectively, based on the theoretical throughput. The aerosol fluorination parameters are given in Table A-5. Characterizations of (XII) and (XIII) are given in Table B-1.

Neopentyl Chloride

Neopentyl chloride was made from addition of neopentyl alcohol to triphenylphosphine dichloride by the method of Wiley, et al. Neopentyl chloride has a vapor pressure at -7°C such that a helium flow of 80 mL/min produces a throughput of 0.38 g/h (3.6 mmol/h). A 3 hour run produced 2.56 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (15°C/5 min; 10°C/min to 75°C/0 min to 75°C/0 min; 50°C/min to 150°C/7 min) produced 2.03 g of F-neopentyl chloride (XIV), 79.6% at 7 min, 74% yield based on the theoretical throughput. Other products included 3.4% F-iso-butane (I) at 3 min, 14.6% F-neopentane at 4 min and 2.4% partially fluorinated material between 17-19 min. The aerosol fluorination parameters for this reaction are given in Table A-6 as run 3. Runs 1 and 2 were carried out with a lower main helium carrier flow and lower fluorine flows. The yields of F-neopentyl chloride were also lower, 15% and 13% respectively. F-Neopentyl chloride (XIV) is characterized in Table B-5.

Propyl Chloride

1-Chloropropane (Matheson) has a vapor pressure at -45°C such that a helium flow of 75 mL/min produces a throughput of 0.24 g/h (3.0 mmol/h). A 2 hour run produced 0.909 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (isothermally at -20°C) gave 85% 1-chloro-F-propane (XV) at 6 min for a 63% yield. The aerosol fluorination parameters are given in Table A-7. 1-chloro-F-propane (XV) is characterized in Table B-1.

Butyl Chloride

1-Chlorobutane (Fisher) has a vapor pressure at -10°C such that a helium flow of 58 mL/min produces a throughput of 0.29 g/h (3.1 mmol/h). A 2 hour run produced 1.168 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/5 min; 10°C/min to 30°C/0 min; 25°C/min to 180°C/10 min) gave 6.9% F-n-butane at 3 min and 60.2% 1-chloro-F-butane (XVI) at 6 min (43.8% yield). The aerosol fluorination parameters are given in Table A-8. 1-Chloro-F-butane is characterized in Table B-6.

Iso-Butyl Chloride

1-Chloro-2-methylpropane (Eastman) has a vapor pressure at -10°C such that a helium flow of 25 mL/min produces a throughput of 0.13 g/h (1.4 mmol/h). A 2 hour run produced 0.3881 g of crude material after fractionation. Separation on the SE-52 column (0°C/5 min; 15°C/min to 120°C/min; 25°C/min to 200°C/10 min) gave 15.6% F-iso-butane (I) at 3 min and 76.4% F-iso-butyl chloride (XVII) at 6 min, (41.6% yield). The aerosol fluorination parameters are given in Table A-9 as run 1. F-Iso-butyl chloride (XVII) is characterized in Table B-7.

1-Chloro-2-Methylbutane

1-Chloro-2-methybutane was prepared in 80% yield from the addition of $SOCl_2$ to an ice cold solution of 2-methyl-1-butanol and pyridine. 1-Chloro-2-methylbutane has a vapor pressure at 22°C such that a helium flow of 12 mL/min produces a throughput of 0.42 g/h (3.0 mmol/h). A 3 hour run produced 1.629 g of crude product after

fractionation on the vacuum line. Separation on the SE-52 column (15°C/5 min; 10°C/min to 75°C/0 min; 50°C/min to 160°C/10 min) gave 19% F-iso-pentane (XVIII) at 3.5 min and 66% 1-chloro-F-2-methylbutane (XIX) at 7 min in 39% yield. The aerosol fluorination parameters are given in Table A-10. Characterizations are given: (XVIII) in Table B-1, (XIX) in Table B-8.

1-Chloro-3-Methylbutane

1-Chloro-3-methylbutane was prepared in 83% yield from the addition of $SOCl_2$ to an ice cold solution of iso-amyl alcohol (Mallinckrodt) and pyridine. 1-Chloro-3-methyl-butane has a vapor pressure at 22°C such that a helium flow of 12 mL/min produces a throughput of 0.42 g/h (3.0 mmol/h). A 3 hour run produced 1.323 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (15°C/5 min; 10°C/min to 75°C/0 min; 50°C/min to 160°C/10 min) gave 19% F-iso-pentane (XVIII) at 3.5 min and 67% 1-chloro-F-3-methylbutane (XX) at 7 min in 32% yield. The aerosol fluorination parameters are given in Table A-11. 1-Chloro-F-3-3-methylbutane (XX) is given in Table B-9.

Iso-Propyl Chloride

2-Chloropropane (Eastman) has a vapor pressure at -45°C such that a helium flow of 75 mL/min produces a throughput of 0.31 g/h (4.0 mmol/h). A 2.5 hour run produced 1.239 g of crude product after fractionation on the vacuum line. Separation isothermally at -20°C on either the SE-52 or QF-1 columns gave an unresolved peak (80%) at 6

min and 18 min respectively of a 1:2 mixture of 1-chloro-F-propane (XV) and 2-chloro-F-propane (XXI). The combined calculated yield for both products is 48.5%. The aerosol fluorination parameters are given in Table A-12. F-Iso-propyl chloride (XXI) is characterized in Table B-1.

2-Chlorobutane

2-Chlorobutane (Eastman) has a vapor pressure at -10°C such that a helium flow of 33 mL/min produces a throughput of 0.26 g/h (2.8 mmol/h). A 3 hour run produced 0.971 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/5 min; 10°C/min to 30°C/0 min; 25°C/min to 180°C/10 min) gave two overlapping peaks of 30% 2-chloro-F-butane (XXII) at 5.5 min and 43% 1-chloro-F-butane (XVI) at 6 min. The combined and calculated yield for both is 33.1%. The aerosol fluorination parameters are given in Table A-13. 2-Chloro-F-butane (XXII) is characterized in Table B-10.

3-Chloropentane

3-Chloropentane was prepared in 78% yield by addition of $SOCl_2$ to an ice cold solution of 3-pentanol and pyridine. It has a vapor pressure at 28°C such that a helium flow of 20 mL/min produces a throughput of 0.17 g/h (1.2 mmol/h). A 1.5 hour run produced 0.191 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (15°C/5 min; 10°C/min to 75°C/0 min; 25°C/min to 180°C/10 min) gave a mixture of 30% 3-chloro-F-pentane (XXIII) and 45% 2-chloro-F-pentane (XXIV) at 6 min, and 15% 1-chloro-F-pentane (XXV)

at 6.5 min. The combined calculated yield for all three products was 31%. All three products are characterized in Table B-11. The aerosol fluorination parameters are given in Table A-14.

Chlorocyclopentane

Chlorocyclopentane (Aldrich) has a vapor pressure at -10°C such that a helium flow of 135 mL/min produces a throughput of 0.21 g/h (2.0 mmol/h). A 3 hour run produced 1.30 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (10°C/13 min; 10°C/min to 60°C/5 min; 50°C/min to 180°C/5 min) gave 2.6% F-butane at 5 min, 12.5% F-cyclopentane (XXVI) at 12 min, 5% $C_4F_{11}Cl$ (XVI) and (XXII) at 15 min, 12.5% F-pentane at 18 min, 49.5% 1-chloro-F-cyclopentane (XXVII) at 22 min, and 15.5% $C_5F_{11}Cl$ isomers (XXIII), (XXIV), (XXV) at 25-26 min. The yield of (XXVII) was 40.2%. Aerosol fluorination parameters are given in Table A-15. Characterizations are given: (XXVI) in Table B-1, (XXVII) in Table B-12.

Tert-Butyl Chloride

2-Chloro-2-methylpropane (Eastman) has a vapor pressure at -10°C such that a helium flow of 13 mL/min produces a throughput of 0.28 g/h (3.0 mmol/h). A 2 hour run produced 0.8884 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/5 min; 15°C/min to 120°C/0 min; 25°C/min to 200°C/10 min) gave 15.6% F-iso-butane (I) at 3 min and 76.4% 1-chloro-F-2-methylpropane (XVII) at 6 min in 41.6% yield. A second 2 hour run with the same throughput and only 6.0 mmol/h fluorine and no photochemical finishing

gave about the same amount of partially fluorinated material. Separation with the same GC program gave 30% unreacted tert-butyl chloride at 12 min, 30% 1-chloro-2-fluoro-2-methylpropane (XXVII) at 11 min, 2% 1,2-difluoro-1-chloro-2-methylpropane (XXVIII) at 13 min, and 20% 1,2-difluoro-3-chloro-2-methylpropane (XXIX) at 15 min. The aerosol fluorination parameters are given in Table A-16. Characterizations are given: (XVII) in Table B-7, (XXVII) in Table B-1, (XXVIII) and (XXIX) in Table B-13.

Tert-Amyl Chloride

2-Chloro-2-methylbutane (Eastman) has a vapor pressure at 0°C such that a helium flow of 53 mL/min produces a throughput of 0.27 g/h (2.5 mmol/h). A 2.5 hour run produced 0.963g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (15°C/5 min; 10°C/min to 75°C/0 min; 50°C/min to 180°C/10 min) gave 6.2% F-iso-butane (I) at 3 min, 22.1% F-iso-pentane (XVIII) at 3.5 min, and 62.8% of an unresolved mixture at 7 min of 1-chloro-F-2-methylbutane (XIX), 1-chloro-F-3-methylbutane (XX), and 2-chloro-F-3-methylbutane (XXX) in a 16:6.5:1 ratio respectively. The combined calculated yield for the three perfluorinated chlorides (XIX, XX, XXX) was 31.8%. The aerosol fluorination parameters are given in Table A-17. Characterization of (XXX) is given in Table B-14.

1,2-Dichloroethane

1,2-Dichloroethane (Fischer) has a vapor pressure at -23°C such that a helium flow of 45 mL/min produces a throughput of 0.20 g/h (2.0

mmol/h). A 2 hour run produced 0.601 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/2 min; 5°C/min to 25°C/0 min; 50°C/min to 140°C/6 min) gave 10% 1-chloro-F-ethane at 3 min and 90% 1,2-dichloro-F-ethane (XXXI) at 8 min in 79% yield. The aerosol fluorination parameters are given in Table A-18. 1,2-Dichloro-F-ethane is characterized in Table B-1.

1,2-Dichloro-2-Methylpropane

1,2-Dichloro-2-methylpropane (Chemical Samples Co.) has a vapor pressure at 22°C such that a helium flow of 33 mL/min produces a throughput of 0.25 g/h (2.0 mmol/h). A 2 hour run produced 0.731 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/5 min; 10°C/min to 30°C/0 min; 25°C/min to 190°C/10 min) gave 90% 1,3-dichloro-F-2-methylpropane (XXXII) at 12 min in 63% yield. The aerosol fluorination parameters are given in Table A-19. This compound is characterized in Table B-15.

Trans-1,2-Dichlorocyclopentane

Trans-1,2-dichlorocyclopentane was prepared by chlorination of cyclopentene according to the method of Mousseron, Granger and Valette.[49] It has a vapor pressure at 22°C such that a helium flow of 175 mL/min produces a throughput of 0.14 g/h (1.0 mmol/h). A 3 hour run produced 0.8426g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (10°C/13 min; 10°C/min to 60°C/15 min; 50°C/min to 180°C/15 min) gave 1% C_4F_{10} at 5 min, 6% F-cyclopentane (XXVI) at 12 min, 1% $C_5F_{11}Cl$ at 15 min, 24%

chloro-F-cyclopentane (XXVII) at 22 min, a mixture of 10% trans-1,2-dichloro-F-cyclopentane (XXXIII), 10% trans-1,3-dichloro-F-cyclopentane (XXXIV), 9% cis-1,3-dichloro-F-cyclopentane (XXXV) at 30 min, and 9% cis-1,2-dichloro-F-cyclopentane (XXXVI) at 31 min. The calculated yields are the same as the above distribution yields. The aerosol fluorination parameters are given in Table A-20. Characterizations are given: (XXXIII), (XXXIV), (XXXV) in Table B-16 and (XXXVI) in Table B-17.

1,1-Dichloropropane

1,1-Dichloropropane was prepared by addition of propionaldehyde (Eastman) to ice-cold PCl_5 (Aldrich) with several portions of water, followed by fractional distillation of the organic layer gave 1,1-dichloropropane in 60% yield. It has a vapor pressure of 0°C such that a helium flow of 50 mL/min produces a throughput of 0.42 g/h (3.7 mmol/h). A 2 hour run produced 1.09 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (-10°C/4 min; 4°C/min to 30°C/1 min; 10°C/min to 90°C/5 min) gave 8% C_3F_7Cl at 5.5 min and 90% of a 1:1 mixture of 1,1-dichloro-F-propane (XXXVII) and 1,2-dichloro-F-propane (XXXVIII) at 14 min. The combined calculated yield for both compounds is 60%. The aerosol fluorination parameters are given in Table A-21. Both compounds are characterized in Table B-1.

2,2-Dichloropropane

2,2-Dichloropropane prepared by the addition of acetone (Fischer) to PCl_5 followed by fractional distillation, was run by Mark Robin.[45] A syringe pump delivered 0.51 mL/hr (2.9 mmol/h) 2,2-dichloropropane to a heated inlet. A 1 hour run produced 0.242 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (-10°C/4 min; 4°C/min to 30°C/1 min; 10°C/min to 180°C/5 min) gave one major peak (85%) at 14 min which contained a 2:3 mixture of 1,2-dichloro-F-propane (XXXVIII) and 1,3 dichloro-F-propane (XXXIX). The aerosol fluorination parameters are given Table A-22. Both compounds are characterized in Table B-1.

1,3-Dichloropropane

1,3-Dichloropropane, prepared by the addition of $SOCl_2$ to 1,3-propanediol and pyridine followed by fractional distillation, was delivered by a syringe pump at 0.51 ml/hr (2.9 mmol/h) to a heated inlet. A 4.5 hour run produced 1.71 g of crude product after fractionation on the vacuum line. Separation with the 2,2-dichloropropane GC program gave 70% 1,3-dichloro-F-propane (XXXIX) at 14 min in 43% yield. The aerosol fluorination parameters are given in Table A-22.

3,3-Dichloropentane

3,3-Dichloropentane was prepared by addition of 3-pentanone (Aldrich) to PCl_5. A helium flow of 30 mL/min through mini-evaporator at 28°C produces a throughput of 0.20 g/h (0.7 mmol/h). A 2 hour run period produced 0.185 g of crude product after fractionation on the

vacuum line. Separation on the SE-52 column (15°C/5 min; 10°C/min to 75°C/0 min; 25°C/min to 180°C/7 min) gave 58% of a mixture of chloro-F-pentane isomers at 5.5 min and 38% of a mixture of dichloro-F-pentane isomers at 12.5 min. Four dichloro isomers were tentatively identified as 1,3-di-chloro-F-pentane (XL), 1,4-dichloro-F-pentane (XLI), 2,3-dichloro-F-pentane (XLII), and 2,4-dichloro-F-pentane (XLIII). Tentative ^{19}F NMR characterizations of these four isomers are given in Table B-18. The aerosol fluorination parameters are given in Table A-23.

1,1-Dichlorocyclopentane

1,1-Dichlorocyclopentane was prepared by addition of cyclopentanone (Aldrich) to PCl_5. A helium flow of 45 mL/min through the mini-evaporator at 28°C produces a throughput of 0.25 g/h (1.8 mmol/h). A 3-hour run produced 1.0 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/5 min; 10°C/min to 60°C/5 min; 10°C/min to 180°C/10 min) gave 8.6% F-cyclopentane (XXVI) at 4 min, 29.7% chloro-F-cyclopentane (XXVII) at 10 min, 57.8% of a mixture of four dichloro-F-cyclopentane isomers (XXXIII), (XXXIV), (XXXV), (XXXVI) at 18 min. The calculated yield of chloro-F-cyclopentane is 37% while the combined yield for the dichloro-F-cyclopentane isomers is 20%. The aerosol fluorination parameters are given in Table A-24.

1,1-Dichloroneopentane

1,1-Dichloroneopentane was prepared by addition of trimethylacetaldehyde (Aldrich) to PCl_5. A helium flow of 25 mL/min through

the mini-evaporator at 28°C produces a throughput of 0.32 g/h (2.3 mmol/h). A 1.5 hour run produced 0.85 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (25°C/10 min; 10°C/min to 75°C/10 min; 25°C/min to 160°C/10 min) gave 30% 1-chloro-F-neopentane (XIV) at 6 min and 34% 1,1-dichloro-F-neopentane (XLII) at 16 min. The calculated yields of (XIV) and (XLII) are 24% and 26% respectively. 1,1-Dichloro-F-neopentane (XLIV) is characterized in Table B-19. The aerosol fluorination parameters are given in Table A-25.

1,1,1-Trichloroethane

1,1,1-Trichloroethane (Eastman) has a vapor pressure at 0°C such that a helium flow of 15 mL/min produces a throughput of 0.25 g/h (1.9 mmol/h). A 2 hour run produced 0.333g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (25°C/10 min; 10°C/min to 75°C/10 min; 25°C/min to 160°C/7 min) gave 82.4% 1,1,2-trichloro-F-ethane (XLV) at 14 min and 15.7% of 3 unidentified products between 20-22 min. The aerosol fluorination parameters are given in Table A-26. The calculated yield of (XLV) is 77%. It is characterized in Table B-1.

1,1,2,2-Tetrachlorethane

1,1,2,2-Tetrachloroethane (Eastman) has a vapor pressure at 28°C such that a helium flow of 70 mL/min produces a throughput of 0.67 g/h (4.0 mmol/h). A 2 hour run produced 1.010 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column

(0°C/2 min; 5°C/min to 25°C/0 min; 50°C/min to 180°C/10 min) gave 10% 1,2-dichloro-F-ethane (XXXI) at 7 min and 80% 1,1,2,2-tetrachloro-F-ethane (XLVI) at 21 min. The calculated yield of (XLVI) is 50%. It is characterized in Table B-1. The aerosol fluorination parameters are given in Table A-27.

2,3-Dichloro-1,4-Dioxane

2,3-Dichloro-1,4-dioxane was prepared by chlorination of 1,4-dioxane (Fischer) by $SOCl_2$ with U.V. irradiation.[50] A helium flow of 120 mL/min through the mini-evaporator at 75°C produces a throughput of 0.28 g/h (1.8 mmol/h). A 2 hour run produced 0.67% g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (-10°C/6 min; 5°C/min to 60°C/0 min; 20°C/min to 160°C/10 min) gave 24.1% F-1,4-dioxane (XLVII) at 4.5 min in 20% yield, 45.5% 2-chloro-F-1,4-dioxane (XLVIII) at 13 min in 35% yield, and 29.6% 2,3-dichloro-F-1,4-dioxane (XLIX) at 23 min in 21% yield. The aerosol fluorination parameters are given in Table A-28. Characterizations are given: (XLVII) in Table B-1, (XLVIII) in Table B-20, and (XLVIX) in Table B-21.

Bis-(2-Chloroethyl) Ether

Bis-(2-Chloroethyl) ether (Eastman) has a vapor pressure at 28°C such that a helium flow of 140 mL/min produces a throughput of 0.37 g/h (2.6 mmol/h). A 2 hour run produced 1.215 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (25°C/5 min; 5°C/min to 75°C/5 min; 20°C/min to 180°C/10 min)

gave 66.9% bis-(2-chloro-F-ethyl) ether (L) at 7 min in 54% yield. It is characterized in Table B-22. The aerosol fluorination parameters are given in Table A-29.

Neopentyl Bromide

1-Bromo-2,2-dimethypropane was prepared from neopentyl alcohol and triphenylphosphine dibromide by the method of Wiley, et al.[48] It has a vapor pressure at -10°C such that a helium flow of 25 mL/min through the hydrocarbon evaporator produces a throughput of 0.30 g/h (1.4 mmol/h). A 2 hour photochemically finished run produced 0.629 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (10°C/4 min; 2°C/min to 55°C/1 min; 50°C/min to 125°C/10 min) gave 80% F-iso-pentane (XVIII) at 3 min. This corresponds to a 63% yield for this reaction (run 1). Four additional fluorination runs were carried out without photochemical finishing and with lower fluorine:hydrocarbon mole ratios. They produced similar amounts of material. The aerosol fluorination parameters for all five reactions are given in Table A-30. The distribution of the products collected from the five GC separations are given in Table 1. Characterizations are given: (LI) Table B-23, (LII) Table B-24, (LIII) Table B-25. (LIV) Table B-26, (LV) Table B-27, (LVI) Table B-28, (LVII) Table B-29.

Iso-Amyl Bromide

Iso-amyl bromide was prepared by adding iso-amyl alcohol (Mallinckrodt) to a cold solution of NaBr and sulfuric acid. It has a

TABLE 1

Aerosol fluorination of neopentyl bromide: GC product distribution

Time (Min)	Product Number	Product Name	Reaction Numbers 1	2	3	4	5
2.5	I	F-isobutane	10	-	-	-	-
3	XVIII	F-isopentane	80	-	-	-	-
12	LI	2,3,3-trifluoro-2-methylbutane	-	10	2	4	-
13	LII	3,3-difluoro-2-methylbutane	-	18	14	6	-
14	LIII	1,1,3,3-tetrafluoro-2-methylbutane	-	5	2	2	-
15	LIV	2,3-difluoro-2-methylbutane	-	11	20	20	-
16	LV	1,3,3-trifluoro-2-methylbutane	-	18	6	2	-
17	LVI	1,3,3-trifluoro-2-fluoromethylbutane } a	-	16	5	5	-
18	LVII	1,2,3,3-tetrafluoro-2-methylbutane } a					
10	LVIII	2-methyl-2-butene	-	-	-	-	30
24	LVIX	neopentyl bromide	-	-	15	28	50
25-27		? residule peaks	10	27	38	35	20

[a] Overlapping peaks collected together.

vapor pressure at -7°C such that a helium flow of 63 mL/min produces a throughput of 0.45 g/h (3.0 mmol/h). A 3 hour run produced 2.0 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (20°C/min; 5°C/min to 10°C/0 min; 10°C/min to 180°C/10 min) gave approximately 60% yield of F-iso-pentane. The rest of the material was bromine, bromine fluorides, and partially fluorinated iso-pentanes. A second run with only 1.5 mL/min fluorine flow and no photochemical finishing gave unreacted iso-amyl bromide and incompletely characterized, partially-fluorinated iso-pentanes. The aerosol fluorination parameters given in Table A-31.

1-Bromo-2-Methylbutane

1-Bromo-2-methylbutane (Columbia Organic Chemicals) has a vapor pressure at -7°C such that a helium flow of 63 mL/min produces a throughput of 0.47 g/h (3.1 mmol/h). A 3 hour run produced 2.2 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (20°C/2 min; 5°C/min to 100°C/0 min; 10°C/min to 180°C/10 min) gave approximately 65% F-iso-pentane. The remaining products were free bromine and partially fluorinated iso-pentanes. A second run with only 2 mL/min fluorine flow and no photochemical finishing gave unreacted starting material, free bromine, and partially fluorinated isopentanes. The aerosol fluorination parameters are given in Table A-32.

Iso-Pentane

Iso-pentane (Aldrich) has a vapor pressure at -45°C such that a helium flow of 40 mL/min produces a throughput of 0.24 g/h (3.3

mmol/h). A 3 hour run produced 1.31 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (25°C/10 min; 10°C/min to 75°C/10 min; 50°C/min to 125°C/10 min) gave 80% F-iso-pentane (XVII) in 46% yield. It is characterized in Table B-1. The aerosol fluorination parameters are given in Table A-33.

Neopentane

Neopentane (K and K Laboratories) has a vapor pressure at -63°C such that a helium flow of 100 mL/min produces a throughput of 0.12 g/h (1.7 mmol/h). A 1 hour run produced 0.31 g of crude product after fractionation on the vaccum line. Separation on the QF-1 column (25°C/10 min; 10°C/min to 75°C/10 min; 50° min to 125°C/20 min) gave 70% distribution of F-neopentane (LX) in 43% yield, 5% hydryl-F-neopentane (LXI) 7% 1,3-dihydryl-F-neopentane (LXII) and other partially fluorinated neopentanes. The aerosol fluorination parameters are given in Table A-34. Characterizations are given: (LX) Table B-30, (LXI) Table B-31, (LXII) Table B-32.

Tetrachloroethylene

Tetrachloroethlyene (Aldrich) has a vapor pressure at 22°C such that a helium flow of 30 mL/min produces a throughput of 0.35 g/h (2.1 mmol/h). A 2 hour run produced 0.68g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/2 min; 5°C/min to 25°C/0 min; 50°C/min to 100°C/10 min) gave 75% distribution of 1,2-difluoro-1,1,2,2-tetrachloroethane (XLVI) in 50% yield. The aerosol fluorination parameters are given in Table A-35.

1,2-Dichloroethylenes

A mixture of cis and trans 1,2-dichloroethylenes (Aldrich) was separated gas chromatographically before use. As less than 1 g of each was collected, the mini-evaporator was used. A flow of 10 mL/min carried 0.116 g/h of cis-1,2-dichloro-ethene and 0.136 g/h of trans-1,2-dichloro-ethene into the reactor. The major product in each reaction was 1,2-dichloro-F-ethane (XXXI). The yields were not calculated. The aerosol fluorination parameters are given in Table A-36.

Ethyl 3-Chloropropanoate

Ethyl 3-chloropropanoate (Aldrich) has a vapor pressure at 22°C such that a helium flow of 190 mL/min produces a throughput of 0.24 g/h (1.75 mmol/h). A 3 hour run produced a large number of perfluorinated products. These included F-propanoyl fluoride, acetyl fluoride, and carbonyl fluoride. The aerosol fluorination parameters are given in Table A-37.

Iso-Propyl Propanoate

Iso-propyl propanoate (Baker) has a vapor pressure at 28°C such that a helium flow of 15 mL/min produces a throughput of 0.44 g/h (3.8 mmol/h). A 2 hour run produced many perfluorinated products. These included F-propanoyl fluoride, F-acetyl fluoride, F-propanone, and a small amount of fluoroxy compounds. The aerosol fluorination parameters are given in Table A-37.

Iso-Amyl Alcohol

Iso-amyl alcohol (Mallinckrodt) has a vapor pressure at 23°C such that a helium flow of 125 mL/min produces a throughput of 0.15g/hr (1.7 mmol/h). A 3 hour run produced a mixture of F-iso-pentane, F-iso-butane and several F-alkyl acid fluorides. The aerosol fluorination parameters are given in Table A-38.

2-Butanol

2-Butanol (Fischer) has a vapor pressure at 28°C such that a helium flow of 30 mL/min produces a throughput of 0.15 g/h (2.0 mmol/h). A 2 hour run produced a mixture of products containing F-butane, F-propanoyl fluoride, F-acetyl fluoride, carbonyl fluoride, and F-2-butane. The aerosol fluorination parameters are given in Table A-38.

Tert-Butanol

Tert-butanol (Fischer) has vapor pressure at 24°C such that a helium flow of 20 mL/min produces a throughput of 0.28 g/h (3.8 mmol/h). A 1 hour run produced a mixture of F-iso-butane, F-iso-butene, F-acetyl fluoride, carbonyl fluoride, and F-2-propanone. The aerosol fluorination parameters are given in Table A-38.

Nitropropane

Nitropropane (Eastman) has a vapor pressure at 28°C such that a helium flow of 80 mL/min produces a throughput of 0.22 g/h (2.5 mmol/h). A 2 hour run produced F-propane and NO_2. The aerosol fluorination parameters are given in Table A-39.

D. DERIVATION OF CHLORO-F-ALKANES

Reactions with Zinc/Dioxane

F-iso-butyl chloride (0.08 g) was sealed in a glass ampule with zinc dust (Fischer), brought to room temperature, then heated for 12 hours at 100°C. Examination of the nearly pure F-iso-butyl chloride by IR and GC showed a trace amount of F-iso-butene was present. The reaction was repeated with dioxane as a solvent for 24 hr at 100°C. Examination of the products indicated a mixture of approximately 30% F-iso-butene and starting material.

This same procedure was repeated for chloro-F-cyclopentane (0.042 g), chloro-F-butane (0.035 g), and chloro-F-neopentane (0.038 g) with zinc dust and dioxane, heated to 100°C for 12 h. Products produced were 20% F-cyclopentene and 70% chloro-F-cyclopentane; 10% F-butene, 80% chloro-F-butane, 10% 1-hydryl-F-butane; 50% 1-hydryl-F-neopentane and 50% chloro-F-neopentane respectively.

Formation and Reactions of Perfluoro Tertiary Butyl Fluorocarbene

F-neopentyllithium was prepared by the metallation of chloro-F-neopentane by n-butyllithium similarly to the metallation of hydryl-F-neopentane.[51] Chloro-F-neopentane (0.113 g, 0.37 mmole) was condensed into a tube containing 0.35 mL of 1.2 M (0.42 mmole) n-butyllithium and 0.10 mL (1.15 mmole) of cyclohexene. The tube was sealed, placed in dry ice-methanol, and shaken every hour until it warmed to room temperature. Fractionation on the vacuum line and GC

separation gave 30% unreacted chloro-F-neopentane, 10% 7-fluoro-7-nonafluoro-tert-butyl-norcarane (LXIII), 20% trans-1,1,1-trifluoro-2,2-bis-(trifluoromethyl)-3-heptene (LXIV) and 5% of the cis isomer. This reaction was repeated with the addition of 0.5 mL of bis(dimethylamino)ethane, $(CH_3)_2NCH_2CH_2(CH_3)_2$, and produced 15% (LXIII), 35% (LXIV) respectively. Characterizations are given: LXIII in Table B-33, LXIV in Table B-34.

Reaction of F-neopentyl chloride (0.130 g, .4 mmol) and an excess of butyllithium (1.0 mL, 1.2 mmol) over a 12-hour period as the ampule warmed from -78°C to 20°C produced 45% trans-1,1,1-trifluoro-bis-(trifluoromethyl)-3-heptene, (LXIV), 10% cis-1,1,1-trifluoro-bis-(trifluoromethyl)-3-heptene, and 25% recovered F-neopentyl chloride.

Addition of an ether solution of I_2, to an ether solution of F-neopentyl chloride and 1.2 mL methyllithium which had been allowed to warm from -78°C to -20°C over an eight hour period produced 35% F-neopentyl iodide (LXV) and 25% recovered and unreacted F-neopentyl chloride. A similar reaction quenched with I_2 after 2 hours at -40°C produced 20% F-neopentyl iodide and 30% recovered F-neopentyl chloride. F-Neopentyl iodide (LXV) is characterized in Table B-1.

E. PHOTOCHEMICAL HALOGENATIONS OF HYDRYL-F-FLUOROCARBONS

Experimental Conditions

Hydryl-F-neopentane (LXI), 1,3-dihydryl-F-neopentane (LXII), 2-difluoromethyl-2-trifluoromethyl-F-1,3-dioxolane, (LXXVI),

2-hydryl-F-1,4-dioxane were major products isolated from nonphotochemically finished, aerosol direct fluorinations of neopentane, 2,2-dimethyl-1,3-dioxolane and 1,4-dioxane respectively.[39] Some 2-hydryl-F-1,4-dioxane, 1-hydryl and 1,3-dihydryl-F-neopentanes and all of the 1-hydryl-F-2,5-dioxahexane were produced by LTG direct fluorination techniques.[36,51] Bromine (Fischer), chlorine (Linde) and bromine trifluoride (Matheson) were commercial products which were purified by vacuum line fractionation, using flexible "Teflon" PTFE tubing as traps in the case of BrF_3. Photolysis reactions were conducted in a 170 mL cylindrical quartz vessel (40 mm x 135 mm) fitted with a Kontes 0-4 mm "Hivac" stopcock through a graded seal. Contents were irradiated using a 125W Hanovia medium pressure mercury vapor arc lamp. Ambient temperature inside the enclosure was approximately 35°C during operation. The reaction was monitored at half day intervals by withdrawing some of the gas phase products into a 10 cm gas infrared cell (KCl windows). Following the reaction, excess halogens were absorbed by condensation of the product into a tube containing a filter paper wet with oleic acid. Nonreactive products were vacuum transferred and subjected to a work-up which consisted of vacuum line fractionation; infrared assay of fractions; and gas chromatographic separation of components.

Hydryl-F-Neopentane: Cl_2

Hydryl-F-neopentane (0.178 mmol, 0.048 g) and chlorine (0.190 mmole, 0.013 g) were condensed into the evacuated quartz cylindrical bulb. The contents were warmed to ambient temperature, until all

reactants were evaporated. The contents were irradiated for 1 hour. Workup of the products produced 96% chloro-F-neopentane (XIV), 4% hydryl-F-neopentane (LXI).

Hydryl-F-Neopentane: Br_2

Hydryl-F-neopentane (0.504 mmol, 0.136 g) and bromine (0.631 mmol, 0.101 g) were condensed into the evacuated quartz bulb. The contents were warmed to ambient temperatures. The contents were irradiated for 180 hours with no significant bromination. Thermal bromination at 250°C for 100 hours of this mixture also gave no significant bromination.

Hydryl-F-Neopentane: BrCl

Hydryl-F-neopentane (0.508 mmol, 0.1371 g), chlorine (0.480 mmol, 0.340 g) and bromine (0.572 mmol, 0.0915 g) were condensed into the evacuated quartz cylindrical bulb. The contents of the bulb were warmed to ambient temperature, until all reactants were evaporated. The contents were then irradiated for a total of 254 hours. The irradation was interrupted at half day intervals for infrared examination. Workup of the products produced 52% bromo-F-neopentane (LXVI), 45% chloro-F-neopentane (XIV) with 3% recovered starting material. Bromo-F-neopentane (LXVI) is characterized in Table B-35.

1,3-Dihydryl-F-Neopentane: BrCl

1,3-Dihydryl-F-neopentane was reacted with bromine chloride under several sets of conditions which are outlined in Table 2. The effect

TABLE 2

Reaction of 1,3-dihydryl-F-neopentane with BrCl: product distributions versus reaction conditions

Reaction Number	1	2	3	4
1,3-di-H-F-neopentane	0.663	0.302	0.608	0.354
Mole ratios				
1,3-di-H-F-neopentane	1	1	1	1
chlorine	1.113	1.311	0.975	0.93
bromine	1.165	1.315	0.980	1.75
Reaction time (hr)	186	180	302	173
Product distribution (mole %) of 1,3-F-neopentanes				
H, H (LXII)[a]	2.7	2.0	1	10
H, Cl (LXVII)	11.4	9.8	7	8
Cl, Cl (LXVIII)	6.5	9.8	9	3
H, Br (LXIX)	29.2	24.6	35	48
Br, CL (LXX)	18.6	29.6	32	9
Br, Br (LXXI)	31.5	24.5	16	22
Ratio of bromination to chlorination [b]	2.6	1.75	1.74	4.4

[a] Recovered starting material.

[b] Calculated as mmoles C-Br bonds to mmoles C-Cl bonds in 1.3 product distribution.

on product distributions by changes in Cl_2/Br_2 ratios and reaction times are tabulated. Reactions were performed in a manner similar to the hydryl-F-neopentane reactions. Characterizations of products are given: $C_5F_{10}HCl$ (LXVII) Table B-36, $C_5F_{10}Cl_2$ (LXVIII) Table B-37, $C_5F_{10}HBr$ (LXIX) Table B-38, $C_5F_{10}BrCl$ (LXX) Table 39, $C_5F_{10}Br_2$ (LXXI).

F-Neopentyl Bromide: Cl_2

Bromo-F-neopentane (0.03 mmol, 0.010 g) and chlorine (0.09 mmol, 0.0064 g) were condensed into the evacuated quartz cylindrical bulb. The contents were warmed to ambient temperature, and then irradiated with the 125 watt mercury vapor lamp for a total of 30 hours. The irradiation was interrupted three times at 2 hour intervals and at 6 hour intervals thereafter for infrared examination. The C-Cl band of F-neopentyl chloride at 860 cm^{-1} was noticable after two hours as a shoulder on the C-Br band of F-neopentyl bromide at 840 $cm.^{-1}$ Gas chromatographic assay of the total product indicated 90% F-neopentyl bromide, 8% F-neopentyl chloride and 2% F-pivaloyl chloride.

F-Neopentyl Bromide: Hg

Bromo-F-neopentane (0.04 mmol, 0.014 g) and mercury (0.5 mmol, 0.1 g) were combined in the evacuated quartz cylindrical bulb and irradiated for 47 hours with the 125 watt mercury lamp. Gas chromatographic assay of the total product indicated a mixture of 20% dimer, F-2,2,5,5-tetramethylhexane identified by its infrared spectra. The remainder consisted of unchanged starting material. F-2,2,5,5-tetremethylhexane (LXXII) is characterized in Table B-1.

F-Neopentyl Chloride: Hg

Chloro-F-neopentane (0.20 mmol 0.062 g) and mercury (1 mmol, 0.2 g) were combined in a second quartz vessel and the reaction carried out simultaneously with the bromo-F-neopentane reaction. Only a trace of dimer was produced in this reaction. Identification was made by GLC retention time comparison of products with the bromo-F-neopentane run.

1-Hydryl-F-2,5-Dioxahexane: BrCl

1-Hydryl-F-2,5-dioxahexane (0.3077 mmol, 0.075 g), chlorine (0.318 mmol, 0.0225 g) and bromine (0.3206 mmol, 0.0521 g) were condensed into the quartz bulb. On warming, the mixture was irradiated for 302 hours before coming to equilibrium. Workup produced 34.5% 1-bromo-F-2,5-dioxahexane (LXXIII), 37% 1-chloro-F-2,5-dioxahexane (LXXIV) and recovered 28.4% starting material (LXXIV). Characterizations are given: (LXXIII) in Table B-41, (LXXIV) in Table B-42, (LXXV) in Table B-43.

2-Difluoromethyl-2-Trifluoromethyl-4,4,5,5-Tetrafluoro-1,3-Dioxolane: BrCl

The starting material (0.563 mmol, 0.150 g), chlorine (0.588 mmol, 0.0417 g) and bromine (0.588 mmol, 0.0939 g) were condensed into the quartz bulb. On warming, the mixture was irradiated for 192 hours. Workup produced 59.5% 2-bromodifluoromethyl-2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane (LXXVI), 37.5% of the analogous

chloro-F-dioxolane (LXXVII) and 2.3% recovered starting material (LXXVIII). Characterizations are given: (LXXV) in Table B-44, (LXXVII) in Table B-45, (LXXVIII) in Table B-46.

Hydryl-F-Neopentane: BrF

The quartz bulb used in the BrCl reactions was fitted with a 9 mm x 50 mm "Teflon" FEP test tube, supported vertically in the bottom, and charged with approximately 25 g of sodium fluoride, 1/8" pellets (Harshaw). Approximately 1.80 mmol (0.10 ml, 0.25 g) of bromine trifluoride was syringed into the test tube under a nitrogen atmosphere. The quartz bulb was cooled with liquid nitrogen, evacuated, and 0.167 g (0.620 mmol) hydryl-F-neopentane and 0.290 g (1.80 mmol) bromine were condensed into the bulb. On warming, the mixture was irradiated for a total of 108 hours, although infrared assay showed little change after 24 hours. Workup produced bromo-F-neopentane (78.6%), F-neopentane (6.6%) and recovered starting material (14%).

1,3-Dihydryl-F-Neopentane: BrF

1,3-Dihydryl-F-neopentane (0.345 mmol, 0.0868 g) and bromine 0.313 mmol, 0.050 g) were condensed into the quartz bulb containing the bromine trifluoride (0.90 mmol, 0.05 mL, 0.12 g). On warming, the mixture was irradiated for 64 hours with most of the reaction occurring within the first 24 hours. Workup of the product produced 1,2-di-bromo-F-neopentane (20%), 1-bromo-3-hydryl-F-neopentane (15%), hydryl-F-neopentane (trace) and unreacted starting material (60%).

CHAPTER III

RESULTS AND DISCUSSION

A. AEROSOL FLUORINATION OF COMPOUNDS WITH SURVIVABLE FUNCTIONALITY

Acid Chlorides

Preparation of F-alkyl carboxylic acid derivatives. The ability to retain a functional group on a hydrocarbon during fluorination, such as an acyl halide, is desirable in many respects. It predetermines the site of functionality and produces the product in a single reaction. For instance, perfluorinated acids can be prepared indirectly by a number of methods analogous to their hydrocarbon counterparts, but these often require several steps. Some examples are the oxidation of chloro-F-alkanes.[52,53]

$$R_FCFCl_2 \xrightarrow{O_2\ \ U.V.,\ \ H_2O} R_FCOOH$$

$$R_FCCl_3 \xrightarrow{H_2SO_4\text{-}SO_3,\ H_2O} R_FCOOH$$

and chloro-F-alkenes[54,55]

$$CCl_2{=}CClCCl{=}CCl_2 \xrightarrow{SbF_3/SbF_3Cl_2} CF_3CCl{=}CClCF_3 \xrightarrow[heat]{KMnO_4} 2\ CF_3COOH$$

or from additions to fluoro alkenes.[56]

$$CF_3CF{=}CF_2 + F_2CO \xrightarrow[100^\circ]{CsF} (CF_3)_2CFCOF$$

First the appropriate chloro and chlorofluorocarbons must be made before the actual derivation to a carbonyl compound. These methods seem overly involved and wasteful of valuable starting materials when electrochemical fluorination can easily produce perfluorinated acid

fluorides in good yields from simple acid fluorides[57]

$$CH_3COF \longrightarrow CF_3COF \quad (75\text{-}85\%)$$

$$C_2H_5COF \longrightarrow C_2F_5COF \quad (51\%)$$

$$n\text{-}C_3H_7COF \longrightarrow n\text{-}C_3F_7COF \quad (39\%)$$

and somewhat poorer yields from acids, esters, aldehydes, and ketones.[28] Electrochemical fluorination is used industrially to produce simple acid fluorides. However, as the length or complexity of the hydrocarbon portion increases, the yields of perfluorinated acid fluorides decrease.

It had been proposed that highly branched hydrocarbons are more difficult to fluorinate, due to the large amount of steric crowding.[24,58] An unsuccessful attempt to fluorinate pivaloyl fluoride with potassium tetrafluorocobaltate (III) seemed to bear this out.[59] However, the LTG fluorination of pivaloyl fluoride in good yield (52%) dispelled this idea. It appeared that the direct fluorination of highly branched structures required more reaction time at higher fluorine concentrations to replace the last remaining hydrogens. Since the aerosol and LTG systems successfully fluorinated highly branched hydrocarbons such as neopentane,[39,36] it was thought that the aerosol fluorination system could similarly fluorinate the highly-branched, and functional pivaloyl chloride.

The LTG system, as well as most other methods, has an acidic environment due to the presence of HF and metal fluorides formed during the fluorination process. In the aerosol fluorination system, the presence of sodium fluoride particles could be viewed as a more

neutral or basic system in comparison to the metal fluorides of the LTG metal packing. Even the neutralization of HF by NaF to form the less acidic sodium bifluoride ($NaHF_2$) would make the aerosol system less acidic.[40] The successful aerosol fluorination of the acid sensitive 2,2-dimethyl-1,3-dioxolane seems to bear this out.[39] The LTG fluorination of acyl halides is limited to the acyl fluorides because of the tendency of the molecules to decarbonylate when the halogen is chlorine or bromine.[36] Thus pivaloyl chloride became a logical candidate to test the ability of the aerosol fluorination system in retaining carbonyl functionalities.

Aerosol fluorination of acid chlorides. The aerosol fluorination of pivaloyl chloride gave 0.76 g of F-pivaloyl fluoride in 73% purity and 48% yield under high-yield fluorination conditions (run 7, Table A-1). This compares quite favorably to the 52% yield produced by the LTG system. Although the chlorine was replaced by fluorine, very little decarbonylation occurred, unlike the LTG reaction. This tends to support the idea that the aerosol system is less acidic than the LTG system. An important advantage was shown in that the more readily available acid chlorides could be used.

An important point to note is that a 3 hour aerosol reaction gave 0.76 g of F-pivaloyl fluoride while a 7 day LTG reaction gave 2.26 g of the same product in approximately the same yield. Thus the aerosol system can produce significantly more functionalized fluorocarbon in high yields in a shorter time period. It should be noted that the only reason the aerosol reaction was not run longer was that the

researcher wanted to run the reaction and completely separate the products in one day. The aerosol system can obviously be run longer than 3 hours.

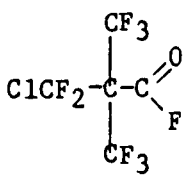
The initial aerosol fluorination runs (2 and 4) of pivaloyl chloride gave moderately high distributions of F-pivalyl fluoride but low yields based on the theoretical throughput. Investigation of this problem found that the loss was due to partially fluorinated material having low volatility collecting in the end coil and NaF trap. For runs 5 and 6 (Table A-1), the end coil was heated by a steam bath. The amount of material collected was greatly improved. However, the extra material collected was partially fluorinated products. Thus yields of F-pivaloyl fluoride were only improved slightly while its per cent distribution went down. In all the runs, a change in hydrocarbon throughput had relatively no effect on the yield obtained. Increasing the fluorine to hydrocarbon ratio in the

run	4	5	6a
hydrocarbon:F_2	1:11	1:16	1:36
stoich. amt. F_2	1.1	1.6	3.6
yields	14.4%	18.1%	19.7%

runs only increased the yields slightly. However, the yield was greatly increased when the main-carrier, helium flow was increased in run 7. The earlier six runs had a main carrier flow of 400 mL/min helium, while this was tripled to 1200 mL/min helium for run 7. In order to keep the percentage of fluorine around 4%, the fluorine flows were also tripled. Some of the increase in yield could be due to

higher fluorine flows, but this is not likely as noted for reactions 5 and 6. Also increasing the main flow reduced the residence or reaction time of the mobile reactants in the reactor. Thus run 6a had a reaction time of 148 sec while run 7 had a reaction time of 52 sec. This should have the effect of reducing, not increasing perfluorination. However, increasing the main carrier flow through the oven produces more and smaller NaF particles with a correspondingly large increase in total surface area. If in the formation of the aerosol particulates, the NaF particles are coated with several layers of hydrocarbon, then the lower layers of hydrocarbon will not be highly fluorinated. This could account for the large amount of partially fluorinated material found. A large increase in surface area allows the formation of more uniform and thinner layers of hydrocarbon. This in turn promotes more uniform attack by fluorine. Thus the yields of run 7 were dramatically improved.

In all the runs, free chlorine was formed. If the crude product mixtures were not kept dark and cold, or worked up just after a run, the free chlorine would slowly react with available hydrogens. This was noted by the gradual disappearance of chlorine in the crude product mixtures of runs 2, 4, and 6a. In these runs, chloro-F-pivaloyl fluoride (IV) was formed in 21%, 10% and 14.5% distribution



(IV)

respectively. However, when the free chlorine was removed by vacuum line fractionation soon after the products were collected, (IV) was not found. This suggests that although free chlorine is formed during the reaction, chlorination does not occur during the reaction as happens in other fluorination methods. This is probably due to the short residence or reaction time and the low temperatures, which are not favorable conditions for chlorination.

As noted for other aerosol fluorination reactions, the products are stable to photochemical fluorination of the last few remaining hydrogens. The percent distribution is typical of other photochemically finished runs.[39] Runs 6a and 6b were run under identical conditions except that 6b was not photochemically finished. The distribution of the partially fluorinated material shown in Figure 15 is not significantly different, except in magnitude.

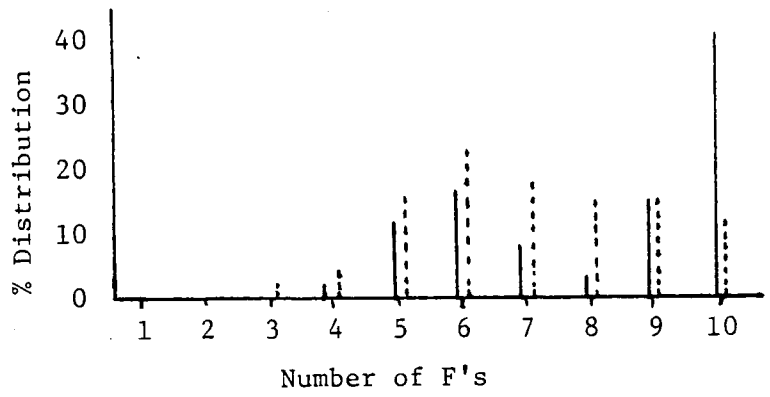


Figure 15. Distribution of F's on products of run 6 from the aerosol fluorination of pivaloyl chloride.

| 6a, photochemically finished.

¦ 6b, nonphotochemically finished.

Photochemical finishing results in singular enhancement of perfluorination at a slight expense of partial fluorination. This effect is obviously due to excited hydrocarbon molecules being produced and scavenging available fluorine molecules in a sustained sequence of reaction steps culminating in perfluorination. Such observations are compatible with a radical chain propagation mechanism modified to allow for reaction energy storage within the partially fluorinated molecule, which supports a finding discovered earlier in neopentane fluorinations.[39]

A single 3-h aerosol fluorination run of butyryl chloride gave 1.13 g of F-butyryl fluoride in 80% distribution and 58% yield. This reaction (Table A-2) was run with a high main carrier flow of 1000 mL/min helium. The hydrocarbon:fluorine ratio of 1:33 was half that of the high yield pivaloyl chloride run. This shows that the high yields are due more to a high main carrier flow than high fluorine flows.

The results of two iso-butyryl chloride reactions (Table A-3) at first glance seem to contradict the above statement about fluorine flows. Both reactions were run with 1000 mL/min main flows and similar conditions except for the hydrocarbon:fluorine ratio. Run 1 had only a 5% yield while run 2 had a 53% yield.

run number	(1)	(2)
hydrocarbon (mmol/h)	4	3
total F_2 flow (mL/min)	40	60
hydrocarbon:F_2 ratio	1:24	1:49
percent yield	5%	53%

However, the distribution of products from run 1 shown in Figure 16 is not that normally seen for photochemically finished reactions while

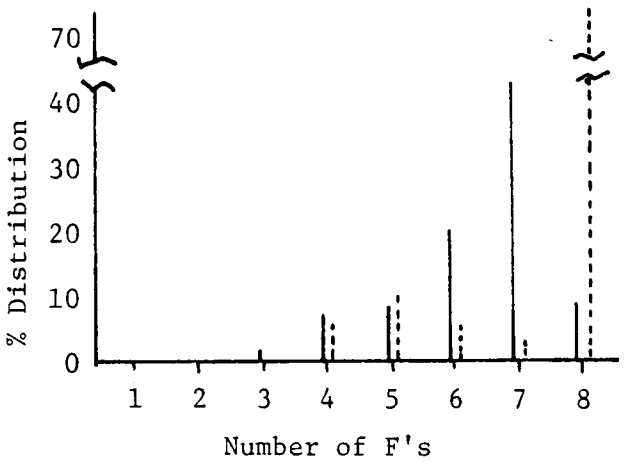
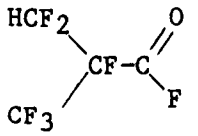


Figure 16. Distribution of F's on products from the aerosol fluorination of iso-butyryl chloride.

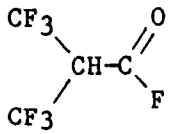
| 1, insufficient fluorine.

⋮ 2, excess fluorine.

run 2 is. This suggests that without sufficient fluorine, the molecules in run 1 were stopping just short of perfluorination. Both monohydryl products were found in 18% distribution. Statistical



(VIII)

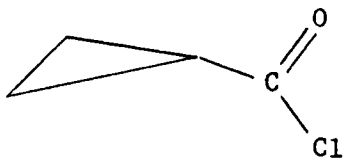


(IX)

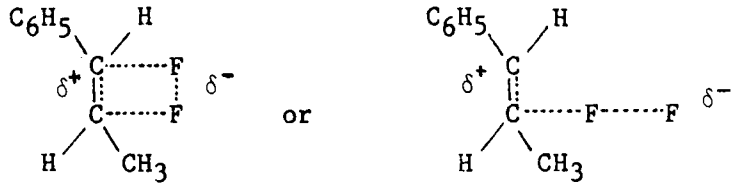
replacement of hydrogens by fluorine would indicate that the Δ-hyrogen would be replaced before all six β-hydrogens would be replaced. Thus the expected amount of (IX) is much smaller than (VIII) on a purely statistical basis. Thus fluorine attack on the Δ-hydrogen is inhibited somehow. Bockemuller[4] observed that fluorine attacked the

α-hydrogen and not the β-hydrogen in iso-butyric acid, while bromine attacked the α-hydrogen preferentially. Both steric and electronic effects could be used to explain this observation. However, Bockemuller also observed that fluorine preferentially attacked the β- and γ-hydrogens of butyric acid. This argues more for an electronic effect of the carbonyl group inhibiting fluorine attack on an adjacent carbon.

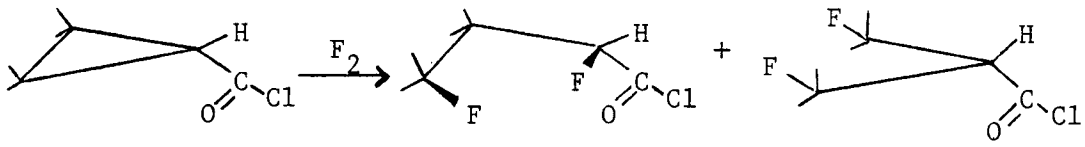
In the aerosol fluorination of cyclopropyl carbonyl chloride



no definite products could be isolated with an intact ring structure. However, of the mixtures collected, a few were thought to contain minor amounts of one or more partially fluorinated ring structures due to the large ^{19}F NMR coupling constants (250 Hz) for peaks in the -100 to -140 ppm range. The perfluorinated ring opened products for several reactions (Table A-4) were generally in a 3:2 ratio of F-butyryl fluoride (V) and F-iso-butyryl fluoride (VI). In many reactions, cyclopropyl rings resemble double bonds. Halogenation of cyclopropane usually gives the 1,3-dihalo-propane. Meritt found that fluorine adds across double bonds predominantly in a cis manner in preference to hydrogen substitution.[22] He proposed that the fluorination involved a polar molecular complex

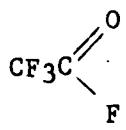


If fluorine added concertedly, a 2:1 ratio of F-butyryl fluoride to F-isobutyryl fluoride would be expected to be formed if there

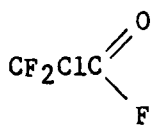


were no steric, electronic or polar effects. A 3:2 ratio seems to indicate some slight preference for fluorine addition opposite the carbonyl group, similar to fluorine attack of the β-hydrogens of isobutyryl chloride. However, there is not enough information to indicate whether this is due to steric or electronic effects of the carbonyl group and/or a polar effect of the attacking fluorine.

Aerosol fluorination of chloroacetyl chloride under high fluorination conditions (Table A-5) gave F-acetyl fluoride (XII) chloro-F-acetyl fluoride (XII)



(XII)



(XIII)

in 20% and 34% yields. The acyl chlorine was always replaced by a fluorine whereas the other chlorine was more resistant to replacement. Chloro-F-acetyl derivatives have been made in 19% yield by fluorination of methyl trichloroacetate with SbF_3,[60] in 31% yield by electrochemical fluorination of chloroacetyl fluoride,[61] and in 77% yield by oxidation of chlorotrifluoroethylene.[51]

These reactions show that replacement of hydrogen by fluorine occurs more readily than replacement of chlorine. The sodium salt of chloro-F-acetic acid has been shown to be a good source of difluorocarbene as shown at the bottom of Table 3. Perfluorocarboxylic acid derivatives undergo many of the same reactions as their hydrocarbon analogues. Some examples are given in Table 3.

Alkyl Chlorides

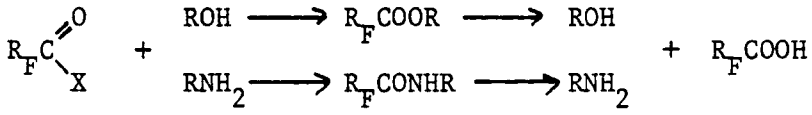
Reactions and preparations of F-alkyl chlorides. The direct fluorination of alkyl chlorides is valuable in several respects. Alkyl chlorides can easily be obtained with one or more chlorines in desired positions. Hydrogens are replaced in preference to those chlorines by fluorine in the aerosol system. This was shown in the aerosol fluorination of $ClCH_2COCl$ and in the many examples of chloroalkanes. Many of the perfluorinated alkyl chlorides produced by the aerosol system cannot be easily made by other methods. Finally, these same products can be easily converted to perfluoroalkenes which can be used in further reactions. Some typical reactions by which F-alkyl chlorides can be derivatized are shown in Table 4. These include elimination of chlorine to form F-alkenes and carbenes, oxidations to form F-carboxylic acids, reductions to hydryl-F-alkanes, and exchange reactions.

Early attempts at direct fluorination of chloroalkanes often gave mixtures of many chlorofluoro compounds.[2-9] Many of these compounds

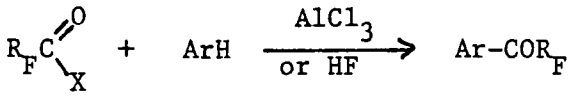
TABLE 3

Typical reactions of perfluorocarboxylic acid derivatives[a]

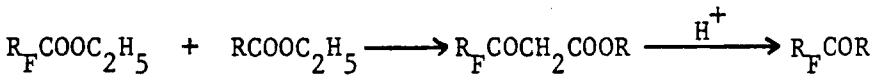
Acylation of Active Hydrogens



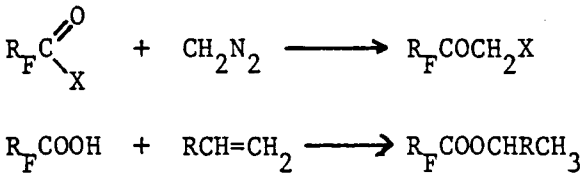
Friedal Crafts Acylations



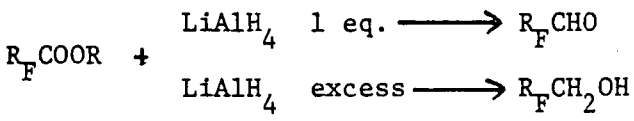
Active Methylene Condensations



Addition Reactions



Reduction



Reactions with Organometallic Reagents

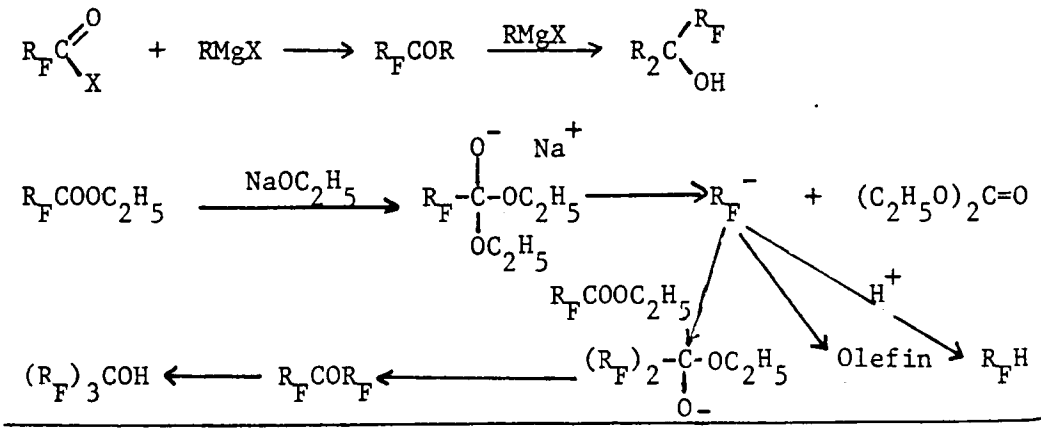
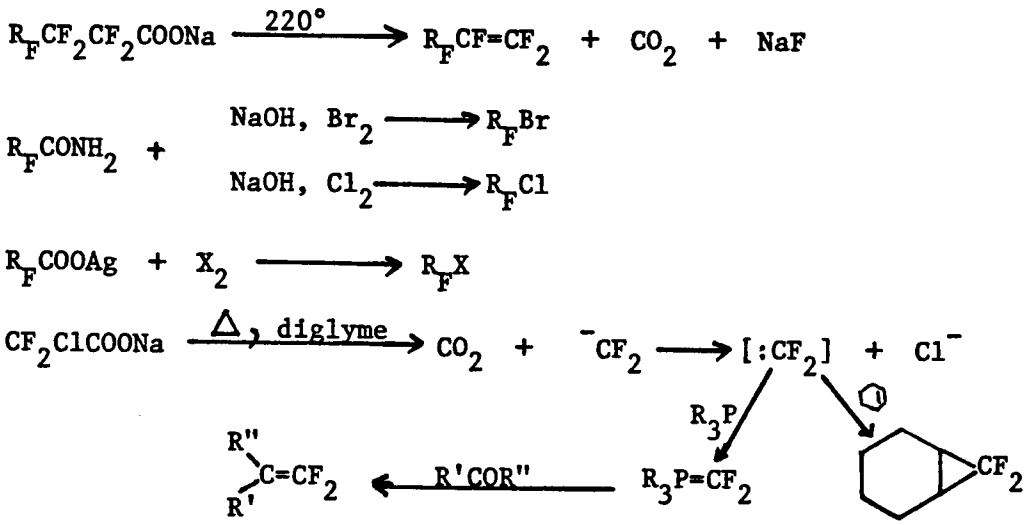


TABLE 3 (Continued)

Decarboxylation



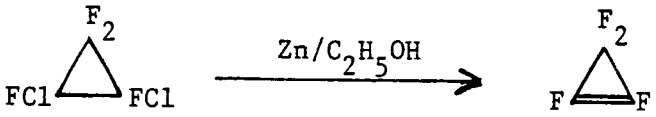
[a] Compiled from Chambers,[63] Hudlicky,[12] and Sheppard and Sharts.[64]

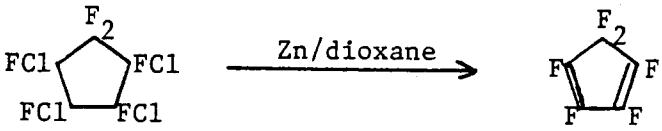
TABLE 4

Reactions of perfluoroalkyl chlorides [a]

Eliminations

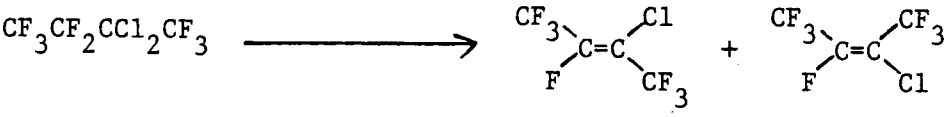
$CFCl_2CF_2Cl \xrightarrow{Zn/C_2H_5OH} CFCl{=}CF_2$





$R_FCF_2CF_2Cl \longrightarrow R_FCF{=}CF_2$

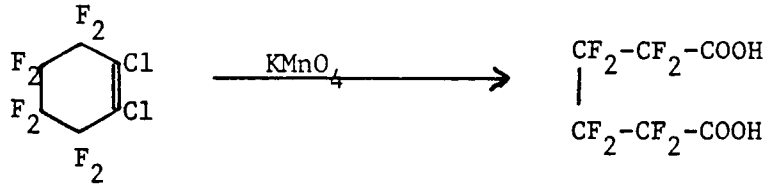
$CF_3CF_2CFClCF_3 \longrightarrow CF_3CF{=}CFCF_3 + CF_3CF_2CF{=}CF_2$



$ClCF_2H \xrightarrow{base} ClCF_2^- \longrightarrow [:CF_2] + Cl^-$

$CCl_2F_2 \xrightarrow{Zn,\ 550°} [:CF_2] \longrightarrow CF_2{=}CF_2$

Oxidations



$R_FCFCl_2 \longrightarrow R_FCOOH$

TABLE 4 (Continued)

Reductions

$$CF_2Cl_2 \xrightarrow{H_2/Pt} CF_2HCl + CF_2H_2$$

$$CClF{=}CF_2 \xrightarrow{H_2/Pd} CH{=}CF_2 + CFH_2CF_2H$$

Rearrangements

$$CFCl_2CFCl_2 \xrightarrow{AlBr_3/70^\circ} CF_2ClCCl_3$$

$$CF_2ClCFCl_2 \xrightarrow{AlCl_3/60^\circ} CF_3CCl_3 + CClF_2CCl_3$$

Exchanges

$$CF_2Br_2 + CF_2ClCFCl_2 \xrightarrow{AlBr_3} CF_2Cl_2 + CF_3Br + CF_2BrCl + CBr_4 + CF_2ClCBrCl_2 + CF_2BrCCl_3 + CF_2ClCFBrCl + CF_3CBrCl_2$$

$$R_FCF_2Cl \xrightarrow{ClSO_3F} R_FOSO_2F \xrightarrow{MOH} R_FCOOM$$

[a] Compiled from Chambers,[63] Hudlicky,[12] and Sheppard and Sharts.[64]

contained more chlorines than the starting materials. Some of these reactions are shown in Table 5.

More recently, Schmeiser, et al.[65] attempted a direct fluorination of 1,2-dichloropropane to synthesize 1,2-dichloro-F-propane from which they expected to produce F-propene. Unfortunately, they conducted the reaction at 100-200°C and produced a complex mixture of products. Some of these products shown in Table 5 contained 3 or 4 chlorines. This demonstrated that free chlorine was formed under the reaction conditions and that chlorination as well as dimerization occurred.

Electrochemical fluorination of chloroalkanes also showed the same marginal stability towards fluorination as shown in Table 5. Electrochemical fluorination of 1,2-dichloroethane produced fluorinated mono-, di- and tri-chloroethanes.[66]

In the indirect fluorination methods, chlorines are replaced in prefence to hydrogens. Some typical reactions are shown in Table 5. Complete fluorination of highly chlorinated materials to only one or two remaining chlorines is difficult and often requires extreme conditions. The mono- and di-chloro compounds obtained are often secondary chlorides, as these have lower reactivity towards fluorination.[14] However, predicting the position of the last remaining chlorine is not easy nor accurate.

Chloro-F-alkanes can also be made from other perfluorinated compounds. These reactions are shown in Table 5. Salts of perfluorocarboxylic acids are converted to chlorides by $ClOSO_2F$.[73,74]

TABLE 5

Formation of F-alkyl chlorides

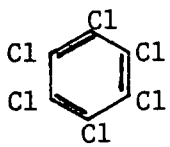
Reaction	Reference
Direct Fluorination	
$C_2Cl_6 \xrightarrow{F_2/N_2} CFCl_2CFCl_2$	5
$C_2H_5Cl \xrightarrow{F_2} CF_4,\ CF_3Cl,\ CF_3CF_2Cl,\ CHF_2CH_2Cl,\ CF_2{=}CCl_2,\ CH_3CHCl_2,\ CHF_2CHCl_2$	7
$CCl_4 \xrightarrow{F_2} CFCl_3,\ CF_2Cl_2,\ CF_3Cl,\ CF_4$	3
$CHCl_2CHCl_2 \xrightarrow{F_2} CHCl_2CFCl_2,\ CCl_3CHCl_2,\ CCl_2{=}CHCl,\ CFCl_2CFCl_2$	9
$CH_3CHClCH_2Cl \xrightarrow[100\text{-}200°]{F_2/N_2} CF_3CFClCF_2Cl,\ CF_2ClCF_2CF_2Cl,\ C_3F_5Cl_3,\ C_3F_4Cl_4$	65
Electrochemical Fluorination	
$CH_2ClCH_2Cl \xrightarrow{5\text{-}6\ V}$ Fluorinated mono-, di-, and trichloroethanes	66
Indirect Fluorination	
$CCl_3CCl_3 \xrightarrow{SbF_3Cl_2} CFCl_2CFCl_2,\ CFCl_2CF_2Cl,\ CF_2ClCF_2Cl$	67
$CH_3CCl_3 \xrightarrow{HF/SbF_3} CH_3CF_2Cl,\ CH_3CFCl_2$	68
$C_4Cl_6 \xrightarrow[2.)\ CoF_3]{1.)\ HF/Cl_2/SbCl_3} CF_3CF_2CFClCF_3$	69
$CF_3CFClCCl_2CF_3 \xrightarrow[AlBr_3]{F_2 \text{ or } ClF_3} CF_3CF_2CFClCF_3$	70
 $\xrightarrow[350°]{CoF_3} C_6F_{12-n}Cl_n$	71

TABLE 5 (Continued)

Substitution of Perfluoroalkyl Derivatives	
$R_FCOOM \xrightarrow{ClOSO_2F} R_FCl$	73,74
$R_FCOOAg \xrightarrow{Cl_2} R_FCl$	75-78
$R_FI \xrightarrow{Cl_2,\ U.V.} R_FCl$	79-81
$R_FH \xrightarrow{Cl_2,\ U.V.} R_FCl$	79-81
$R_FCOR_F \xrightarrow{PCl_5} R_FCCl_2R_F$	82
Pyrolytic Addition of Chlorine	
$R_FR'_F \xrightarrow[900°]{Cl_2} R_FCl + R'_FCl$	83
Addition of Chlorine to Perfluoroalkenes	
$R_FCF=CF_2 \xrightarrow{Cl_2,\ U.V.} R_FCFClCF_2Cl$	84
$R_fCF=CF_2 \xrightarrow{HCl/\ 230°} R_FCHFCF_2Cl$	83

The silver salts are also converted to halides by a Hunsdiecker type of reaction.[75-78] Perfluoroalkyl iodides and hydrides are easily chlorinated.[79-81] Perfluoroketones can be converted to gem-dichlorides by PCl_5.[82] Perfluorinated alkanes can be thermally decomposed by chlorine at 900°C into smaller fragment chloro-F-alkanes.[83] Chlorine and hydrogen chloride can also be added across the double bond of F-alkenes.

The unsuccessful fluorination of 1,2-dichloroethane by Schmeiser, et al.[65] probably resulted from the high temperatures used. The success of the aerosol fluorination reactions was probably due to the low temperatures, low fluorine concentration, extremely low chlorine concentration if any was formed, and short reaction times. Thus hydrogens were preferentially replaced by fluorine. If some small amount of free chlorine was formed, the reaction conditions did not favor chlorination.

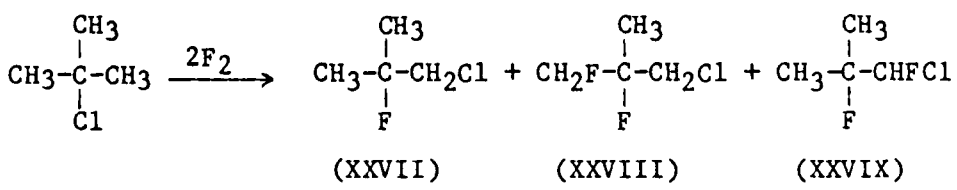
Aerosol Fluorination of Monochloroalkanes. The fluorination of neopentyl chloride showed the stability of an attached chlorine towards fluorination. Only 18% of the 2.56 g collected products had no chlorine, while 79.6% was F-neopentyl chloride. There was no rearrangement of the carbon skeleton. This implies that there was no formation of a carbocation, since neopentyl structures are susceptible to carbocation rearrangement,[86] but not to radical rearrangement.[87] Thus the fluorination process probably occurs by a free radical mechanism. There were no products observed which contained more than one chlorine. As was observed with the fluorination of acid

chlorides, an increase in the main-carrier helium flow of 400 to 1000 mL/min increased the yield of F-neopentyl chloride from 15% to 74%.

Aerosol fluorination of other primary alkyl chlorides also showed the same exceptional stability and gave good yields. Aerosol fluorination of 1-chloropropane gave 1-chloro-F-propane in 85% distribution and 63% yield. Similarly, aerosol fluorination of 1-chlorobutane gave 1-chloro-F-butane in somewhat lower distribution (60%) and yield (44%). The yields of the above two reactions were produced with 1000 mL/min main carrier flows. An earlier run of 1-chlorobutane at a 400 mL/min main flow gave only 15% yield of 1-chloro-F-butane. As with other reactions, this shows that the main carrier flow is critical for high perfluorination yields. The aerosol fluorination of iso-butyl chloride produced F-iso-butyl chloride in 76.4% purity and 41.6% yield.

The aerosol fluorination of tertiary butyl chloride did not give the expected F-tert-butyl chloride. Instead, the only major product observed was F-iso-butyl chloride in 80.4% purity and 47% yield. No products were observed that corresponded to spectra of F-tert-butyl chloride.[88] No tertiary chlorines were found on any of the products.

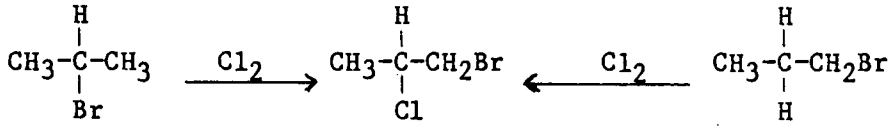
A second reaction (run 2, Table 16), with only 6 mmol/h of fluorine, 3 mmol/h tert-butyl chloride, and without photochemical finishing gave 30% unreacted tert-butyl chloride, 30% (XXVII), 20%



(XXVII) (XXVIII) (XXVIX)

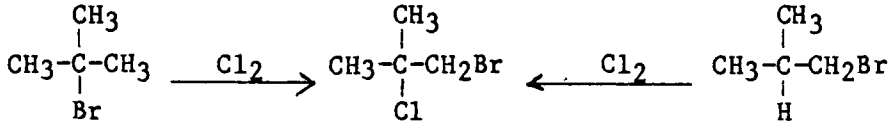
(XXVIII), 2% (XXVIX), and more highly fluorinated material (15%). The only tertiary chlorine observed was for unreacted starting material. No free chlorine was observed, nor were any products found to contain more than one chlorine. This showed that a chloride shift occurs upon initial fluorination and not by photolysis. Also, chlorine fission due to photolysis or fluorine displacement apparently does not occur with any significance.

Skell, Allen, and Gilmour[89] observed a similar rearrangement when chlorination of 2-bromopropane gave 15% 1-bromo-2-chloropropane (a)



(a)

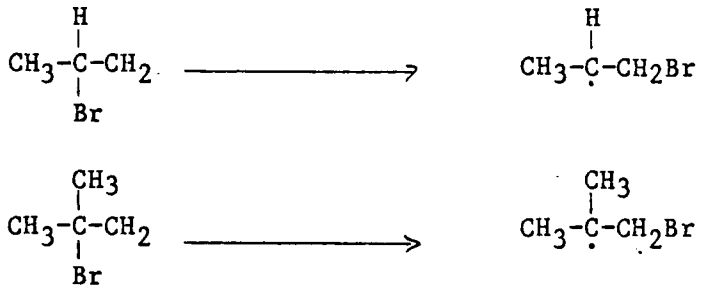
and 2-bromo-2-methylpropane gave 92% 1-bromo-2-chloro-2-methylpropane (b)



(b)

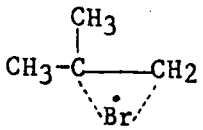
Chlorination of 1-bromo-propane gave (a) in 40% yield and 1-bromo-2-methylpropane gave (b) in 57% yield. These experiments indicated 100% rearrangement occurred when a hydrogen atom was removed from the methyl groups of iso-propyl and tert-butyl bromides. These rearrangements to give more stable radicals occurred much more rapidly than the

attack by chlorine on these radicals. Bromine migration was shown to



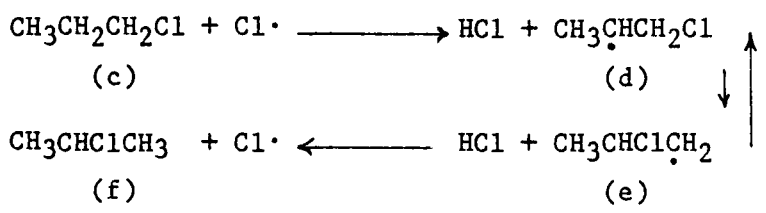
be much faster than methyl migration.[89]

Juneja and Hodnett[90] observed that the same 1,2 bromine shift occurred during the chlorination of tert-butyl bromide. They proposed that this occurred by the formation of an intermediate bridged radical



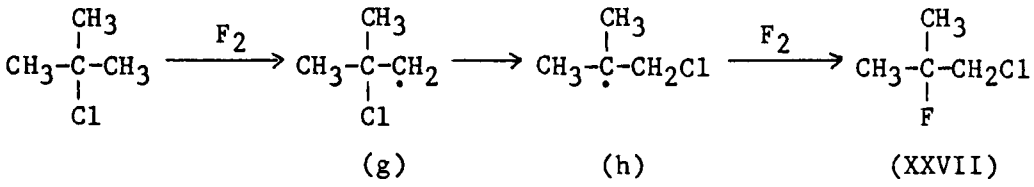
This would open preferentially at the tertiary position when attacked by a chlorine atom because of the electron-releasing ability of the methyl groups. They observed no rearrangements during either the chlorination of iso-butyl bromides, or in the bromination of iso-butyl and tert-butyl chlorides.

Wiley, et al.[91] noticed the isomerization of n-propyl chloride to isopropyl chloride during radioloysis, but not the reverse reaction. Benson and Willard[92] observed that this reaction was catalyzed by HCl and that the H atom exchanges, not the Cl atom. Mayo[93] postulated that an equilibrium between a secondary and a primary radical could explain this rearrangement.



In reactions of radicals (d) and (e) which require little activation, the products correspond to the more stable radical (d). In reactions of radicals (d) and (e) which require a large activation energy and are therfore relatively difficult, as with HCl, then the more stable product (f) is formed from minor proportions of the less stable,[92] but more reactive radical (e).

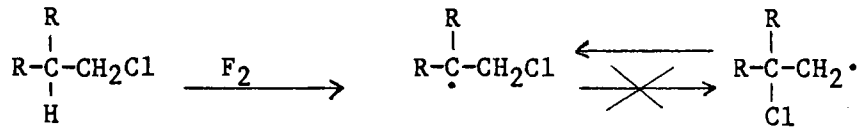
The fluorination of alkyl chlorides requires little or no activation energy (1 to 4 Kcal/mole). Thus if such an equilibrium existed in the fluorination of tert-butyl chloride, the more stable radical would be expected to add a fluorine atom. Thus initial reaction of fluorine would form the radical (g)



which would rearrange to the more stable radical (h). This 1,2-chlorine shift occurs faster than reaction with a fluorine molecule or or than a methyl migration. Reaction of (XXVII) with additional fluorine causes no further rearrangements and gives the difluoro products (XXVIII) and (XXIX).

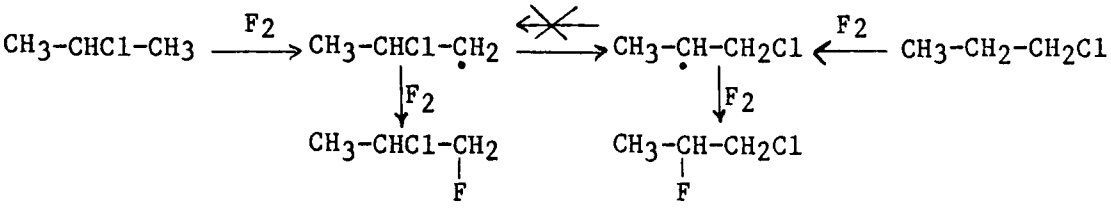
Such a mechanism also helps explain why no rearrangements occur during the aerosol fluorination of primary chlorides. The chlorine

rearrangement of a secondary or tertiary free radical adjacent to a



primary radical would not be favorable. If an equilibrium existed between the two radicals, it would favor the more stable secondary or tertiary radical. The aerosol fluorination of iso-butyl chloride to give only F-iso-butyl chloride seems to bear this out.

The aerosol fluorination of 2-chloropropane gave another opportunity to test this equilibrium. This reaction gave both 1-chloro-F-propane and 2-chloro-F-propane. Since the fluorination



of 1-chloropropane gave only 1-chloro-F-propane, this suggests that the secondary radical is more stable than the primary radical and/or that the secondary radical does not rearrange to the primary radical.

A similar mechanism is expected for the aerosol fluorination of 2-chlorobutane as both 2-chloro-F-butane (30%) and 1-chloro-F-butane (43%) were produced, while 1-chlorobutane gave only 1-chloro-F-butane.

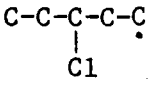
The question of whether a chlorine migration could occur for a secondary chlorine to another secondary position was not answered by the aerosol fluorination of chlorocyclopentane. As all the carbons are secondary, a chlorine migration could not be observed unless the carbons were labeled. This reaction did demonstrate that

chloro-F-cyclopentane could be produced directly in a decent yield of 40% without significant ring opening.

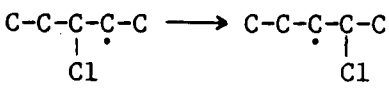
The aerosol fluorination of 3-chloropentane provided an indication that a chlorine could shift from one secondary carbon to another secondary carbon. All three possible mono-chloro isomers were formed

$CF_3CF_2CFClCF_2CF_3$ (XXIII) $CF_3CF_2CF_2CFClCF_3$ (XXIV) $CF_3CF_2CF_2CF_2CF_2Cl$ (XXV)

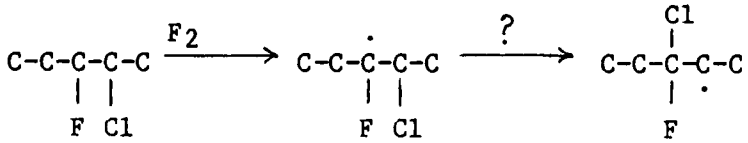
in the ratio 2:3:1 respectively. Initial fluorination is most likely to occur at the ends and thus no rearrangement is expected.



The chlorine migration occurs only when an adjacent secondary free radical is formed. This gives the possibility of moving in either direction. Since there is no large difference in the



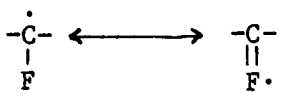
stabilities or energies of the two radicals, and hence no significant driving force, the chloride shift is not encouraged. Thus some chlorine remains on the original carbon and some migrates. Unfortunately, the data do not indicate whether a chlorine could migrate to a carbon after it had added a fluorine. Of the two possible radicals,



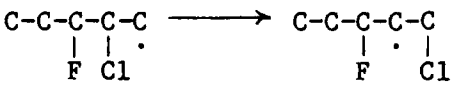
(i) (j)

it is likely that (i) is more stable due to the resonance effect of

the attached fluorine. The lack of such resonance stabilization for (j) would thus prevent its formation.

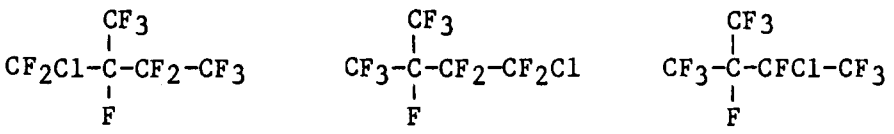


Thus it is not likely that chlorine will shift back to its original carbon that already has accumulated a fluorine. However, migration of the chlorine to the primary carbon could readily ocur as indicated



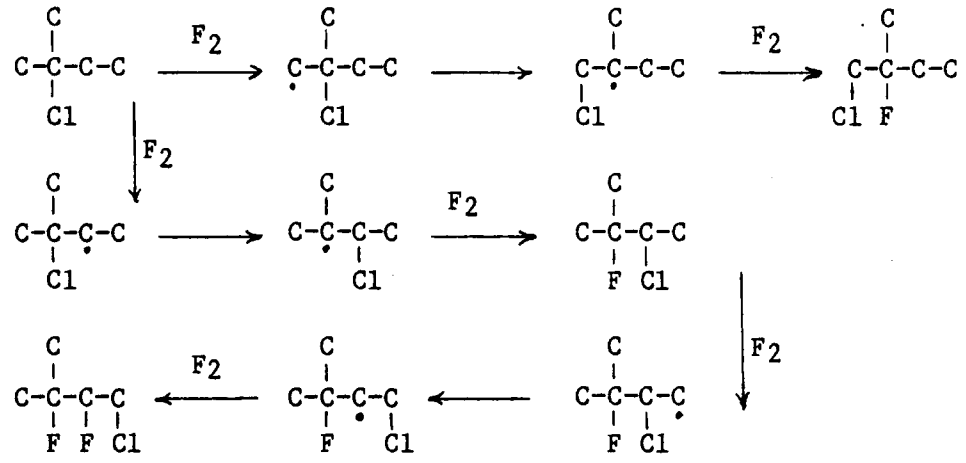
from the fluorination of 2-chlorobutane which gave 2-chloro- and 1-chloro-F-butane. Also, formation of the primary radical is much more likely than formation of the secondary radical (i) due to higher statistical probability and more active primary hydrogens.

The aerosol fluorination of tert-amyl chloride gave three isomers



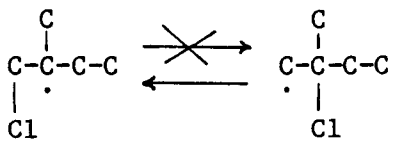
(XIX) (XX) (XXX)

in the ratio of 16:6.5:1 respectively. Again the tertiary chlorine can rearrange from a primary to a tertiary radical by a 1,2-chloride shift giving the primary chloride. The tertiary chlorine can also shift from an adjacent secondary radical to a tertiary radical by a 1,2-chloride shift giving the secondary chloride.



The secondary chloride can subsequently rearrange upon formation of an adjacent primary radical by another 1,2-chlorine shift giving a slightly more stable secondary radical and eventually a primary chloride. Thus the observed ratio is close to that expected statistically although weighted more in favor of initial secondary radical formation.

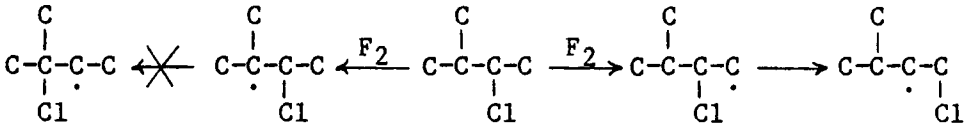
The aerosol fluorination of 1-chloro-2-methylbutane gave 1-chloro-F-2-methylbutane in 39% yield. The other two chloro-F-isomers (XX) and (XXX) were not formed. As with iso-butyl chloride, this showed that primary chlorides do not rearrange to tertiary chlorides.



As the initially formed tertiary radical is much more stable than a possible primary radical that would be formed by a 1,2-chloride shift. This also supports the reverse reaction, i.e., rearrangement of a primary radical to a more stable tertiary radical by a 1,2-chloride shift.

The aerosol fluorination of 1-chloro-3-methylbutane was uneventful as it produced 1-chloro-F-3-methylbutane as the only major product in 36% yield. The other chloro-F- isomers were not formed. As was typical with other primary chlorides, no rearrangement occurred.

Aerosol fluorination of 2-chloro-3-methyl butane gave a mixture of 2-chloro-F-3-methylbutane and 1-chloro-F-3-methylbutane. This showed that the secondary chloride partially migrated to a primary position similar to the partial migrations of other secondary



chlorides. However, the chlorine did not migrate to or through the tertiary position as neither 1-chloro-F-2-methylbutane nor 2-chloro-F-2-methylbutane were found. This is expected as the initial tertiary radical would not rearrange to the less stable secondary radical. These last three aerosol reactions also showed that 1,3 chloride shifts were not occuring.

A summary of the 1,2-chloride rearrangements observed and their possible equilibria are shown in Table 6. These same possible 1,2-chlorine shifts and the corresponding free radical rearrangements are given in Table 7. It appears that a 1,2-chloride shift occurs completely whenever a very stable tertiary radical can be formed from from such a rearrangement. A 1,2-chloride shift does not occur whenever a primary radical would be formed by such a process. Whether secondary chlorides rearrange is dependent on the initial radical

TABLE 6

Alkyl chloride rearrangements

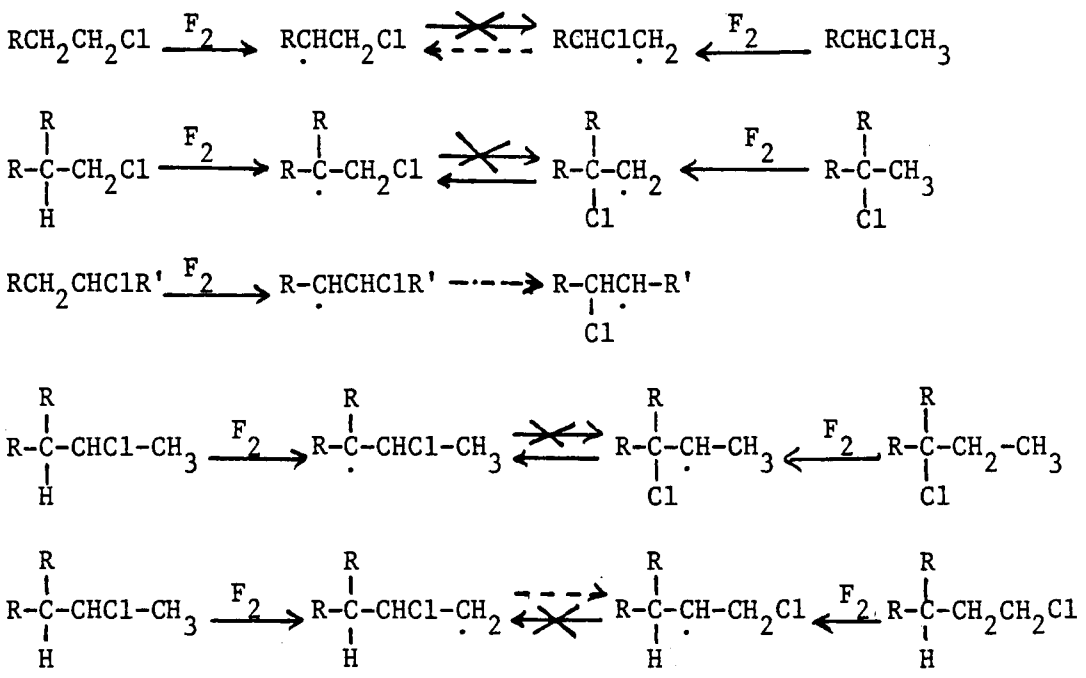


TABLE 7

Summary of 1,2-chloride shifts

Chlorides	Radicals
1° ⟶✕⟵ 3°	3° ⟶✕⟵ 1°
1° ⟶✕⟵ 2°	2° ⟶✕⟵ 1°
1° ⟶?⟵ 1°	1° ⟶?⟵ 1°
2° ⟶✕⟵ 3°	3° ⟶✕⟵ 2°
2° ⟵- - -⟶ 2°	2° ⟵- - -⟶ 2°
2° ⟵- - -⟶ 1°	1° ⟵- - -⟶ 2°
3° ⟶?⟵ 3°	3° ⟶?⟵ 3°
3° ⟵——⟶ 2°	2° ⟵——⟶ 3°
3° ⟵——⟶ 1°	1° ⟵——⟶ 3°

⟶✕⟵ Shifts do not proceed in this direction

⟶?⟵ Unknown

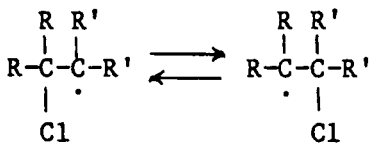
⟵- - -⟶ Shifts procede partially

⟵——⟶ Shifts procede completely

formed. Thus an initially formed tertiary radical would not rearrange to a secondary radical. Initially formed primary or secondary radicals allow partial rearrangement to secondary radicals. A primary to primary chloride shift would be possible but quite rare and would only be observable by labeling a carbon.

$$\overset{\cdot}{C}H_2\text{-}CH_2Cl \rightleftharpoons CH_2Cl\text{-}\overset{\cdot}{C}H_2$$

A tertiary to tertiary chlorine shift would also be possible but not common. The equilibrium, stabilities of the radicals, and the



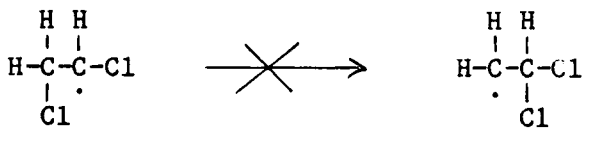
products formed would depend on the substituent groups. However, a 1,2-chloride shift to one of the groups, if possible, would be more likely.

Aerosol fluorination of dichloroalkanes. The aerosol fluorination of 1,2-dichloroethane gave 1,2-dichloro-F-ethane in very high 90% purity and 79% yield. This is quite an improvement over the lower yields obtained by other methods. This reaction showed an important relationship between the temperature and helium flow in the hydrocarbon evaporator and the yields obtained. Two reactions were run under similar conditions (Table A-18) except for the temperature and helium flow

temperature	0°C	-23°C
He flow, mL/min	13	45
yield	66%	79%

of the hydrocarbon evaporator. The lower temperature required a higher helium flow to maintain a comparable throughput in the second reaction. This points out that if the hydrocarbon helium flow is low, then the yields are lower than comparable reactions with higher hydrocarbon helium flows. This may be due to several factors. The throughputs are not as accurately measured and controlled at lower helium flows. The lower helium flows may not be as able to effectively deliver hydrocarbon into the aerosol generator against its slight back pressure. An assumption was made that the pressure in the reactor was atmospheric, but it may be slightly greater. Another assumption was made that the hydrocarbon collected in a liquid nitrogen trap just prior to delivery into the aerosol generator for throughput determinations would be the same as during operating conditions. These approximations tend to make the theoretical throughput slightly higher than the actual throughputs. Thus calculated yields are probably a little lower than actual yields. This would also help explain why less material is collected than expected. Of course some hydrocarbon does not leave the aerosol generator or reactor because it freezes to the walls while some may remain in an aerosol state and consequently passes through the liquid nitrogen product collection trap.

As no 1,1-dichloro-F-ethane was observed upon fluorination of 1,2-dichloroethane, the rearrangement



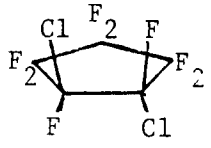
(k) (l)

probably did not occur. A primary to primary radical rearrangement might occur, especially for chloroethane, similarly to secondary radicals. However, since this does not happen in the above reaction, the initially formed radical (k) must be more stable than the rearranged primary radical (l). This implies that the attached chlorine stabilizes the radical (k). Freidlina has reviewed several chlorine rearrangements in which radicals are stablized by attached chlorines.[97] Thus radical (k) may be closer to a secondary radical and rearrangement to a primary radical is not favored.

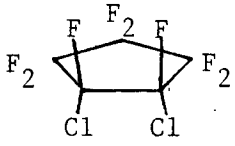
The aerosol fluorination of 1,2-dichloro-2-methylpropane gave 90% of 1,3-dichloro-F-2-methylpropane as the only perfluorinated dichloride in 63% yield. This showed once again that a tertiary chlorine rearranges to a primary position, while a primary chlorine does not rearrange. Since no 1,1-dichloro-F-2-methylpropane was found, this implies that the initial fluorine attack is directed away from the chlorine to the unhalogenated methyl groups.

The aerosol fluorination of 1,3-dichloropropane was uneventful in producing 1,3-dichloro-F-propane in 80% purity and 45% yield. As might be expected, the primary chlorines did not rearrange to a secondary position.

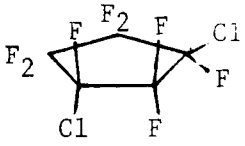
The aerosol fluorination of 1,2-dichlorocyclopentane gave four dichloro-F-isomers in 38% total yield (10%, 9%, 10%, 9% respectively).



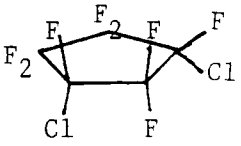
trans-1,2



cis-1,2



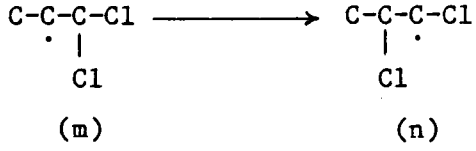
trans-1,3



cis-1,3

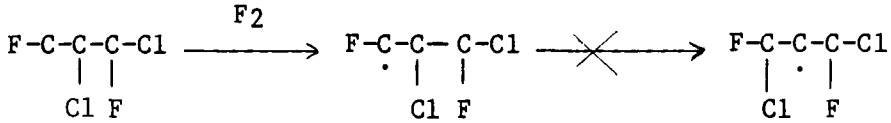
This shows that secondary chlorides can rearrange to other secondary positions. It also shows that cis/trans isomerization also occurs as might be expected in a free radical process.

Aerosol fluorination of geminal dichloroalkanes. The aerosol fluorination of geminal dichloroalkanes gave the opportunity to further study the stability of chlorine stablized radicals. The aerosol fluorination of 1,1-dichloropropane gave a 1:1 ratio of 1,1-dichloro-F-propane and 1,2-dichloro-F-propane in an inseparable mixture. This suggests that the chlorine stabilized radical (n)



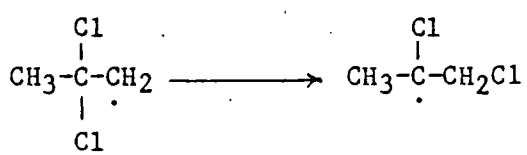
(m) (n)

has about the same stability as the initially formed secondary radical (m). Further migration might be possible, but would not be expected as the terminal methyl carbon would be statistically likely to already have been fluorine substituted before the initial chlorine shift.

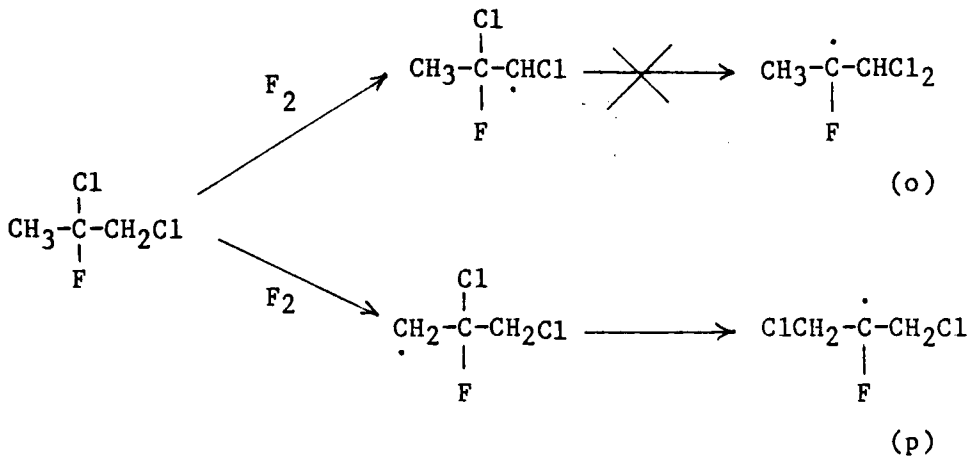


This would tend to inhibit a second fluorine attack and formation of a radical.

In the aerosol fluorination of 2,2-dichloropropane, initial attack by fluorine can only occur on the terminal methyl hydrogens, forming a primary radical on the terminal methyl.

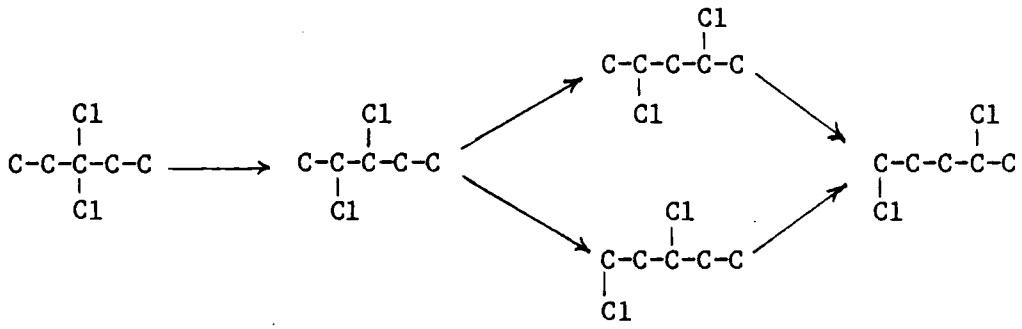


If the chlorine atom stablizes the radical as presumed, then migration of chlorine would be equivalent to a primary to tertiary radical rearrangement. This rearrangement evidently occurs completely in the same manner as the tertiary chloride rearrangement since no 2,2-dichloro-F-propane was found. The major products obtained in 26% combined yield were 1,2-dichloro-F-propane and 1,3-dichloro-F-propane in a 2:3 ratio. This is the statistically expected result since the next fluorine attack could be on either terminal carbon.

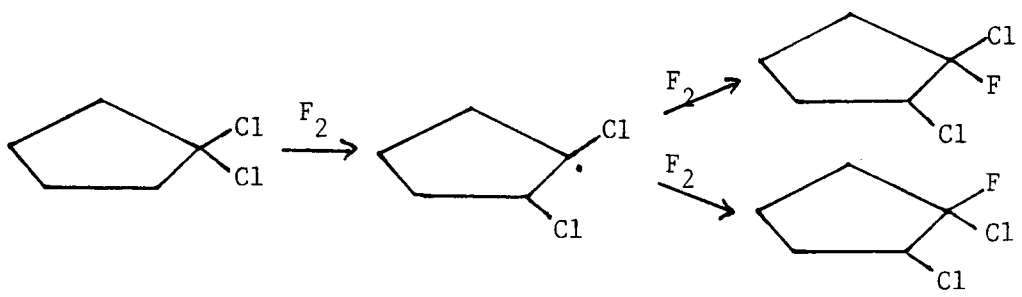


Rearrangement to give the dichloro radical (o) is not expected and no 1,1-dichloro-F-propane was found. Recall the reverse rearrangement for the fluorination of 1,1-dichloropropane. It is possible that the migrating chlorine cannot form a bridge due to steric or electronic repulsions of the primary chlorine. No such problems exist for the chlorine to migrate to the opposite carbon, which would statistically be more likely to be attacked by fluorine to form a primary radical that could rearrange by a 1,2-chloride shift to the more stable tertiary radical (p).

The aerosol fluorination of 3,3-dichloropentane gave four dichloro-F-pentane isomers as major products: 1,3-dichloro-F-pentane (XL); 1,4-dichloro-F-pentane (XLI); 2,3-dichloro-F-pentane (XLII); and 2,4-dichloro-F-pentane (XLIII). These products were isolated as an inseparable mixture and tentively identified by ^{19}F NMR. These products could be formed by chloride shifts similar to chloride shifts in 3-chloropentane.



Aerosol fluorination of 1,1-dichlorocyclopentane gave a mixture of isomers similar to the mixture produced from trans-1,2-dichlorocyclopentane, namely the perfluorinated trans-1,2- ; cis-1,2-; trans-1,3- ; and cis-1,3- dichlorocyclopentanes. No 1,1-dichloro-F-cyclopentane was produced. Initial fluorination adjacent to the gem-dichloride carbon would result in a chloride shift giving a tertiary-like radical. This radical would yield either a cis or trans



1,2-dichloride. Both of these products could rearrange further to give the cis or trans 1,3-dichlorides. Thus complete scrambling of the chlorine atoms results as would be expected for a free radical process.

Aerosol fluorination of 1,1-dichloroneopentane gave 1,1-dichloro-F-neopentane. No rearrangement was observed. Chlorine shifts were blocked by the adjacent quarternary carbon. No 1,3-chloride shifts were observed, indicating that 1,3-shifts would require two sequential 1,2-shifts. However, the yields were not high; 26% 1,1-dichloro-F-neopentane and 24% 1-chloro-F-neopentane. This indicated that it is easier to remove a chlorine from a $CHCl_2$ group than from a CH_2Cl. This is similar to the stability of chlorines noted for the Swarts reaction.[12]

The aerosol fluorination of 1,1,1-trichloroethane gave 1,1-2-trichloro-F-ethane in 77% yield. Initial fluorination gives

$$\dot{C}H_2\text{-}CCl_3 \longrightarrow CH_2Cl\text{-}\dot{C}Cl_2$$

a primary radical. A chlorine shift gives a more stable tertiary radical. It should be noted was that the CCl_3 group was not stable with respect to rearrangement, but that it was stable to chlorine fission.

The aerosol fluorination of 1,1,2,2-tetrachloroethane gave 1,2-difluoro-1,1,2,2-tetrachloroethane in 50% yield. The initial fluorination would give a tertiary radical. A chloride shift would

give a less stable secondary radical which apparently does not occur.

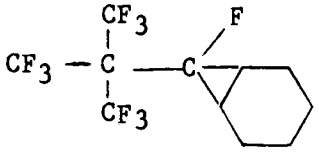
$\dot{C}Cl_2$-$CHCl_2$ ⇸ CCl_3-$\dot{C}HCl$

A summary of the chlorine and radical rearrangements for the dichloroalkanes is the same as that observed for the monochloroalkanes in Table 7, p.94. The geminal dichlorides are quite susceptible to free radical rearrangement. A migration of a chlorine from a terminal geminal group leaves a fairly stable secondary-like radical, while migration of a chlorine from a nonterminal geminal group or a trichloromethyl group leaves behind a very stable tertiary-like radical. Thus geminal dichlorides are difficult to retain during fluorination. They can only be retained by blocking possible migration sites such as with 1,1-dichloroneopentane. Fortunately, perfluoroketones have been successfully prepared with the aerosol fluorination system.[45] These and other F-ketones can easily be converted to geminal dichlorides with PCl_5.[82]

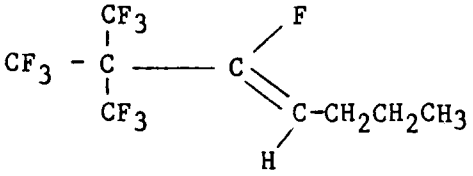
Derivation of F-Alkyl Chlorides

Reactions with zinc/dioxane. A zinc/dioxane system was used to eliminate chlorine and form F-alkenes. Thus F-iso-butyl chloride produced 30% F-iso-butene. F-Cyclopentyl chloride produced 20% F-cyclopentene. Interestingly enough, F-butyl chloride produced F-butene and 1-hydryl-F-butane. F-neopentyl chloride produced 50% hydryl-F-neopentane under the same conditions. No elimination occurred because of the adjacent quarternary carbon.

Reactions with methyl and butyllithium. F-neopentyllithium was produced from F-neopentyl chloride and butyllithium at -78°C. Trapping the F-tert-butyl carbene, formed by elimination of LiF, with cyclohexene gave a F-tert-butyl substituted norcarnene, (nonafluoro-tert-butyl-7-fluoro-norcarnane) (LXIII).



Some of the F-neopentyl lithium reacted with excess butyl lithium to form trans-2,2-bis-(trifluoromethyl)-1,1,1-trifluoro-3-heptene (LXIV).



A small amount of cis isomer was also formed. Repeating this reaction with the addition of bis(dimethylamine)ethane produced slightly higher yields. Reaction without any trapping agent produced even more of the trans heptene (LXIV).

A reaction of F-neopentyl chloride with methyllithium was quenched with iodine after warming from -78°C to -20°C over 8 hours. This produced 35% F-neopentyl iodide (LXV) and 25% recovered and unreacted F-neopentyl chloride. A similar reaction quenched with iodine after 2 hours at -40°C produced only 20% F-neopentyl iodide and 30% F-neopentyl chloride. Apparently F-neopentyllithium is somewhat

stable at temperatures below -20°C. An additional research project would be useful in studying this chemistry.

Chloro Ethers

Formation and reactions of perfluoroalkyl ethers. Fluoroalkyl ethers can be formed by classical Williamson synthesis.[95]

$$CHF_2CF_2Cl \xrightarrow{C_2H_5ONa} CHF_2CF_2OC_2H_5$$

They can also be formed by addition to F-alkenes of alcohols,[96]

$$CF_2CF_2 \xrightarrow{C_2H_5OH} CHF_2CF_2OC_2H_5$$

F-ketones,[97]

$$CF_2CF_2 + (CF_3)_2C{=}O \xrightarrow{KF,\ I_2CH_3CN} (CF_3)_2CFOCF_2CF_2I$$

or F-fluoroxy compounds,[98]

$$CFCl{=}CFCl + CF_3OF \longrightarrow CF_3OCFClCF_2Cl$$

The most commonly used method is the electrochemical fluorination of ethers, cyclic ethers, or glycol ethers.[27] However, chloro-F-ethers are not readily made by this method due to the ease of chlorine replacement.

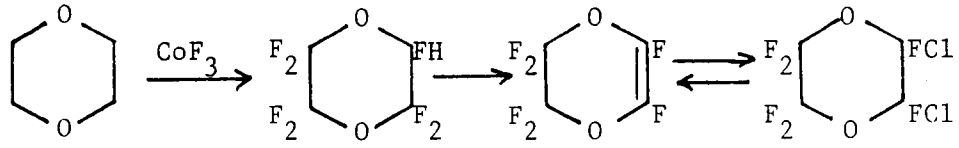
Perfluoroalkyl ethers are characterized by high chemical and thermal stability similar to perfluoroalkanes. They show few properties of their hydrocarbon analogues. They are generally inert to chemical reagents and can usually only be cleaved by $AlCl_3$[99] or concentrated sulfuric acid at elevated temperatures.[100] Thus derivatizing perfluoroalkyl ethers is extremely difficult unless a

potential reaction site is available. Such an example is the preparation of F-vinyl ethers.[98]

$$CF_3OCFClCF_2Cl \xrightarrow{Zn/DMSO} CF_3OCF{=}CF_2$$

Thus if a chlorine could be retained on an ether during fluorination, this would be a distinct advantage over other methods of derivatizing F-ethers.

Aerosol fluorination of chloro ethers. Aerosol fluorination of 2,3-dichloro-1,4-dioxane gave a mixture of cis and trans-2,3-dichloro-F-1,4-dioxane in 21% yield and 2-chloro-F-1,4-dioxane in 35% yield. This showed that chloro ethers could be fluorinated directly and still retain the desired chlorine. The same dichloro-F-dioxane was synthesized in several steps by Coe, Dodman, and Tatlow.[101]



Their initial fluorination of 1,4-dioxane with CoF_3 gave a complex mixture, of which the monohydryl compound was isolated in low yield. Drastic conditions were necessary to form the F-dioxene (fused KOH at 150°C) in low yields. The F-dioxane was easily chlorinated to the dichloro-F-dioxane. However the dichloro-F-dioxane once formed is easily converted back to the F-dioxene. Thus the aerosol fluorination system can produce a chloro-perfluoro ether which can then be easily derivatized. However, chlorines are more easily lost due to the presence of an adjacent oxygen atom which can stablize the radical

formed. Thus the yield of dichloro-F-dioxane is lower than the yield of F-dioxane produced from the aerosol fluorination of dioxane.[39]

The aerosol fluorination of 2,2'-dichloro-diethyl ether produced 2,2'-dichloro-F-diethyl ether in a better yield of 54% with respect to dichloro-F-dioxane.

$$CH_2ClCH_2OCH_2CH_2Cl \longrightarrow CF_2ClCF_2OCF_2CF_2Cl$$

This higher yield may be due to the chlorines not being on the carbon atoms adjacent to the oxygen atom. This chlorinated F-ether might easily be derivatized.

B. AEROSOL FLUORINATION OF COMPOUNDS WITH NONSURVIVABLE FUNCTIONALITY

Alkyl Bromides

Selective fluorination of alkyl bromides. The ease with which bromine is replaced by fluoride ion makes alkyl bromides quite useful for selective fluorination. Various metal fluorides, such as SbF_3, AgF, HgF, and KF, have been used to selectively replace a bromo group. Bromines are more easily replaced than chlorines. Many examples are given by Hudlicky[12] and Sheppard and Sharts[64]. Electrochemical fluorination also selectively replaces bromine.[102] Reaction with high valency metal fluorides or elemental fluorine easily replaces both bromides and hydrogens.[12]

Aerosol fluorination of alkyl bromides. The aerosol fluorination of alkyl bromides was studied to determine whether their stability to

fluorination is similar to the exceptional stability of alkyl chlorides. The aerosol fluorination of neopentyl bromide was carried out under conditions similar to those for neopentyl chloride. A perfluorination reaction (run 1, Table A-30) produced 80% F-isopentane 10% F-iso-butane and elemental bromine.

The most significant result of the neopentyl bromide fluorinations is the near total rearrangement of the neopentyl moiety to the iso-pentyl. Such rearrangements must certainly occur early in the fluorination because low fluorine, control runs without photochemical finishing (runs 2 to 5 Table A-30) produce exclusively rearranged products or unreacted starting material. Reactions 2 through 5 represent stepwise reductions in neopentyl bromide to fluorine mole ratios from approximately 1:12 to 1:1. Product distributions for neopentyl bromide reactions (1) through (5) are given in Table 8.

The major product isolated at 1:1 stoichiometry (Run 5) is 2-methyl-2-butene (LVIII). As the fluorine to neopentyl bromide ratio is increased (Run 4) 2-methyl-2-butene (LVIII) disappears and 2,3-difluoro-2-methylbutane (LIV) becomes the prevalent product. However "abnormal" products having the geminal difluoromethylene group are collectively of near equal prevalence. These abnormal products increase as the relative amount of fluorine increases (Runs 3 and 2) and the amount of 2,3-difluoro-2-methylbutane actually decreases in reaction 2. Compounds having this geminal difluorosubstitution [(LI), (LII), (LIII), (LV), (LVI) and (LVII), Table 8] are classified "abnormal" because none are the statistically probable products

TABLE 8

Results of aerosol fluorinations of neopentyl bromide

Reaction number		1[a]	2	3	4	5
Fluorine:hydrocarbon mole ratio		105	12	4	2.5	1
Product distribution						
LVIX	Neopentyl bromide[b]	-	-	15	28	50
LVIII	2-Methyl-2-butene	-	-	-	-	30
LIV	2,3-Difluoro-2-methylbutane	-	11	20	20	-
LII	3,3-Difluoro-2-methylbutane	-	18	14	6	-
LI	2,3,3-Trifluoro-2-methylbutane	-	10	2	4	-
LV	1,3,3-Trifluoro-2-methylbutane	-	18	6	2	-
LVII	3,3,4-Trifluoro-2-methylbutane	-				
LVI	1,3,3-Trifluoro-2-fluoromethylbutane	-	(c) 16	5	5	-
LIII	1,1,3,3-Tetrafluoro-2-methylbutane	-	5	2	2	-
XVIII	F-Isopentane	80	-	-	-	-
I	F-Isobutane	10	-	-	-	-

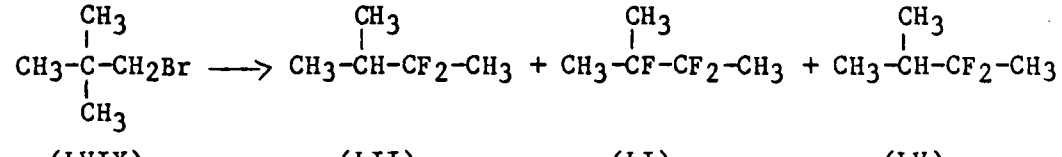
[a]Photochemical stage operative here only.

[b]Unreacted starting material.

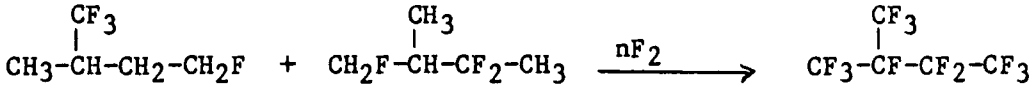
[c]Inseparable mixture, tentative identification by ^{19}F and ^{1}H NMR.

expected from fluorine attack on the products (LVIII) (LIV) are prevalent at the lowest stoichiometries.

The facility with which neopentyl cations rearrange to isopentyl cations is a well known phenonmenon.[86] It is also known that neopentyl radicals do not show a pronounced tendency to rearrange.[87] This leads to the conclusion that the fluorination of neopentyl bromide produces intermediate carbocations, although highly polar species or carbene type intermediates cannot be totally eliminated. Furthermore these carbocations and their precursor intermediate(s) must account for the "abnormal" fluorine products containing the difluoromethylene group.

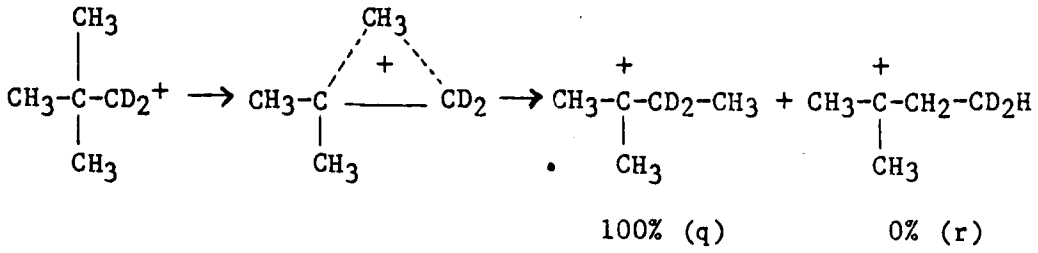


(LVIX) (LII) (LI) (LV)



(LVII) (LVI) (XVII)

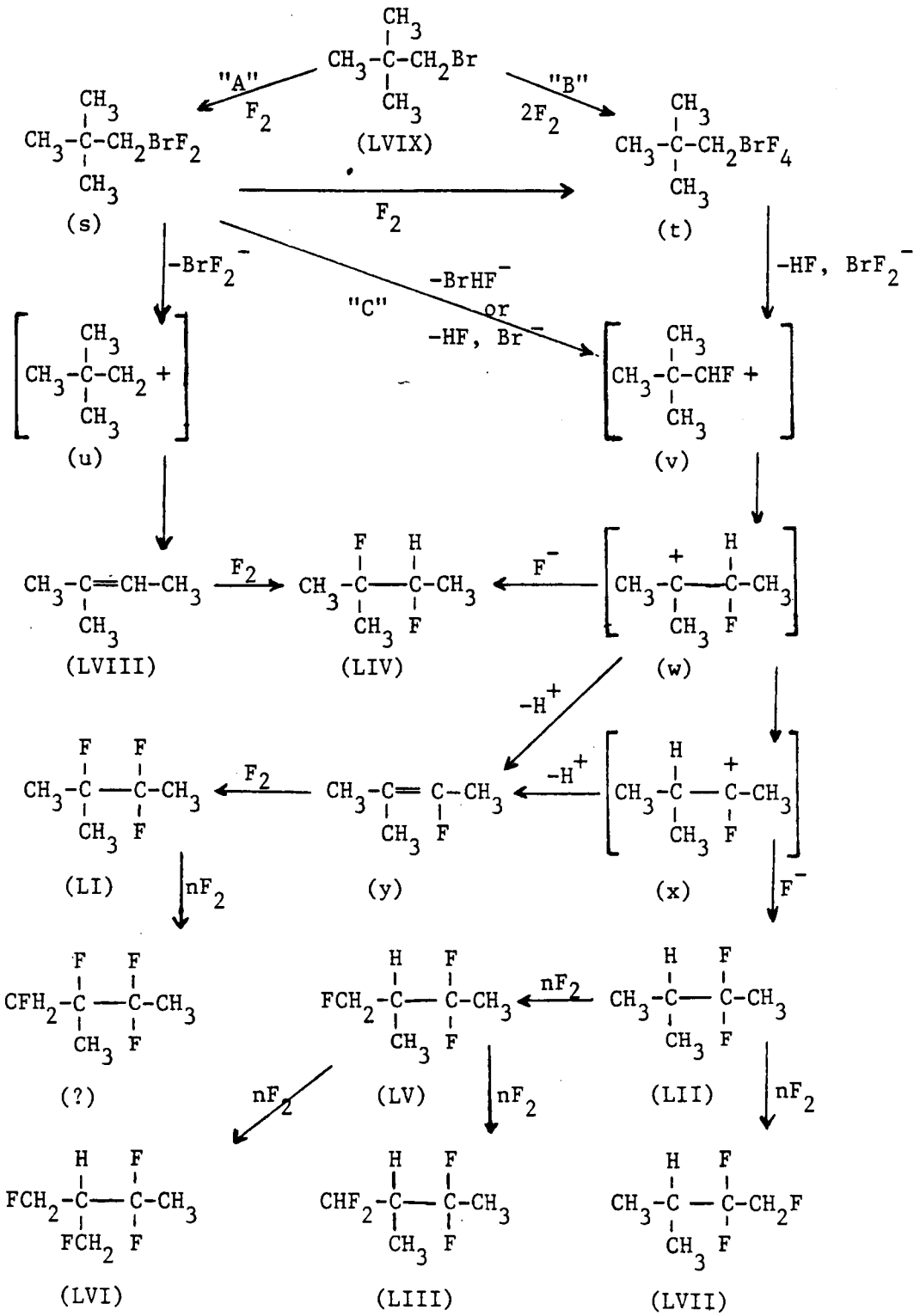
The nature of these intermediates are not known but their behavior bears a striking resemblence to the rearrangements of the neopentyl cation observed by Skell, et al.[103] Skell, et al. observed that all derived products of the rearrangement of neopentyl cation labeled with deuteriums in the 1-position were consistent with the deuterium label in the 3-position, i.e. exclusively derived from (q).



100% (q) 0% (r)

A protonated cyclopropane derivative was thus discounted because it could cleave either of two ways producing tert-amyl derivatives consistent with the deuterium label in the observed 3-position derived from (q), or in the unobserved 4-position derived from (r). Karabatsos, et al. observed this rearrangement of neopentyl cations using a 13-C label and obtained the same result.[104]

One hypothetical scheme (Scheme 1) which not only provides a reasoned approach to all of the products produced, but also addresses the change in product distribution as the fluorine stoichiometry is increased, is in effect two schemes. The basic postulate supported by run 5 (Table 8) is that fluorine preferentially attacks only the bromine and that depending on the stoichiometry either (or both) and alkylbromine difluoride (s) or an alkylbromine tetrafluoride (t) is formed. Conceivably (s) may disproportionate giving the known interhalogen anion, BrF_2^-, and the carbocation (u). Carbocation (u) rearranges to give a tert-amyl cation similar to (q) which by loss of a proton produces 2-methyl-2-butene (LVIII), the largest single product in reaction 5. As the fluorine to alkylbromide ratio is increased, significant amounts of the alkylbromine tetrafluoride (t) are produced leading to formation of the fluorinated carbocation (v) which rearranges to a (q)-like fluorinated tert-amyl cation (w). The

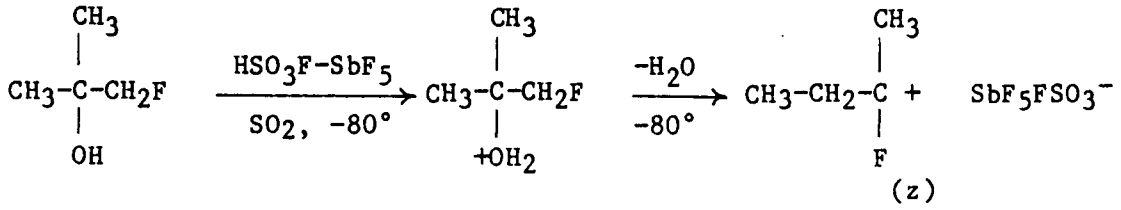


Scheme I

major product in run 4, 2,3-difluoro-2-methylbutane, (LIV) may be produced by fluorine addition to (LVIII) or by fluoride ion trapping of (w). Both routes "A" and "B" are probably operating. As the fluorine:alkylbromide ratio is increased further (reactions 3 and 2) the proportion of route "A" is diminished over route "B" since the other products produced by route "B" alone, (LI) (LII) (LV), are increasing while that product (LIV) produced by route(s) "A" (and "B") is diminishing. It is also likely that the beta fluorinated tert-amyl cation (w) contributes less to product (LIV) than expected because of its ready rearrangement (1,2-hydride shift) to the alpha fluorinated secondary butyl cation (x). The sigma inductive destabilization of (w) by the beta fluorine coupled to the resonance (π-donor) stabilization of (x) by the alpha fluorine inverts the usual $1° < 2° < 3°$ carbocation stablization.[105] Fluoride ion trapping of (x) leads to 3,3-difluoro-2-methylbutane (LII), which by statistically-directed, radical-chain, direct fluorination leads either to product (LV) 1,3,3-trifluoro-2-methylbutane or to the tentaviely identified 3,3,4-trifluoro-2-methylbutane (LVII). 1,3,3-Trifluoro-2-fluoromethylbutane (LVI) and 1,1,3,3-tetrafluoro-2-methylbutane (LII) are statistically produced from (LV). A tentatively identified product, 1,1,3,3-tetrafluoro-2-methylbutane (?) could be statistically produced from (LI). Exhaustive fluorination of any of the products would lead to F-iso-pentane (XVIII). Together products (LII), (LIII), (LV), (LVI), and (LVIII) make up 57% of the total products in reaction 2. Product (LI) produced by proton loss from (w) or (x) to give the olefin

(y), followed by addition of fluorine contributes an additional 10% to the total.

Support for this hypothesis is provided by Olah and Bollinger in which the protonation studies of 1-fluoro-2-methyl-2-propanol in "magic acid," HSO_3F-SbF_5/SO_2, at -80°C produced a rearranged carbocation (z).[105]



The only carbocation detected in this system was (z) although the chloro analog produced the chloro-t-butyl cation. Carbocation (z) requires, in effect two hydride shifts and one methide shift to occur for it to be produced from a transient fluoro-t-butyl cation which was not detected by Olah and Bollinger.[105]

The only unsubstantiated or unsupported parts of this hypothesis (Scheme I) is the formation of (s) and (t) and their "disproportionation" to (u) and (v) respectively. The formation of perfluoroalkyl bromine tetrafluorides is however documented.[108] F-Propylbromine(V)tetrafluoride was synthesized by allowing F-propyl bromide and fluorine to react in a Monel cylinder at 0°C for 15 hours.[106] F-Alkyliodine(V)tetrafluorides have also been made in a similar manner.[107] Also, in a crossed beam study of F and CH_3I, at a collisional energy of 2.6 Kcal/mol, the angular distribution of scattered IF product shows some bimodal symmetry about a center of

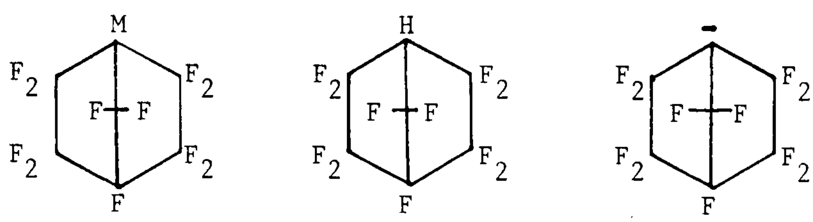
mass centroid suggesting a long-lived, highly-prolate complex.[108] Time-of-fight M.S. velocity data confirm that this angular distribution is symmetric about $\Theta = \pi/2$ as would be expected from decomposition of a complex which exists for many rotational periods. A separate cross-beam study with F_2 and CH_3I also indicated that the complex CH_3IF_2 is "bound" by at least 25 Kcal.[109] Thus it appears possible that complexes (s) and (t) would form upon initial fluorination but would be short lived and would likely disproportionate.

Although a potential route "C" from (s) to (v) is shown in Scheme I, the evidence does not support or require it, although it cannot be eliminated a priori. It is also problematical whether (s) will have sufficient lifetime to interact with a second mole of fluorine to form (t), or whether two moles of fluorine must act in concert as implied by route "B" Scheme I. Whatever the mechanism, insufficient data exist to more than simply pose the question. The solution of this problem might be obtained through matrix isolation studies. It is however clear that fundamental differences in the mode of fluorine attact on alkyl chlorides and bromides exist and that the consequences will likely involve "carbocation" type rearrangements of the organic substituent.

The aerosol fluorinations of 1-bromo-2-methylbutane and 1-bromo-3-methylbutane under high fluorination conditions gave F-iso-pentane and free bromine. No apparent rearrangement of the carbon structures was observed. However this does not preclude carbocation formation and rearrangement by hydrogen migration.

Alkanes and Ethers

Residual hydrogen may serve as a site of functionalization. Selectively not subtituting certain hydrogens on a hydrocarbon by fluorine allows a site for derivation. Certain hydrogens have low reactivity towards radical abstracton by fluroine. These include hydrogens at bridge head sites[110, 111] and positions relative to halogens and carbonyls.[4] The bridgehead position in [2.2.1] bicycloheptane is very resistant to radical abstraction due to the inability of the hydrocarbon to form a planar radical.[110] However this resistant hydrogen can easily be replace by



active metals to form grignard or lithium compounds which can be further reacted.[111] Similarly, the perfluoralkyl anion can also be produced.[112]

Another method of derivatizing hydrylfluorocarbons is halogenation. Photochemical bromination and chlorination of hydryl-F-alkanes have been previously reported in early work by Haszeldine[79] and by Benning and Park.[113] Thermal brominations of hydryl-F-alkanes have been studies by Amphlett & Whittle at temperatures in excess of 400°C.[114]

The aerosol direct fluorination process can produce mono- and di- hydryl-F-alkanes.[39] However these are not the major products obtained. The major products produced using the photochemical stage are perfluorinated. Without the photochemical stage the distribution of products tends to favor partially fluorinated materials.[39] Although mono- and di- hydryl fluorocarbons are produced on small yield, they can be separated and collected. The LTG system is better suited for mono- and di- hydryl fluorocarbons. The aerosol fluorination of neopentane produced 70% F-neopentane (LX) in 43% yield. However, this distribution gave only 5% hydryl-F-neopentane (LXI) and 7% 1,3-dihydryl-F-neopentane. This shows that the hydryl compounds can be made, but not in high yield. An optimized LTG reaction produced 31% F-neopentane, 34% 1-hydryl-F-neopentane and 14% 1,3-F-neopentane. Both processes were used to produce these products.

Photochemical Chlorination and Bromination of F-Alkyl Hydrides

Despite the deactivation of the hydrogen, reaction of hydryl-F-neopentane with an equimolar amount of chlorine produced 96% chloro-F-neopentane (XIV). However a similar bromination reaction, also at ambient temperatures, gave no significant bromination, even after 180 hours of irradiation. These two reactions showed that substitution of fluorines for hydrogens raises the activation energy for abstraction of the remaining hydrogen sufficiently such that chlorination occurs while bromination doesn't.

Thermal bromination was unsuccessful at 250°C, and higher temperatures resulted in significant fluorocarbon skeletal fragmentation.

Efforts were then directed toward interhalogen compounds as potential bromination reagents.

Because the reactivity of chlorine with hydryl-F-neopentane was high and that for bromine was so low, the first interhalogen which suggested itself was bromine chloride. A search of literature produced many instances where bromine chloride was used as a reactive electrophilic brominating agent but far fewer instances where it was used as a free radical brominating agent. These examples have been reviewed in some detail by Mills and Schneider.[115] Among the free radical reaction examples was a reference to the bromination of fluoroform by bromine chloride which reportedly produced exclusively bromotrifluoromethane.[116]

Bromine chloride (mp -66°C, bp 5°C) is approximately 40% dissociated at 25°C ($k°_d$ = 0.34) into bromine (mp -7.2°C, bp 58.8°C) and chlorine (mp -103°C, bp 034.6°C).[117] It is a polar, reactive electrophile and its selectivity as a brominating agent is apparently due to the attraction of the electron rich radical to the positive (bromine) end of the molecular dipole of BrCl.[115] Given this hypothesis, the more electrophilic the radical the less selective will be the bromination.

The reaction of hydryl-F-neopentane with bromine chloride was much slower (100 hrs) than the ambient temperature chlorination of that compound (10 minutes). The reaction was followed by gas phase infrared spectroscopy. Although bromo-F-neopentane formed much faster initially than chloro-F-neopentane, the latter compound was negligible in yields only for overall conversions of less than 10%. As the

reaction reached completion (304 hrs) the percentages of bromo- to chloro-F-neopentane was 48% to 43%. A slight excess of bromine to chlorine and a slightly shorter (254 hrs) reaction time slightly increases the yield of bromo-F-neopentane (LXVI).

The reactions of 1,3-di-hydryl-F-neopentane under similar conditions are summarized in Table 2, page 61. All possible products were produced. For example in Rxn. 1, 31.5% 1,3-dibromo-(LXXI), 18.6% 1-bromo-3-chloro-(LXX), 29.2% 1-bromo-3-hydryl-(LXIX), 6.5% 3,3-di-chloro (LXVIII) and 11.4% 1-chloro-3-hydryl- (XVII) were produced. The overall ratio of chlorination to bromination was 1:2.6. Increases in chlorine concentration (Rxn. 2) and increases in overall reaction time (Rxn. 3) markedly increased the yield of 1-bromo-3-chloro-Fneopentane (29.4% and 32%, respectively). Decreases in chlorine concentration (or increases in bromine concentration), Rxn. 4, significantly increased the yield of 1-bromo-3-hydryl-F-F-neopentane (48%) and recovered starting material (10%). The optimum reaction (Rxn. 1) for making 1,3-di-bromo-F-neopentane produced 2.6 times as much bromination as chlorination products, however, optimal bromination (4.4:1) occurred for reaction 4 which produced predominately 1-bromo-3-hydryl-F-neopentane (48%).

It is apparent from these results that the proportion of chlorination to bromination increases both with the concentration of chlorine and with overall reaction time. Conversely, the ratio of brominated to chlorinated products decreased with reaction time.

In a set of control experiments F-neopentyl bromide and chlorine gas irradiated for 30 hours produced approximately 8% F-neopentyl

chloride, 90% recovered F-neopentyl bromide and 2% F-pivaloyl chloride. The converse reaction of F-neopentyl chloride with bromine did not occur. Furthermore F-neopentyl bromide plus hydrogen (and also deuterium) did not react. The reaction of F-neopentyl bromide with mercury, however, produced 20% F-2,2,5,5-tetramethylhexane (F-dineopentyl) (LXXII) after 47 hours of irradation. The chloride produced only a trace of the coupled product under similar conditions.

These experiments suggest that although the bromides are produced faster, they are more reactive and are gradually consumed, i.e. converted to the chlorides in the interhalogen reactions.

The reaction of 2-di-fluoromethyl-2-tri-fluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane (LXXVIII) with BrCl produced much higher yields of perhalogenated products: 59.5% bromo- (LXXVI) and 37.5% chloro-F-dioxolanes (LXXVII). This is likely a result of the increased reactivity of the hydrogen on the starting compound. The reaction of BrCl and 1-hydryl-F-2,5-dioxohexane (hydryl-F-glyme, $CF_3OCF_2CF_2OCF_2H$), however, does not go to completion but "equilibrates" at 37.1% chloro-, 34.5% bromo and 28.4% starting material. This equilibration may be due to the neighboring oxygen atom.

The reactions of BrCl with 2-hydryl-F-dioxane and 4-hydryl-F-2,2-dimethyl-1,3-dioxolane result in extensive decomposition of both fluorocarbons. Neither reaction produced identifiable amounts of the chloro- or bromo- analogs, nor were significant amounts of starting material recovered in either case.

The "chlorobromination" reaction is a significant improvement over the metallation-bromination of hydryl-F-neopentane; the only previously reported route to bromo-F-neopentane.[51] The metallation route, however, remains the preferred route to iodo-F-neopentane. Photoloysis of ICl and hydryl-F-neopentane produced chloro-F-neopentane, HCl and I_2. This failure is not surprising because of the photo-liability of F-alkyl iodides, the low reactivity of iodine atoms, and formation of relatively non-volatile, solid I_2 at ambient temperatures. Conceivably this reaction might work at higher temperatures with gaseous I_2 and I atoms present.

Despite the improvement in convenience of the chlorobromination over the metallation route, it is still slow and produces considerable amounts of undesired chlorofluorocarbons. In search of a faster, more efficient brominating agent, an investigation was begun for the possibility of using bromine fluoride, BrF. Bromine monofluoride (mp -33°C, bp 20°C) is not stable but disproportionates extensively (55% at 55°C; 55 torr) to bromine (mp -7.2°C, bp 58.8°C) and bromine trifluoride (mp 9°C, bp 126°C). Dissociation to the elements is not appreciable at room temperature ($K°_d = 8x10^{-3}$). Because of the disproportionation of BrF to BrF_3 and Br_2, special techniques were required to minimize contact between the hydryl-fluorocarbons and BrF_3 and to prevent the liquid BrF_3 from attacking the quartz reactor. The net reaction: $BrF + R_FH \rightarrow R_FBr + HF$, also requires a hydrogen fluoride scavenger to prevent HF attack on the quartz. These conditions were met relatively easily by placing a 9 mm x 50 mm

"Teflon" FEP[14] test tube vertically in the bottom of the cylindrical quartz reactor (170mL) surrounded by anhydrous sodium fluoride pellets to absorb HF and support the "Teflon" tube. A threefold stoichiometric amount of BrF_3 was syringed into the teflon test tube. The tube was cooled and evacuated. Then the stoichiometric amount of hydryl fluorocarbon and a threefold stoichiometric amount of bromine were introduced. Photolysis began as soon as frost cleared the tube and the fluorocarbon and bromine evaporated. The much lower vapor pressure of BrF_3 and the large vapor phase excess of bromine maintained the disproportionation substantially toward BrF. Some BrF and BrF_3 evidently form adducts with the NaF because at the completion of the reaction (24 hrs) all of the volatile BrF_3 had been consumed.

"Fluorobromination" of hydryl-F-neopentane produced 78.6% bromo-F-neopentane and 6.6% F-neopentane. The remainder consisted of recovered starting material plus, occasionally, an unidentified F-acid fluoride probably formed by contaminant oxygen from attack by BrF_3 on the quartz. "Fluorobromination" of 1,3-dihydryl-F-neopentane produced 20% 1,3-dibromo-F-neopentane, 15% 1-bromo-3-hydryl-F-neopentane with 60% of the starting material recovered. No traces of bromo-F-neopentane or F-neopentane were found.

Unlike the radical mechanisms proposed for fluorination and chlorination in reactions (1-1) through (1-13), the interhalogen photochemical reactions proposed in Scheme II do not comprise a true chain mechanism. The inability of Br (y·) to abstract a F-alkyl hydrogen limits propogation. The reactions which produce Br· (y·)

x = F, Cl

y = Br

(3-1)	Initiation	$xy \xrightarrow{h\nu} x\cdot + y\cdot$
(3-2)		$[x_2 \xrightarrow{h\nu} 2x\cdot]$
(3-3)	Propagation	$R_FH + x\cdot \longrightarrow R_F\cdot + Hx$
(3-4)		$R_F\cdot + xy \longrightarrow R_Fy + x\cdot$
(3-5)		$R_F\cdot + x_2 \longrightarrow R_Fx + x\cdot$
(3-6)	Termination	$R_F\cdot + xy \longrightarrow R_Fx + y\cdot$
(3-7)		$R_F\cdot + x\cdot \longrightarrow R_Fx$
(3-8)		$R_F\cdot + y\cdot \longrightarrow R_Fy$
(3-9)		$R_F\cdot + y_2 \longrightarrow R_Fy + y\cdot$
(3-10)		$R_F\cdot + R_F\cdot \longrightarrow R_F - R_F$
(3-11)		$x\cdot + y\cdot \longrightarrow xy$
(3-12)		$x\cdot + x\cdot \longrightarrow x_2$
(3-13)		$x\cdot + y_2 \longrightarrow xy + y\cdot$
(3-14)		$y\cdot + y\cdot \longrightarrow y_2$
(3-15)		$y\cdot + x_2 \longrightarrow xy + x\cdot$
(3-16)		$y\cdot + Hx \longrightarrow Ry + x\cdot$

Scheme II

do not readily lead to further propagation and are therefore essentially termination reactions. The fact that reactions (3-15) and (3-16) do not occur also tends to limit propagation. That reaction (3-10) is not observed to produce the dimer $R_F - R_F$ implies that the concentration of $R_F\cdot$ is quite low and that reaction (3-3), the initial abstraction of the F-alkyl hydrogen by x· may be the rate determining reaction.

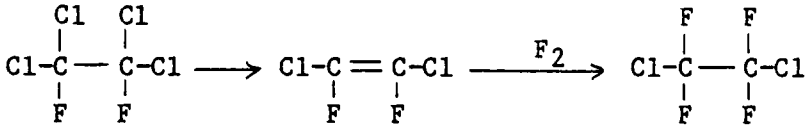
The much faster BrF reaction implies that the hydrogen abstraction reaction (3-3) is much more efficient or that an alternate abstraction reaction such as (3-3a) is responsible.

(3-3a) $R_FH + BrF \longrightarrow R_F\cdot + HF + Br\cdot$

Either way, "bromofluorination" produces greater amounts of brominated products than by "bromochlorination".

Chloroalkenes

Chloroethylenes were subjected to aerosol fluorination to determine the stability of the chlorines and to study the addition of fluroine to the double bond. Tetrachloroethylene gave 1,2-difluorotetrachloroethane (XLVI) in 75% purity, indicating fairly high stability of the attached chlorines to attack by fluorine. No apparent chlorine migration was observed. However the mode of fluorine addition could not be determined from this experiment. A small amount of 1,2-dichloro-F-ethane (XXXI) was observed. This product may have been formed by elimination of Cl_2 from excited 1,2-difluoro-tetrachloroethane followed by addition of fluorine across the double bond.



This is supported by the lack of any observed trichloro-trifluoroethane which might be expected for a stepwise loss of just one chlorine.

This reaction proceeds much more cleanly than a similar reaction carried out in CCl_2F_2 solution at -80°C which gave only 25% yield of 1,2-difluoro-tetrachloroethane (XLVI).[4] Addition of chlorine to the double bond, dimerization, and significant cleaveage of the C-C bond were not observed in contrast to the solution reaction.[4]

The aerosol fluorination of 1,2-dichloroethylenes gave 1,2-dichloro-F-ethane (XXXI) as the major product. The chlorines were stable to fluorine attack. No chloride migrations were observed. The mode of fluorine attack could not be determined from perfluorination reactions. Partial fluorination seems to indicate that fluorine adds across the double bond before attacking the hydrogens. However, this could not be definitely established because of the difficulty in accurately controlling the aerosol fluorination parameters with the minibubbler. Also, more suitable compounds, as well as purer compounds, would give better data on this question.

Esters

Unlike the LTG reaction,[35] esters did not survive aerosol fluorination. The major products obtained from both ethyl 3-chloropropanoate and isopropyl propanoate were F-propanoyl fluoride

and F-acetyl fluoride. Small amounts of fluoroxy compounds were observed. Some F propane was also produced from the isopropyl propanoate reaction. This failure is likely due to the large amount of free fluoride ion in the aerosol process which is known to catalize F-ester F-acid fluoride equilibria.[118] It may be possible to fluorinate esters if fluoride ion could be eliminated by use of compounds such as $NaBF_4$ for aerosol production.

Alcohols

The aerosol fluorination of alcohols resulted in extensive cleavage of the hydroxy group and of the adjacent C-C bond producing F-alkanes. Considerable amounts of F-acid fluorides were also produced. Since fluoroxy compounds were also produced, these reactions were not extensively worked up. Tert-butyl alcohol produced a small amount of F-propanone, most likely by cleavage of methy group.

Nitroalkanes

The aerosol fluorination of nitropropane resulted in complete cleavage of the nitro group. The two major products produced were F-propane and NO_2. This is not unexpected as nitro groups are easily cleaved and the resulting NO_2 is quite stable.

CHAPTER IV

CONCLUSION

The ability to retain a functional group on a hydrocarbon during aerosol direct fluorination was demonstrated. Acid chlorides were easily fluorinated to the corresponding F-alkyl acid fluorides. The yields and purity were comparable to electrochemical fluorination. Thus aerosol direct fluorination provides an alternate method of producing F-alkyl acid fluorides, especially highly branched compounds.

The remarkable stability of chlorides towards aerosol direct fluorination was also demonstrated. Primary F-alkyl chlorides are easily produced from the analogous alkyl chlorides in high purity and good yields. This is in contrast to the instability of the chloride group to other fluorination methods. No products were found which might result from chlorination by free chlorine or dimerization of radicals as is common with other fluorination methods of alkyl chlorides. Although F-alkyl chlorides can be made indirectly with difficulty, aerosol fluorination provides the only method by which preselected, primary F-alkyl chlorides can easily be produced in a single reaction.

Aerosol direct fluroination also provides a method for studying the basic fluorination reactions of alkyl chlorides without the competing side reactions so common in other fluorination reactions.

The aerosol direct fluorination of tertiary chlorides results in complete rearrangement of the chlorine to adjacent primary or secondary positions. For example, tert-butyl chloride, upon fluorination gave F-isobutyl fluoride. Presumably, initial fluorination produces a primary radical, which rearranges to a more stable tertiary radical by a 1,2-chloride shift. Aerosol direct fluorination of secondary chlorides resulted in only partial rearrangement of the chlorine. For example, 2-chloropropane gave both 1-chloro-F-propane and 2-chloro-F-propane.

In the aerosol direct fluorination of secondary geminal dichlorides, a 1,2-chloride shift results in chlorine-stabilized tertiary-like radicals. Thus complete rearrangement occurs as for 2,2-dichloropropane gave 1,2-dichloro-F-propane and 1,3-dichloro-F-propane. In the aerosol fluorination of primary geminal dichlorides, the partial 1,2-chloride shifts result in chlorine-stabilized secondary-like radicals which have about the same stabilities as other secondary radicals. 1,1-Dichloropropane gave a 1:1 mixture of 1,1-dichloro-F-propane and 1,2-dichloro-F-propane.

Chloroethers are easily fluorinated without significant cleavage to chloro-F-ethers by the aerosol direct fluorination method. However, esters and alcohols do not survive aerosol fluorination. Considerable cleavage occurs to produce F-acyl fluorides and F-alkanes.

Aerosol direct fluorination of alkyl bromides did not give F-alkyl bromides. Instead, F-alkanes and free bromine were produced.

Initial fluorination of neopentyl bromide apparently occurs on the bromine to give neopentyl bromine fluorides, $(CH_3)_3$-C-CH_2BrF_x. Disproportionation of this species resulted in a series of fluorine-stabilized carbocation rearrangements. Perfluorination yielded F-isopentane.

Although F-alkyl bromides could not be synthesized directly from the alkyl bromides, they could be produced indirectly. The gas phase photolysis of mixtures of F-alkyl hydrides, obtained from the aerosol fluorination of the analogous hydrocarbons, and one of the interhalogen compounds, BrCl or BrF, provided a simple route to F-alkyl bomides and chlorides in high conversion. The use of BrF decreased reaction times from approximatey 180 h to less than 24 h and gave considerably more bromination than fluorination.

Conversion of the relatively unreactive F-alkyl chlorides to more reactive compounds, such as the bromides or iodides, would be useful. Although conversion to F-alkenes is one well known route, other methods need to be developed. One such method briefly investigated was the metalation by lithium alkyls. F-Neopentyllithium was produced at -78°C from F-neopentyl chloride and either methyllithium or butyllithium. This reactive species could react with iodine to form F-neopentyl iodide or excess butyl lithium to form trans-2,2-bis-(trifluoromethyl)-1,1,1-trifluoro-3-heptene. Alternatively, F-neopenyllithium which eliminates fluoride ion to form F-tert-butyl fluoro carbene could be trapped by cyclohexene to give a F-tert-butyl substituted norcarane.

Aerosol direct fluorination successfully fluorinated acyl chlorides, alkyl chlorides and chloro ethers. This makes new compounds available that are otherwise difficult to obtain and opens up new areas for the exploration of their chemistry. Aerosol direct fluorination also provides a means of studying basic fluorination reactions.

LIST OF REFERENCES

LIST OF REFERENCES

1. Moissan, H.; Chavanne, G. Compt. Rend., 1905, 140, 407.

2. Miller, W. T.; Koch, S. D. J. Am. Chem. Soc., 1957, 79, 3084.

3. Ruff, O.; Keim, R. Z. Anorg. Allgem. Chem., 1931, 201, 245.

4. Bockemuller, W. Ann., 1933, 506, 20.

5. Miller, W. T.; Calfee, J. D.; Bigelow, L. A. J. Am. Chem. Soc., 1937, 59, 198.

6. a) Calfee, J. D.; Bigelow, L. A. J. Am. Chem. Soc., 1937, 59, 2072. b) Young, D. S.; Fukuhara, N.; Bigelow, L. A. J. Am. Chem. Soc., 1940, 62, 1171.

7. Calfee, J. D.; Fukuhara, N.; Young, D. S.; Bigelow, L. A.; J. Am. Chem. Soc., 1940, 62, 267.

8. Hadley, E. H.; Bigelow, L. A. J. Am. Chem. Soc., 1940, 62, 3302.

9. Miller, W. T. J. Am. Chem. Soc., 1940, 62, 341.

10. Swarts, F. S. Bull. Acad. Roy. Belg., 1892, 24, 474.

11. Midgley, T., Jr.; Henne, A. L. Ind. Eng. Chem., 1930, 22, 542.

12. Hudlicky, M. "Chemistry of Organic Fluorine Compounds"; MacMillan: New York, 1962.

13. Pacini, H. A.; Teach, E. G.; Walker, F. H.; Pavlath, A. E. Tetrahedron, 1966, 22, 1747.

14. Henne, A. L. Org. Reactions, 1944, 2, 49.

15. Barbour, A. K.; Belf, L. J.; Buxton, M. W. Advan. Fluorine Chem., 1963, 3, 189.

16. Miller, C. B.; Woolf, C. U. S. Pat. 2,803,665, 1957, Chem. Abs., 1958, 52, 2047.

17. Stacey, M.; Tatlow, J. C. Advan. Fluorine Chem., 1960, 1, 166.

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

19. Jessup, R. S.; Brickwedde, F. G.; Wechsler, M. T. J. Res. Nat. Bur. Stand., 1950, 44, 457.

20. Smith, R. P.; Tatlow, J. C. J. Chem. Soc., 1957, 2505.

21. Cady, G. H.; Grosse, A. V.; Barbour, E. J.; Burger, L. L.; Sheldon, Z. D. Ind. Eng. Chem., 1947, 39, 290.

22. a) Meritt, R. F.; Stevens, T. E. J. Am. Chem. Soc., 1966, 88, 1822. b) Meritt, R. F. J. Org. Chem., 1966, 31, 3871. c) Meritt, R. F. J. Am. Chem. Soc., 1967, 89, 609.

23. Tyczkowski, E. A.; Bigelow, L. A. J. Am. Chem. Soc., 1955, 77 3007.

24. Maxwell, A. F.; Detoro, F. E.; Bigelow, L. A. J. Am. Chem. Soc., 1960, 82, 5827.

25. Bishop, B. C.; Hynes, J. B.; Bigelow, L. A. J. Am. Chem. Soc., 1964, 86, 1827.

26. Simons, J. H. Trans Electrochem. Soc., 1949, 95, 47.

27. Simons, J. H. "Fluorine Chemistry",; Vol. 1; Academic: New York, 1950, p. 401.

28. Nagase, S. Fluorine Chem. Revs., 1967, 1, 77.

29. Margrave, J. L.; Lagow, R. J. Chem. Eng. News, 1970, 40.

30. Lagow, R. J.; Margrave, J. L. Proc. Natl. Acad. Sci., 1970, 67, 4.

31. Lagow, R. J.; Margrave, J. L. J. Polym. Sci., 1974, 12, 177.

32. Maraschin, N. J.; Lagow, R. J. J. Am. Chem. Soc., 1972, 94, 8601.

33. Maraschin, N. J.; Lagow, R. J. Inorg. Chem., 1973, 12, 1459.

34. Adcock, J. L.; Lagow, R. J. J. Org. Chem., 1973, 38, 3617.

35. Adcock, J. L.; Lagow, R. J. J. Am. Chem. Soc., 1974, 96, 7588.

36. Adcock, J. L.; Beh. R. A.; Lagow, R. J. J. Org. Chem., 1975, 40, 3271.

37. Adcock, J. L.; Lagow, R. J., unpublished results.

38. Adcock, J. L.; Catsikis, B. D.; Thompson, J. W.; Lagow, R. J. J. Fluorine Chem., 1976, 7, 197.

39. Adcock, J. L.; Horita, K.; Renk, E. B. J. Am. Chem. Soc., 1981, 103, 6937.

40. Lagow, R. J.; Margrave, J. L. Prog. Inorg. Chem., 1979, 26, 161.

41. Davis, C. N., ed. "Aerosol Science"; Academic Press: New York, 1966, Chapter 1.

42. Cadle, R. D. "Particle Size, Theory and Industrial Applications"; Reinhold: New York, 1965.

43. Hidy, G. M. "Aerosols and Atmospheric Chemistsry"; Reinhold Papers contributed to Kendall Award Symposium; American Chemical Society, Los Angeles, CA, March, 1971; Academic Press: New York; Shahriari, S.; Sarmiento, A. N.; Goodrich, F. C., 1972, "The Kinetics of Growth of an Aerosol in a Flow Reactor", p.67.

44. Sutugin, A. G. "Advances in Aerosol Physics"; Vol. 4; Fedoseer, V. A., ed.; Israel Program for Scientific Translations: Jerusalem, 1971, translated from Russian in 1973, p.36.

45. Adcock, J. L.; Robin, M. L. J. Org. Chem., 1983, 48, 2437.

45. a) Adcock, J. L.; Evans, W. D.; Heller-Grossman, L.; Robin, M. L. "Low Temperature Fluorination of Aerosol and Suspensions of Hydrocarbons Utilizing Elemental Fluorine", Office of Naval Research, Contract Technical Report No. 4. b) Adcock, J. L.; Horita, K.; Renk, E. B. Contract Report No. 3.

47. Dadson, B. A; Minta, A. J. Chem. Soc. Perkin 1, 1976, 146.

48. Wiley, G. A.; Herskowitz, R. L.; Rein, B. M.; Chung, B. C. J. Am. Chem. Soc., 1964, 86, 964.

49. Mousseron, M.; Granger, R.; Valette, J. Bull. Soc. Chem. France, 1946, 249.

50. Kucera, J. J.; Carpenter, P. C. J. Am. Chem. Soc., 1935, 57, 2346.

51. Adcock, J. L.; Renk, A. J. Org. Chem., 1979, 44, 3431.

52. Francis, W. C.; Hasezeldine, R. N. J. Chem. Soc., 1955, 2151.

53. Kim, Y. K. J. Org. Chem., 1967, 32, 3673.

54. Burdon, J.; Tatlow, J. C. J. Appl. Chem. (London), 1958, 8, 293.

55. Henne, A. L.; Trott, P. J. Am. Chem. Soc., 1947, 69, 1820.

56. Fawcett, F. S.; Tallock, C. W.; Coffman, D. J. Am. Chem. Soc., 1962, 84, 4275.

57. Halpern, E.; Goldenson, J. J. Phys. Chem., 1956, 60, 1372.

58. Barber, E. J.; Burger, L. L.; Cady, G. H. J. Am. Chem. Soc., 1951, 73, 4241.

59. Bagnall, R. D.; Coe, P. L.; Tatlow, J. C. J. Fluorine Chem., 1974, 3, 329.

60. Yarovenko, N. N.; Motorny, S. P., Kirenskeya, L. I. Zh. Obshch Khim., 1947, 27, 2796; Chem. Abstr., 1958, 52, 8042b.

61. Dvorak, F.; Dedek, V. Collection Czech. Chem. Commun., 1966, 31, 2727.

62. Birchall, J. M.; Cross, G. W.; Haszeldine, R. N. Proc. Chem. Soc., 1960, 81.

63. Chambers, R. D. "Fluorine in Organic Chemistry"; Wiley-Interscience: New York, 1973.

64. Sheppard, W. A.; Sharts, C. M. "Organic Fluorine Chemistry"; W. A. Benjamin, Inc.: New York, 1969.

65. Schmeisser, M.; Ehlers, K. P.; Sartori, P. Angew. Chem., Int. Ed. Eng., 1967, 6, 627.

66. Fox, H. M.; Ruehlen, F. N.; Childs, W. V. Electrochem. Soc., 1971, 118, 1246.

67. Henne, A. L.; Ladd, E. C. J. Am. Chem. Soc., 1936, 58, 402.

68. Locke, E. G.; Brode, W. R.; Henne, A. L. J. Am. Chem. Soc., 1934, 56, 1934.

69. Gochenour, C. I.; Kyker, G. D. U. S. Patent, 2,436,357; Chem Abstr., 1948, 42 5465d.

70. Tyczkowski, E. A.; Woolf, C., U. S. Patent, 2,831,035; Chem. Abstr., 1958, 52, 14648g.

71. Edwards, A. J.; Plevey, R. G.; Sallomi, I. J.; Tatlow, J. C. Chem. Comm., 1972, 1028.

72. Banks, R. E.; Haszeldine, R. N.; Walton, J. B. J. Chem. Soc., 1963, 5581.

73. Shack, C. J.; Christie, K. O. J. Fluorine Chem., 1980, 16, 63.

74. Johri, K. K.; DesMarteau, D. D. J. Org. Chem., 1981, 46, 5081.

75. Haszeldine, R. N. J. Chem. Soc., 1952, 4259.

76. Hauptschein, M.; Nodiff, E. A.; Grosse, A. V. J. Am. Chem. Soc., 1952, 74, 1347.

77. Hauptschein, M.; Stokes, C. S.; Grosse, A. V. J. Am. Chem. Soc., 1952, 74, 848.

78. Hauptschein, M.; Kinsman, R. L.; Grosse, A. V. J. Am. Chem. Soc., 1952, 74, 849.

79. Haszeldine, R. N. J. Chem. Soc., 1953, 3761.

80. Haszeldine, R. N.; Steele, B. R. J. Chem. Soc., 1957, 2193.

81. Haszeldine, R. N.; Steele, B. R. J. Chem. Soc., 1957, 2800.

82. Farah, B. S.; Gilbert, E. E. J. Org. Chem., 1965, 30, 1241.

83. Henne, A. L.; Nager, M. J. Am. Chem. Soc., 1951, 73, 5527.

84. Kunyants, I. L.; Shokina, V. V.; Kuleshova, N. D. Izv. Akad. Nauk. SSSR, 1960, 1693; Chem. Abstr., 1961, 55, 9254g.

85. Brice, T. J.; Pearlson, W. H.; Simmons, J. H. J. Am. Chem. Soc., 1949, 71, 2499.

86. March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure"; McGraw-Hill: New York, 1968, p.781.

87. Whitmore, F. C.; Popkin, A. N.; Bernstein, H. J.; Wilins, J. P. J. Am. Chem. Soc., 1941, 63, 124.

88. Burger, H.; Pawelke, G. Spectrochim. Acta, 1979, 35A, 559.

89. Skell, P. S.; Allen, R. G.; Gilmour, N. D. J. Am. Chem. Soc., 1961, 83, 504.

90. Juneja, P. S.; Hodnett, E. M. J. Am. Chem. Soc., 1967, 89, 5685.

91. Wiley, R. H.; Miller, W.; Jarboe, C. H.; Harell, J. R.; Parish, D. J. Radiation Research, 1960, 13, 479.

92. Benson, H. L.; Willard, J. E. J. Am. Chem. Soc., 1961, 83, 4672.

93. Mayo, F. R. J. Am. Chem. Soc., 1962, 84, 3964.

94. Freidlina, R. KH. Advan. Free Radical Chem., 1965, 1, 211.

95. McBee, E. T.; Bolt, R. O. Ind. Eng. Chem., 1947, 39, 412.

96. Young, J. A.; Tarrant, P. J. Am. Chem. Soc., 1950, 72, 1860.

97. Evans, F. W.; Litt, M. H.; Weidler-Kubanek, A. M.; Avonda, F. P. J. Org. Chem., 1968, 33, 1837.

98. Durell, W. S.; Stump, E. C.; Westmoreland, G.; Padgett, C. D. J. Polymer Sci., Part A, 1965, 3, 4065.

99. Tiers, G. V. D. J. Am. Chem. Soc., 1955, 77, 6703.

100. Lovelace, A. M.; Rausch, D. A.; Postelnek, W. "Aliphatic Fluorine Compounds", Reinhold: New York, 1958.

101. Coe, P. L., Dodman, P.; Tatlow, J. C. J. Fluorine Chem., 1975, 6, 115.

102. Thiebault, A.; Colin, J. P., Oliva, P. C. R. Acad. Sc. Paris, 1977, 285 Ser C, 373.

103. Skell, P. S.; Starer, I.; Krapcho, A. P. J. Am. Chem. Soc., 1960, 82, 5257.

104. Karabatsos, G. J.; Graham, J. D. J. Am. Chem. Soc., 1960, 82, 5250.

105. Olah, G. A.; Bollinger, J. M. J. Am. Chem. Soc., 1968, 90, 947.

106. Habibi, M. H.; Sams, L. C. J. Fluorine Chem., 1981, 18, 277.

107. Rondestvedt, C. S., Jr. J. Am. Chem. Soc., 1969, 91, 3054.

108. Farrar, J. M.; Lee, Y. T. J. Chem. Phys., 1975, 63, 3639.

109. Farrar, J. M.; Lee, Y. T. J. Am. Chem. Soc., 1974, 96, 7570.

110. Robertson, G.; Liu, E. K.; Lagow, R. J. J. Org. Chem., 1978, 43, 4981.

111. Campbell, S. F.; Stephens, R.; Tatlow, J. C. Tetrahedron, 1965, 21, 2997.

112. Campbell, S. F.; Stephens, R.; Tatlow, J. C. Chem. Commun. 1965, 134.

113. Benning, A. F.; Park, J. D. U.S. Patent, 1949; 2,490,764.

114. Amphlett, J. C.; Whittle, E. Trans. Faraday Soc., 1968, 64, 2130.

115. Mills, J. F.; Schneider, J. A., Ind. Eng. Prod. Res. Develop., 1973, 12, 161.

116. Ruh, R. P.; Davis, R. A.; The Dow Chemical Co., U.S. Patent, 1953, 2,658,086.

117. Cotton, F. A.; Wilkinson, G., "Advanced Inorganic Chemistry", Wiley Interscience; New York, 1980, pp 562-5.

118. DeMarco, R. A.; Couch, D. A.; Schreeve, J. M. J. Org. Chem., 1972, 37, 332.

APPENDIXES

APPENDIX A

AEROSOL FLUORINATION PARAMETERS

TABLE A-1

Aerosol fluorination of pivaloyl chloride

Run Parameters	2[a]	4[a]	5	6a[b]	7
Hydrocarbon Throughput					
mmole/hour	0.9	4.0	4.5	2.0	2.0
He Carrier (mL/min)	32	130	140	65	65
Temperature (°C)	0°	0°	0°	0°	0°
F_2 Flow (mL/min)					
Stage 1	6	10	15	10	20
Stage 2	6	8	15	20	20
Stage 3	-	-	-	-	20
He Diluent (mL/min)					
Stage 1	30	30	25	25	80
Stage 2	30	30	25	25	80
Stage 3	-	-	-	-	80
Reactor Temps (°C)					
Aerosol Generator	50	50	50	50	50
Module 1	-45	-45	-45	-45	-45
Module 2	-35	-40	-35	-30	-30
Module 3	10	10	20	20	20
Main He Carrier (mL/min)	400	400	400	400	1200
Hydrocarbon : F_2 Ratio	1:32	1:11	1:16	1:36	1:73
Percent F_2 by Last Stage	2.3%	3.0%	4.8%	5.5%	4.5%
Run Time (hour)	3.5	3	2	3	3
Products Collected (g)	0.120	0.767	1.112	0.789	1.05
Theoretical Percent Yields of Perfluorinated Products					
II	10.5%	14.4%	18.1%	19.7%	48%

[a] runs 1 and 3 not collected, similar to 2 and 4 respectively.

[b] run 6b similar to 6a except no UV, yield 6%.

TABLE A-2

Aerosol fluorination of butyryl chloride

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	3.0
He Carrier (mL/min)	30
Temperature (°C)	23
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	40
Module 1	-40
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:33
Percent F_2 by Last Stage	3.3%
Run Time (hour)	3
Products Collected (g)	1.41
Theoretical Percent Yield of Perfluorinated Product	
V	58%

TABLE A-3

Aerosol fluorination of iso-butyryl chloride

Run Parameters	1	2
Hydrocarbon Throughput		
mmole/hour	4.0	3.0
He Carrier (mL/min)	30	24
Temperature (°C)	23	23
F_2 Flow (mL/min)		
Stage 1	20	20
Stage 2	20	20
Stage 3	-	20
He Diluent (mL/min)		
Stage 1	80	80
Stage 2	80	80
Stage 3	-	80
Reactor Temps (°C)		
Aerosol Generator	40	40
Module 1	-40	-45
Module 2	-30	-30
Module 3	10	10
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:24	1:49
Percent F_2 by Last Stage	3.3%	4.5%
Run Time (hour)	3	3
Products Collected (g)	1.48	1.37
Theoretical Percent Yield of Perfluorinated Product		
VI	5%	53%

TABLE A-4

Aerosol fluorination of cyclopropyl carbonyl chloride

Run Parameters	1	2	3	4
Hydrocarbon Throughput				
mmole/hour	3.9	2.0	1.8	2.0
He Carrier (mL/min)	42	25	23	25
Temperature (°C)	22	22	22	23
F_2 Flow (mL/min)				
Stage 1	12	10	10	20
Stage 2	15	10	10	20
Stage 3	-	-	-	20
He Diluent (mL/min)				
Stage 1	40	30	40	80
Stage 2	40	30	40	80
Stage 3				
Reactor Temps (°C)				
Aerosol Generator	45	45	45	45
Module 1	-40	-35	-45	-40
Module 2	-35	-30	-35	-30
Module 3	10	10	0	10
Main He Carrier (mL/min)	500	450	500	1200
Hydrocarbon : F_2 Ratio	1:17	1:24	1:27	1:73
Percent F_2 by Last Stage	4.1%	3.6%	3.2%	3.9%
Run Time (hour)	3	3	2.5	3
Products Collected (g)	-	-	0.583	-
Theoretical Percent Yields of Perfluorinated Products				
V [a]	43%	30%	20%	30%
VI [b]	17%	20%	13%	20%

[a] F-butyryl chloride

[b] F-iso-butyryl chloride

TABLE A-5

Aerosol fluorination of chloroacetyl chloride

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	3.0
He Carrier (mL/min)	10
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	-
Stage 3	-
He Diluent (mL/min)	
Stage 1	120
Stage 2	-
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	40
Module 1	-45
Module 2	-35
Module 3	0
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:16
Percent F_2 by Last Stage	1.7%
Run Time (hour)	3
Products Collected (g)	0.80
Theoretical Percent Yields of Perfluorinated Products	
XII [a]	20%
XIII [b]	34%

[a] F-acetyl fluoride

[b] chloro-F-acetyl fluoride

TABLE A-6.

Aerosol fluorination of neopentyl chloride

Run Parameters	1	2	3
Hydrocarbon Throughput			
mmole/hour	1.9	4.0	3.6
He Carrier (mL/min)	40	90	80
Temperature (°C)	-7	-7	-7
F_2 Flow (mL/min)			
Stage 1	5	10	20
Stage 2	5	9	20
Stage 3	-	-	20
He Diluent (mL/min)			
Stage 1	20	40	80
Stage 2	20	40	80
Stage 3	-	-	80
Reactor Temps (°C)			
Aerosol Generator	40	40	40
Module 1	-50	-45	-45
Module 2	-30	-30	-30
Module 3	10	10	10
Main He Carrier (mL/min)	400	400	1000
Hydrocarbon : F_2 Ratio	1:13	1:12	1:41
Percent F_2 by Last Stage	2.0%	3.3%	4.3%
Run Time (hour)	2	3	3
Products Collected (g)	0.40	0.90	2.56
Theoretical Percent Yield of Perfluorinated Product			
XIV	15%	13%	74.6%

TABLE A-7

Aerosol fluorination of propyl chloride

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	3.0
He Carrier (mL/min)	75
Temperature (°C)	-45
F_2 Flow (mL/min)	
Stage 1	15
Stage 2	15
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	40
Module 1	-40
Module 2	-30
Module 3	0
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:25
Percent F_2 by Last Stage	2.4%
Run Time (hour)	2
Products Collected (g)	0.909
Theoretical Percent Yield of Perfluorinated Product	
XV	63%

TABLE A-8

Aerosol fluorination of butyl chloride

Run Parameters	1	2
Hydrocarbon Throughput		
mmole/hour	2.0	3.1
He Carrier (mL/min)	32	48
Temperature (°C)	-7	7
F_2 Flow (mL/min)		
Stage 1	10	20
Stage 2	20	20
Stage 3	-	20
He Diluent (mL/min)		
Stage 1	30	80
Stage 2	30	80
Stage 3	-	80
Reactor Temps (°C)		
Aerosol Generator	50	50
Module 1	-45	-45
Module 2	-30	-30
Module 3	0	10
Main He Carrier (mL/min)	400	1000
Hydrocarbon : F_2 Ratio	1:36	1:42
Percent F_2 by Last Stage	3.3%	4.3%
Run Time (hour)	3	2
Products Collected (g)	0.880	1.17
Theoretical Percent Yield of Perfluorinated Product		
XVI	15%	44%

TABLE A-9

Aerosol fluorination of iso-butyl chloride

Run Parameters	1	2
Hydrocarbon Throughput		
mmole/hour	1.4	3.0
He Carrier (mL/min)	20	40
Temperature (°C)	-7	-7
F_2 Flow (mL/min)		
Stage 1	20	20
Stage 2	20	20
Stage 3	-	-
He Diluent (mL/min)		
Stage 1	80	80
Stage 2	80	80
Stage 3	-	-
Reactor Temps (°C)		
Aerosol Generator	45	45
Module 1	-45	-45
Module 2	-30	-35
Module 3	10	10
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:54	1:33
Percent F_2 by Last Stage	3.2%	3.2%
Run Time (hour)	2	2
Products Collected (g)	0.388	1.038
Theoretical Percent Yield of Perfluorinated Product		
XVII	42%	51%

TABLE A-10

Aerosol fluorination of 1-chloro-2-methylbutane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	3.0
He Carrier (mL/min)	12
Temperature (°C)	22
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	40
Module 1	-40
Module 2	-35
Module 3	0
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:40
Percent F_2 by Last Stage	4.5%
Run Time (hour)	3
Products Collected (g)	1.629
Theoretical Percent Yields of Perfluorinated Products	
XIX	39%

TABLE A-11

Aerosol fluorination of 1-chloro-3-methylbutane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	3.0
He Carrier (mL/min)	12
Temperature (°C)	22
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	45
Module 1	-40
Module 2	-35
Module 3	0
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:40
Percent F_2 by Last Stage	4.5%
Run Time (hour)	3
Products Collected (g)	1.323
Theoretical Percent Yields of Perfluorinated Products	
XX	32%

TABLE A-12

Aerosol fluorination of iso-propyl chloride

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	4.0
He Carrier (mL/min)	75
Temperature (°C)	-45
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	35
Module 1	-40
Module 2	-30
Module 3	0
Main He Carrier (mL/min)	800
Hydrocarbon : F_2 Ratio	1:25
Percent F_2 by Last Stage	3.9%
Run Time (hour)	2.5
Products Collected (g)	1.239
Theoretical Percent Yields of Perfluorinated Products	
XXI [a]	33%
XV [b]	17%

[a] 2-chloro-F-propane

[b] 1-chloro-F-propane

TABLE A-13

Aerosol fluorination of 2-chlorobutane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	2.8
He Carrier (mL/min)	33
Temperature (°C)	-10
F_2 Flow (mL/min)	
Stage 1	19
Stage 2	19
Stage 3	19
He Diluent (mL/min)	
Stage 1	75
Stage 2	75
Stage 3	75
Reactor Temps (°C)	
Aerosol Generator	45
Module 1	-45
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:46
Percent F_2 by Last Stage	4.5%
Run Time (hour)	3
Products Collected (g)	0.97
Theoretical Percent Yields of Perfluorinated Products	
XVI [a]	20%
XXII [b]	14%

[a] 1-chloro-F-butane

[b] 2-chloro-F-butane

TABLE A-14

Aerosol fluorination of 3-chloropentane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	0.8
He Carrier (mL/min)	20
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-45
Module 2	-35
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:75
Percent F_2 by Last Stage	4.6%
Run Time (hour)	1.5
Products Collected (g)	0.191
Theoretical Percent Yields of Perfluorinated Products	
XXIII [a]	10%
XXIV [b]	15%
XXV [c]	5%

[a] 3 chloro-F-pentane

[b] 2-chloro-F-pentane

[c] 1-chloro-F-pentane

TABLE A-15

Aerosol fluorination of chlorocyclopentane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	2.0
He Carrier (mL/min)	135
Temperature (°C)	-7
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-40
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:73
Percent F_2 by Last Stage	4%
Run Time (hour)	3
Products Collected (g)	1.30
Theoretical Percent Yield of Perfluorinated Product	
XXVII	40.2%

TABLE A-16

Aerosol fluorination of tert-butyl chloride

Run Parameters	1	2	3
Hydrocarbon Throughput			
mmole/hour	2.0	3.0	3.0
He Carrier (mL/min)	8	13	13
Temperature (°C)	-7	-7	-7
F_2 Flow (mL/min)			
Stage 1	10	20	2.5
Stage 2	20	20	-
Stage 3	-	20	-
He Diluent (mL/min)			
Stage 1	30	70	70
Stage 2	30	70	-
Stage 3	-	70	-
Reactor Temps (°C)			
Aerosol Generator	30	30	30
Module 1	-45	-40	-45
Module 2	-30	-30	-30
Module 3			
Main He Carrier (mL/min)	400	1000	800
Hydrocarbon : F_2 Ratio	1:36	1:45	1:2
Percent F_2 by Last Stage	5.9%	4.7%	1.1%
Run Time (hour)	3.2	2	2
Products Collected (g)	0.958	0.888	0.513
Theoretical Percent Yield of Perfluorinated Product			
XVII [a]	20%	47%	-

[a] F-iso-butyl chloride

TABLE A-17

Aerosol fluorination of tert-amyl chloride

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	2.5
He Carrier (mL/min)	53
Temperature (°C)	0
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	30
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	120
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	45
Module 1	-45
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	800
Hydrocarbon : F_2 Ratio	1:44
Percent F_2 by Last Stage	4.5%
Run Time (hour)	2.5
Products Collected (g)	0.9626
Theoretical Percent Yields of Perfluorinated Products	
XIX [a]	21.8%
XX [b]	8.9%
XXX [c]	1.4%

[a] 1-chloro-F-2-methylbutane

[b] 1-chloro-F-3-methylbutane

[c] 2-chloro-F-3 methylbutane

TABLE A-18

Aerosol fluorination of 1,2-dichloroethane

Run Parameters	1	2
Hydrocarbon Throughput		
mmole/hour	3.0	2.0
He Carrier (mL/min)	13	45
Temperature (°C)	0	-23
F_2 Flow (mL/min)		
Stage 1	15	15
Stage 2	20	10
Stage 3	-	-
He Diluent (mL/min)		
Stage 1	80	80
Stage 2	80	80
Stage 3	80	80
Reactor Temps (°C)		
Aerosol Generator	30	30
Module 1	-45	-45
Module 2	-35	-35
Module 3	10	10
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:28	1:30
Percent F_2 by Last Stage	2.7%	1.8%
Run Time (hour)	2	2
Products Collected (g)	0.781	0.601
Theoretical Percent Yield of Perfluorinated Product		
XXXI	66%	79%

TABLE A-19

Aerosol fluorination of 1,2-dichloro-2-methylpropane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	2.0
He Carrier (mL/min)	33
Temperature (°C)	22
F_2 Flow (mL/min)	
Stage 1	18
Stage 2	18
Stage 3	18
He Diluent (mL/min)	
Stage 1	75
Stage 2	75
Stage 3	75
Reactor Temps (°C)	
Aerosol Generator	40
Module 1	-45
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:60
Percent F_2 by Last Stage	4.2%
Run Time (hour)	2
Products Collected (g)	0.731
Theoretical Percent Yield of Perfluorinated Product	
XXXII [a]	63%

[a] 1,3-dichloro-F-2-methylpropane

TABLE A-20

Aerosol fluorination of trans-1,2-dichlorocyclopentane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	1.0
He Carrier (mL/min)	175
Temperature (°C)	22
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	45
Module 1	-40
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:146
Percent F_2 by Last Stage	4%
Run Time (hour)	3
Products Collected (g)	0.843
Theoretical Percent Yields of Perfluorinated Products	
XXVI	6%
XXVII	24%
XXXIII	10%
XXXIV	10%
XXXV	9%
XXXVI	9%

TABLE A-21

Aerosol fluorination of 1,1-dichloropropane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	3.7
He Carrier (mL/min)	50
Temperature (°C)	0
F_2 Flow (mL/min)	
Stage 1	10
Stage 2	20
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	40
Module 1	-45
Module 2	-35
Module 3	-10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:20
Percent F_2 by Last Stage	2.3%
Run Time (hour)	2
Products Collected (g)	1.09
Theoretical Percent Yields of Perfluorinated Products	
XXXVII [a]	30%
XXXVIII [b]	30%

[a] 1,1-dichloro-F-propane

[b] 1,2-dichloro-F-propane

TABLE A-22

Aerosol fluorination of 2,2-dichloropropane and 1,3-dichloropropane

Run Parameters	2,2-	1,3-
Hydrocarbon Throughput		
syringe pump mL/hour	0.51	0.51
run time (hour)	1	4.5
mL delivered	0.30	1.70
mmole/hour	2.9	2.9
He primary mL/min	500	500
He secondary mL/min	50	50
He tertiary mL/min	-	-
F_2 Flow (mL/min)		
Stage 1	5	-
Stage 2	10	15
Stage 3	15	15
He diluent (mL/min)		
Stage 1	150	150
Stage 2	150	150
Stage 3	150	150
Reactor Temperatures (°C)		
Aerosol Generator	100	100
Module 1	-30	-30
Module 2	-20	-20
Module 3	20	20
Main He Carrier (mL/min)	600	600
Hydrocarbon : F_2 Ratio	1:23	1:23
Percent F_2 by Last Stage	1.8%	1.8%
Products collected (g)	0.242	1.71
Theoretical Percent Yields of Perfluorinated Products		
XXXVIII	10%	-
XXXIX	16%	43%

[a] 1,2-dichloro-F-propane

[b] 1,3-dichloro-F-propane

TABLE A-23

Aerosol fluorination of 3,3-dichloropentane

Run Parameters	1
Hydrocarbon Throughput [a]	
mmole/hour	0.7
He Carrier (mL/min)	4
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-45
Module 2	-35
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:208
Percent F_2 by Last Stage	4.5%
Run Time (hour)	2
Products Collected (g)	0.185
Theoretical Percent Yields of Perfluorinated Products	
XL, XLI, XLII, XLIII	51%
XXIII, XXIV, XXV	34%

[a] mini bubbler used

TABLE A-24

Aerosol fluorination of 1,1-dichlorocylopentane

Run Parameters	1
Hydrocarbon Throughput [a]	
mmole/hour	1.8
He Carrier (mL/min)	45
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	40
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-40
Module 2	-35
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:81
Percent F_2 by Last Stage	4.5%
Run Time (hour)	3
Products Collected (g)	1.0
Theoretical Percent Yields of Perfluorinated Products	
XXVII	20%
XXXIII	10%
XXXIV	9%
XXXV	9%
XXXVI	9%

[a] minibubbler used

TABLE A-25

Aerosol fluorination of 1,1-dichloroneopentane

Run Parameters	1
Hydrocarbon Throughput [a]	
mmole/hour	2.3
He Carrier (mL/min)	25
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-40
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:64
Percent F_2 by Last Stage	4.5%
Run Time (hour)	1.5
Products Collected (g)	0.85
Theoretical Percent Yields of Perfluorinated Products	
XLIV [b]	26%
XIV [c]	24%

[a] mini bubbler used

[b] 1,1-dichloro-F-neopentane

[c] chloro-F-neopentane

TABLE A-26

Aerosol fluorination of 1,1,1-trichloroethane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	1.9
He Carrier (mL/min)	15
Temperature (°C)	0
F_2 Flow (mL/min)	
Stage 1	-
Stage 2	20
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	40
Module 1	-45
Module 2	-40
Module 3	-10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:25
Percent F_2 by Last Stage	1.7%
Run Time (hour)	2
Products Collected (g)	0.333
Theoretical Percent Yield of Perfluorinated Product	
XLV [a]	77%

[a] 1,1,2-trichloro-F-ethane

TABLE A-27

Aerosol fluorination of 1,1,2,2-tetrachloroethane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	4.0
He Carrier (mL/min)	70
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	18
Stage 2	-
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-45
Module 2	-35
Module 3	0
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:11
Percent F_2 by Last Stage	1.4%
Run Time (hour)	2
Products Collected (g)	1.010
Theoretical Percent Yield of Perfluorinated Product	
XLVI	50%

TABLE A-28

Aerosol fluorination of 2,3-dichloro-1,4-dioxane

Run Parameters	1
Hydrocarbon Throughput [a]	
mmole/hour	1.8
He Carrier (mL/min)	120
Temperature (°C)	75
F_2 Flow (mL/min)	
Stage 1	10
Stage 2	10
Stage 3	20
He Diluent (mL/min)	
Stage 1	60
Stage 2	60
Stage 3	100
Reactor Temps (°C)	
Aerosol Generator	60
Module 1	-45
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:81
Percent F_2 by Last Stage	2.9%
Run Time (hour)	2
Products Collected (g)	0.679
Theoretical Percent Yields of Perfluorinated Products	
XLVIX [b]	21%
XLVIII [c]	35%
XLVII [d]	20%

[a] mini bubbler used

[b] 2,3-dichloro-F-1,4-dioxane

[c] 2-chloro-F-1,4-dioxane

[d] F-1,4-dioxane

TABLE A-29

Aerosol fluorination of bis-(2-chloroethyl)-ether

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	2.6
He Carrier (mL/min)	140
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	10
Stage 2	20
Stage 3	20
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	80
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-45
Module 2	-30
Module 3	0
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:47
Percent F_2 by Last Stage	3.5%
Run Time (hour)	2
Products Collected (g)	1.215
Theoretical Percent Yields of Perfluorinated Products	
L	54%

TABLE A-30

Aerosol fluorination of neopentyl bromide

Run Parameters	1	2 [a]	3 [a]	4 [a]	5 [a]
Hydrocarbon Throughput					
mmole/hour	1.4	10	1.2	1.4	1.4
He Carrier (mL/min)	25	160	20	25	25
Temperature (°C)	-7	-7	-7	-7	-7
F_2 Flow (mL/min)					
Stage 1	20	20	1.7	1.4	0.6
Stage 2	20	20	-	-	-
Stage 3	20	10	-	-	-
He Diluent (mL/min)					
Stage 1	60	120	100	100	100
Stage 2	60	100	-	-	-
Stage 3	60	100	-	-	-
Reactor Temps (°C)					
Aerosol Generator	40	45	40	40	40
Module 1	-40	-40	-48	-40	-40
Module 2	-30	-30	-30	-30	-30
Module 3	10	10	10	10	10
Main He Carrier (mL/min)	1000	1000	1000	1000	1000
Hydrocarbon : F_2 Ratio	1:105	1:12	1:4	1:2.5	1:1
Percent F_2 by Last Stage	4.7%	3.2%	0.15%	0.12%	0.057%
Run Time (hour)	2	-	-	-	-
Products Collected (g)	0.629	-	-	-	-
Theoretical Percent Yields of Perfluorinated Products					
XVIII [b]	62.5%	-	-	-	-

a no UV

b F-isopentane

TABLE A-31

Aerosol fluorination of iso-amyl bromide

Run Parameters	1	2 [a]
Hydrocarbon Throughput		
mmole/hour	3.0	3.0
He Carrier (mL/min)	63	63
Temperature (°C)	-7	-7
F_2 Flow (mL/min)		
Stage 1	20	1.5
Stage 2	20	-
Stage 3	20	-
He Diluent (mL/min)		
Stage 1	80	40
Stage 2	80	-
Stage 3	80	-
Reactor Temps (°C)		
Aerosol Generator	40	40
Module 1	-45	-45
Module 2	-30	-30
Module 3	10	10
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:48	1:1.2
Percent F_2 by Last Stage	4.4%	0.14%
Run Time (hour)	3	3
Products Collected (g)	2.0	1.5
Theoretical Percent Yields of Perfluorinated Products		
XVIII [b]	60%	-

[a] no UV

[b] F-isopentane

TABLE A-32

Aerosol fluorination of 1-bromo-2-methylbutane

Run Parameters	1	2 [a]
Hydrocarbon Throughput		
mmole/hour	3.1	3.1
He Carrier (mL/min)	63	63
Temperature (°C)	-7	-7
F_2 Flow (mL/min)		
Stage 1	20	2
Stage 2	20	-
Stage 3	20	-
He Diluent (mL/min)		
Stage 1	60	60
Stage 2	60	-
Stage 3	60	-
Reactor Temps (°C)		
Aerosol Generator	40	40
Module 1	-40	-40
Module 2	-30	-30
Module 3	10	10
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:47	1:1.6
Percent F_2 by Last Stage	4.6%	0.18%
Run Time (hour)	3	3
Products Collected (g)	2.2	-
Theoretical Percent Yields of Perfluorinated Products		
XVIII [b]		

[a] no UV

[b] F-isopentane

TABLE A-33

Aerosol fluorination of isopentane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	3.3
He Carrier (mL/min)	40
Temperature (°C)	-45
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	20
Stage 3	-
He Diluent (mL/min)	
Stage 1	100
Stage 2	100
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	30
Module 1	-40
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:30
Percent F_2 by Last Stage	3.3%
Run Time (hour)	3
Products Collected (g)	1.31
Theoretical Percent Yields of Perfluorinated Products	
XVIII	46%

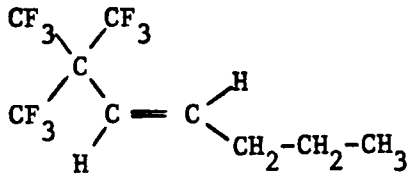
TABLE B-34

Trans-2,2-bis-(trifluoromethyl)-1,1,1-trifluoromethyl-3-heptene (LXIV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -66.5 ppm

J_{HF} = 1.3 Hz



MS: m/e (int) ion

CI 289 (100) M+H, 269 (63.1) M-F, 249 (14.9) $C_9F_7H_8$.

EI 288 (9.7) M, 269 (4.7) M-F, 69 (100) CF_3 and C_5H_9, 42 (84) C_3H_6.

IR: (cm^{-1})

3030(vw), 2977(m), 2940(m), 2930(sh), 2890(w), 2860(w), 1668(w), 1465(w), 1290(vs), 1268(vs), 1250(sh), 1210(w) 1178(w), 1140(m), 1118(s), 980(s), 730(m).

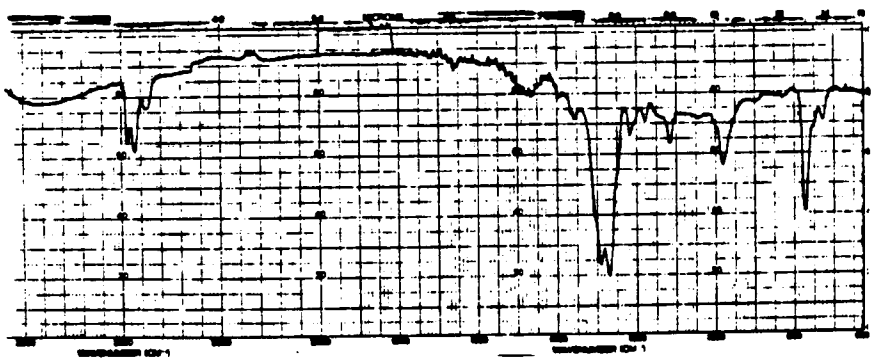


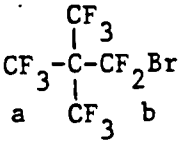
TABLE B-35

F-neopentyl bromide (LXVI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -63.84 ppm (t)

ϕ_b = -47.94 ppm (dect)



J_{ab} = 1o.5 Hz

MS: m/e (int) ion

CI 331 (10.5) and 329 (10.8) M-F, 269 (100) M-Br, 181 (21.6) C_4F_7.

EI 269 (51.9) M-Br, 243 (2.0) and 241 (2.1) C_4F_6Br, 181 (30) C_4F_7, 131 (42.9) and 129 (40.7) CF_2Br, 93 (13.4) C_3F_3, 81 (3.8) and 79 (3.2) Br, 69 (100) CF_3.

IR: (cm^{-1})

1290(vs), 1280(vs), 1225(m), 1040(w), 995(s), 840(m), 760(w), 735(m).

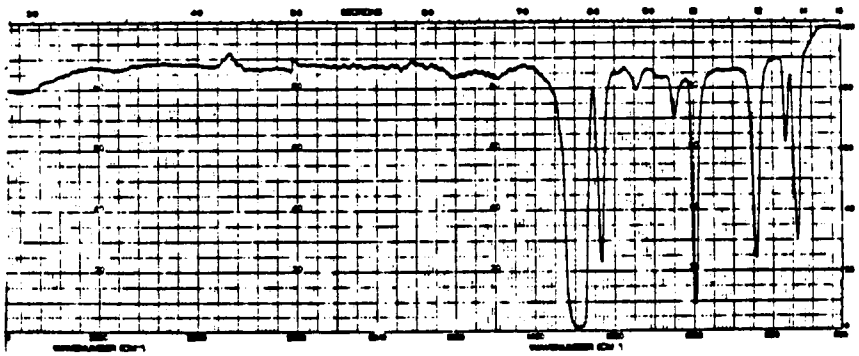


TABLE A-36

Aerosol fluorination of 1,2-dichloroethylenes

Run Parameters	cis	trans
Hydrocarbon Throughput [a]		
mmole/hour	1.2	1.4
He Carrier (mL/min)	10	10
Temperature (°C)	22	22
F_2 Flow (mL/min)		
Stage 1	10	10
Stage 2	10	10
Stage 3	-	-
He Diluent (mL/min)		
Stage 1	60	60
Stage 2	60	60
Stage 3	-	-
Reactor Temps (°C)		
Aerosol Generator	45	45
Module 1	-45	-45
Module 2	-30	-30
Module 3	10	10
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:40	1:35
Percent F_2 by Last Stage	1.7%	1.7%
Run Time (hour)	1	1
Products Collected (g)	-	-
Theoretical Percent Yields of Perfluorinated Products	-	-

[a] minibubbler used

TABLE A-37

Aerosol fluorination of esters

Run Parameters	1 [a]	2 [b]
Hydrocarbon Throughput		
mmole/hour	1.75	3.8
He Carrier (mL/min)	190	15
Temperature (°C)	22	28
F_2 Flow (mL/min)		
Stage 1	20	20
Stage 2	30	30
Stage 3	-	-
He Diluent (mL/min)		
Stage 1	100	80
Stage 2	100	120
Stage 3	-	-
Reactor Temps (°C)		
Aerosol Generator	50	50
Module 1	-40	-45
Module 2	-30	-40
Module 3	10	10
Main He Carrier (mL/min)	800	1000
Hydrocarbon : F_2 Ratio	1:70	1:31
Percent F_2 by Last Stage	4.0%	4.0%
Run Time (hour)	3	2
Products Collected (g)	-	-
Theoretical Percent Yields of Perfluorinated Products	-	-

TABLE A-38

Aerosol fluorination of alcohols

Run Parameters	1 [a]	2 [b]	3 [c]
Hydrocarbon Throughput			
mmole/hour	1.7	2.0	3.8
He Carrier (mL/min)	125	30	20
Temperature (°C)	23	28	24
F_2 Flow (mL/min)			
Stage 1	17	20	20
Stage 2	17	20	20
Stage 3	-	-	20
He Diluent (mL/min)			
Stage 1	80	80	80
Stage 2	80	80	80
Stage 3	-	-	80
Reactor Temps (°C)			
Aerosol Generator	50	50	50
Module 1	-45	-45	-45
Module 2	-30	-30	-30
Module 3	10	10	10
Main He Carrier (mL/min)	1000	1000	1000
Hydrocarbon : F_2 Ratio	1:49	1:49	1:38
Percent F_2 by Last Stage	2.5%	3.2%	4.5%
Run Time (hour)	3	2	1
Products Collected (g)	-	-	-
Theoretical Percent Yields of Perfluorinated Products	-	-	-

[a] iso-amyl alcohol

[b] 2-butanol

[c] tert-butanol

TABLE A-39

Aerosol fluorination of nitropropane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	2.5
He Carrier (mL/min)	80
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	15
Stage 3	-
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	-
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-40
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:34
Percent F_2 by Last Stage	2.8%
Run Time (hour)	2
Products Collected (g)	-
Theoretical Percent Yields of Perfluorinated Products [a]	-

[a] F-propane and NO_2

APPENDIX B

CHARACTERIZATION OF COMPOUNDS

TABLE B-1

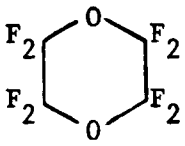
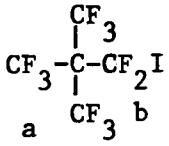
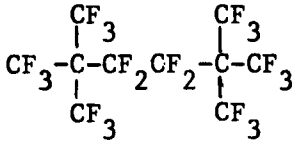
Products in the literature

Number	Compound	NMR (ppm)	IR (cm^{-1})
I	$(CF_3)_3CF$ (a, b)	ϕ_a = -75.3 [a] ϕ_b = -189.0	1325, 1300, 1275, 1205, 1170, 995, 730. [b]
II	$(CF_3)_3C(=O)F$ (a, b)	ϕ_a = -67.1 [c] ϕ_b = +42.3	1880, 1855, 1312, 1290, 1215, 990, 739, 710, 660. [c]
III	$HCF_2-C(CF_3)_2-C(=O)F$ (d, a, b, c)	ϕ_a = -127 [c] ϕ_b = -64 ϕ_c = +40 δ_d = 6.4	3000, 1875, 1850, 1400, 1375, 1290, 1260, 1185, 1080, 990, 730, 690. [c]
V	$CF_3CF_2CF_2C(=O)F$ (a, b, c, d)	ϕ_a = -82 [d] ϕ_b = -128 ϕ_c = -121 ϕ_d = +31	1905, 1370, 1280, 1260, 1225, 1205, 1140, 1090, 1070, 960, 760, 690. [b]
VI	$(CF_3)_2CFC(=O)F$ (a, b, c)	ϕ_a = -75.5 [e] ϕ_b = -182 ϕ_c = +31	1887, 1280, 1250, 1319, 1192, 1155, 999. [e]
IX	$(CF_3)_2CHC(=O)F$ (a, c, b)	ϕ_a = -63 [f] ϕ_b = +38 δ_c = 2.5	1883, 1300, 1275, 1190, 1150, 1000, 705. [f]
XII	$CF_3C(=O)F$ (a, b)	ϕ_a = -75.6 [g] ϕ_b = +15	1912, 1325, 1235, 1200, 1095, 760, 690. [b,g]
XIII	$CF_2ClC(=O)F$ (a, b)	ϕ_a = -68 ϕ_b = +22	1887, 1364, 1269, 1190, 1105, 976, 966, 863, 767, 690. [h]

TABLE B-1 (Continued)

Number	Compound	NMR (ppm)	IR (cm^{-1})
XV	$CF_3CF_2CF_2Cl$ a b c	ϕ_a = -80.7 [i,j] ϕ_b = -125	1350, 1300, 1250, [k] 1160, 1145, 1065, 980, 935, 875, 750, 690.
XVIII	$CF_3-CF_2-CF-(CF_3)_2$ a b c d	ϕ_a = -81.2 [l] ϕ_b = -119.9 ϕ_c = -187.4 ϕ_d = -72.9	1260, 1255, 1225, [m] 1147, 1090, 1060, 980, 930, 888, 720, 635, 610, 525.
XXI	$CF_3CFClCF_3$	ϕ_a = -81.4 [n] ϕ_b = -144.6	1302, 1255, 1190, [o] 1136, 972, 763, 720.
XXVI	cy-C_5F_{10}	ϕ_a = -132.9	1325, 1280, 1220, [b] 1050, 985.
XXVII	$CH_3-\underset{\underset{F}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Cl$ b a c	ϕ_a = -140.5 [p] δ_b = 1.44 δ_c = 3.54	
XXXI	CF_2ClCF_2Cl a a	ϕ_a = -71.2 [q]	1275, 1190, 1140, [r] 1040, 930, 850, 680.
XXXVII	$CFCl_2-CF_2-CF_3$ a b c	ϕ_a = -63 ϕ_b = -121 ϕ_c = -77	1325, 1239, 1212, [s] 1115, 907, 838, 739.
XXXVIII	$CF_2Cl-CFCl-CF_3$ a b c	ϕ_a = -63.8 [t] -64.8 ϕ_b = -133.2 ϕ_c = -76.4	1282, 1239, 1131, [s] 1071, 1044, 970, 851, 727.

TABLE B-1 (Continued)

Number	Compound	NMR (ppm)	IR (cm^{-1})
XXXIX	$CF_2Cl-CF_2-CF_2Cl$ a b a	ϕ_a = - 67.9 [j] ϕ_b = -119.4	1265, 1205, 1150, [u] 1110, 1020, 995, 910, 870, 845, 770.
XLV	$CF_2Cl-CFCl_2$	ϕ_a = -68.4 [v,w] ϕ_b = -72.5	1195, 1155, 1095, [y,x] 1030, 895, 800, 695, 625.
XLVI	$CFCl_2-CFCl_2$ a a	ϕ_a = -67.8 [y,z]	1140, 1110, 1085, [a'] 1025, 930, 900, 880, 835, 780, 750.
XLVII		ϕ_a = -82.0 [b']	1320, 1250, 1165, 1030, 900, 670.
LXV	 a b	ϕ_a = -63.34 [c'] ϕ_b = -42.73	1285, 1270, 1220, [c'] 1120, 1025, 988, 809, 751, 730, 720.
LXXII		ϕ_a = -63.4 [d'] ϕ_b = -99.2	1295, 1280, 1229, [d'] 1170, 1125, 995, 790, 750, 739, 710.

[a] Muller, N; Lauterbur, P.C.; Svatos, G. F. J. Am. Chem. Soc., 1957, 79, 1807.

[b] Weiblen, D. G. "Fluorine Chemistry"; Vol. 2; Simons, J. H., ed; Academic Press: New York, 1950, p. 449.

[c] Adcock, J. L.: Beh, R. A.; Lagow, R. J. J. Org. Chem., 1975, 40, 3271.

[d] Brownstein, S. Chem. Review, 1959, 59, 463.

TABLE B-1 (Continued)

[e] Fawcett, F. S.; Tullock, C. W.; Coffman, D. D. J. Am. Chem. Soc., 1962, 84, 4275.

[f] Halpern, E.; Goldenson, J. J. Phys Chem., 1956, 60, 1372.

[g] Redwood, M. E.; Willis, C. J. Canad. J. Chem., 1967, 45, 389.

[h] Haszeldine, R. N.; Nyman, F. J. Chem. Soc., 1959, 1084.

[i] Pitcher, E.; Buckingham, A. D.; Stone, G. A. J. Chem. Phys., 1961, 36, 124.

[j] White, H. F. Anal. Chem., 1966, 38, 625.

[k] Hauptschein, M.; Nodiff, E. A.; Grosse, A. V. J. Am. Chem. Soc., 1952, 74, 1347.

[l] Dresdner, R. D.; Thimoe, F. N.; Young, J. A. J. Am. Chem. Soc., 1960, 82, 5831.

[m] Sadtler Research Laboratory, IR # 41640P.

[n] Bumgardner, C. L.; Wozny, J. C. J. Fluorine Chem., 1978, 11, 527.

[o] Hauptschein, M.; Braid, M. J. Am. Chem. Soc., 1961, 83, 2383.

[p] Olah, G. A.; Bollinger, J. M. J. Am. Chem. Soc., 1968, 90, 947.

[q] Harris, R. K. J. Mol. Spectr., 1963, 10, 309.

[r] Lacher, J. R.; Mckinley, J. J.; Snow, C. M.; Michel, L. Nelson, G.; Park, J. D. J. Am. Chem. Soc., 1949, 71, 1330.

[s] Haszeldine, R. N.; Steele, B. R. J. Chem. Soc., 1957, 2800.

[t] DeMarco, A.; Gatti, G. J. Magn. Res., 1972, 6, 200.

[u] Hauptschein, M.; Stokes, C. S.; Grosse, A. V. J. Am. Chem. Soc., 1952, 74, 848.

[v] Gutowsky, H. S.; Belford, G. G.; McMahon, P. E. J. Chem. Phys., 1962, 36, 3353.

[w] Lee, J.; Sutcliffe, H. Trans. Faraday Soc., 1959, 55, 880.

TABLE B-1 (Continued)

[x] Sadtler Research Laboratory, IR # 10998K.

[y] Filipovich, G.; Tiers, G. V. D. J. Phys. Chem., 1959, 55, 761.

[z] Tiers, G. V. D. J. Phys. Chem., 1963, 67, 928.

[a'] Sadtler Research Laboratory, IR # 36553K.

[b'] Burdon, J.; Parsons, I. W. Tetrahedron, 1971, 27, 4553.

[c'] Adcock, J. L.; Renk, E. B. J. Org. Chem., 1979, 44, 3431.

[d'] Liu, E. K. S.; Lagow, R. J. J. Fluorine Chem., 1979, 14, 71.

TABLE B-2

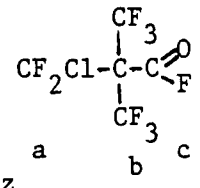
Chloro-F-pivaloyl fluoride (IV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -51.0 ppm (octet)

ϕ_b = -62.7 ppm (m)

ϕ_c = +46.8 ppm (dectet) J_{ab} = 12.2 Hz



MS: m/e (int) ion

CI 265 (31.8) and 263 (100) M-F, 247 (54.7) M-Cl, 181 (64.6) C_4F_7, 87 (3.6) and 85 (16.3) CF_2Cl.

EI 247 (15.7) M-Cl, 181 (10.4) C_4F_7, 169 (22.9) C_4F_5O, 87 (12.7) and 85 (41.5) CF_2Cl, 69 (100) CF_3, 47 (9.2) CFO.

IR: (cm^{-1})

1880(m), 1872(m), 1380(w), 1300(sh), 1270(vs), 1210(m), 1165(m) 1140(m), 1080(w), 1050(w), 988(s), 925(w), 875(m), 760(sh), 735(s).

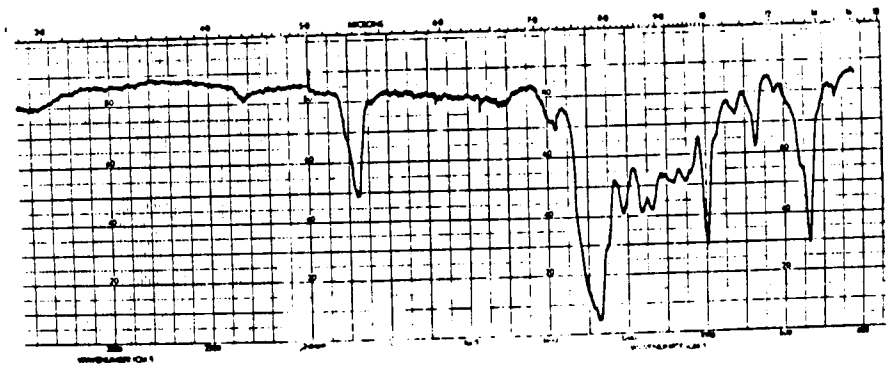
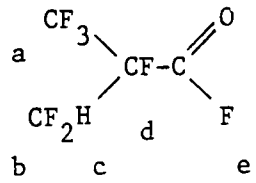


TABLE B-3

3-Hydryl-F-2-methylpropanoyl chloride (VIII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)



ϕ_a = -76 ppm (d.d)

ϕ_b = -125 ppm (d.d.d)

ϕ_d = -184 ppm (d.hext)

ϕ_e = +31 ppm (d.hext)

$J_{ae} = J_{ad} = J_{bd} = J_{de} = J_{be}$ = 5-6 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_c = 6.3 ppm (t.d)

J_{bc} = 42 Hz J_{cd} = 10 Hz

MS: m/e (int) ion

CI 179 (13.0) M-F

EI 132 (2.8) C_3F_5H, 129 (5.2) C_3F_4HO, 128 (16.4) C_3F_4O, 78 (26.3) C_2F_2O, 69 (100) CF_3, 51 (30.1) CF_2H, 47 (48.3) CFO.

IR: (cm^{-1})

3000(vw), 1890(s), 1875(s), 1295(s), 1255(vs), 1230(sh), 1160(s), 1080(m), 955(s), 910(sh), 870(m).

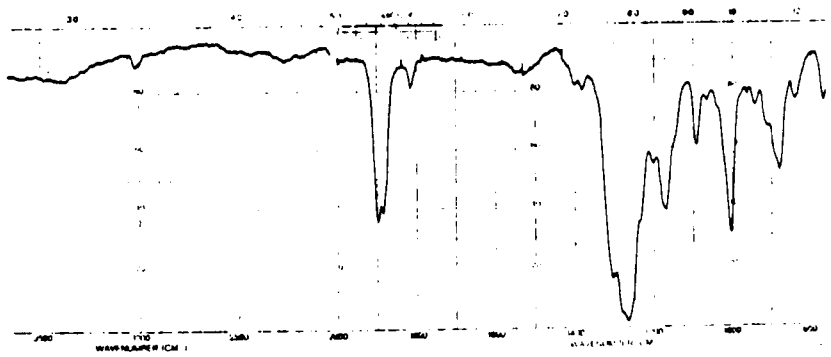
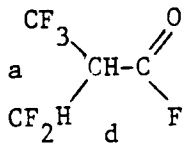


TABLE B-4

Tentative NMR assignments of dihydryl-F-isobutyryl fluorides



(XI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -65 ppm (d.d)

ϕ_b = -126 ppm (d.d.d)

ϕ_e = +30 ppm (hext.d)

$J_{ae} = J_{be} = J_{de}$ = 5-6 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

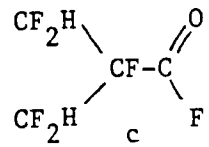
δ_d = 4.0 ppm (hext.d.d)

$J_{ad} = J_{bd}$ = 10 Hz

δ_c = 6.8 ppm (t.d)

J_{bc} = 43 Hz

J_{cd} = 2 Hz



(X)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -132 ppm (d.d.d)

ϕ_c = -186 ppm (t.d.d)

ϕ_d = +32 ppm (p.d)

J_{ac} = 8 Ha

$J_{cd} = J_{ad}$ = 5-6 Hz

^{1}H NMR: (δ_{CHCl_3} = 0 ppm)

δ_b = 6.4 (t.d)

J_{ab} = 45 Hz

J_{bc} = 7 Hz

TABLE B-5

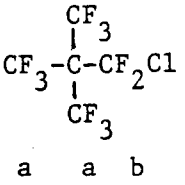
F-Neopentyl chloride (XIV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -64.18 ppm (t)

ϕ_b = -52.29 ppm (dectet)

J_{ab} = 10.7 Hz



MS: m/e (int) ion

CI 287 (10) and 285 (44) M-F, 269 (39.7) M-Cl, 181 (100) C_4F_7, 87 (21) and 85 (70) CF_2Cl, 69 (38) CF_3.

EI 285 (.3) M-F, 269 (20) M-Cl, 181 (31) C_4F_7, 87 (19) and 85 (60) CF_2Cl, 69 (100) CF_3.

IR: (cm^{-1})

1320(sh), 1302(vs), 1294(vs), 1239(m), 1008(s), 880(m), 773(w) 750(m).

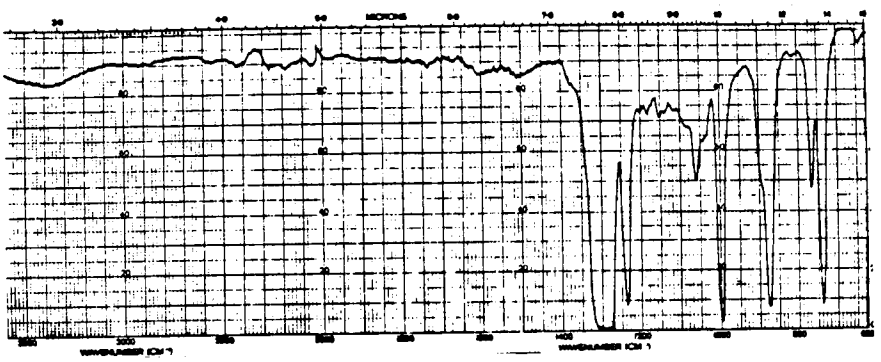


TABLE B-6

1-Chloro-F-butane (XVI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

$CF_3CF_2CF_2CF_2Cl$
a b c d

ϕ_a = -81.7 ppm (t.t)

ϕ_b = -126.1 ppm (t.m)

ϕ_c = -121.6 ppm (q.m)

ϕ_d = -68.9 ppm (t.q)

J_{ac} = 9.89 Hz

$J_{ab} = J_{ad}$ = 1.1 Hz

J_{cd} = 1.46 Hz

J_{bd} = 12.64 Hz

MS: m/e (int) ion

CI 237 (25.4) and 235 (77.6) M-F, 219 (50.3) C_4F_9, 149 (5.2) and 147 (17.5) C_3F_4Cl, 131(9.6) C_3F_5, 119 (12.2) C_2F_5, 87 (4.4) and 85 (15.2) CF_2Cl, 69 (2.7) CF_3.

EI 219 (11.3) C_4F_9, 149 (1.9) and 147 (6.8) C_3F_4Cl, 137 (1.3) and 135 (4.7) C_2F_4Cl, 131 (9.9) C_3F_5, 119 (15) C_2F_5, 100 (11.7) C_2F_4, 87 (18.7) and 85 (58.2) CF_2Cl, 69 (100) CF_3.

IR: (cm^{-1})

1351(m), 1285(sh), 1240(vs), 1213(vs), 1160(w), 1148(s), 1110(s), 1020(sh), 997(m), 866(m), 848(sh), 802(s), 745(sh), 732(s), 694(m).

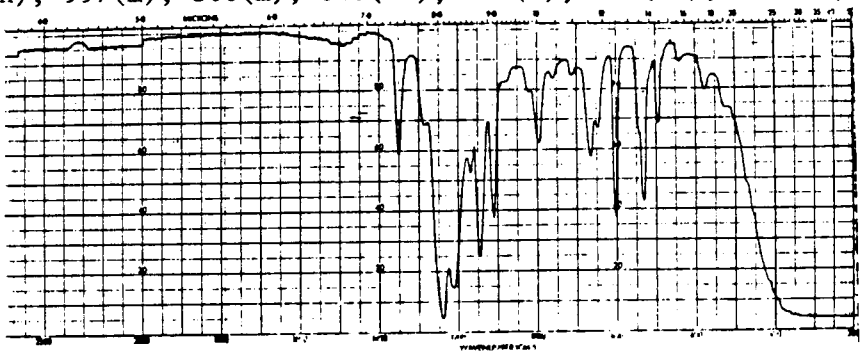


TABLE B-7

F-Iso-butyl chloride (XVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

$(CF_3)_2CF-CF_2Cl$
a b c

ϕ_a = -73.0 ppm (t.d)

ϕ_b = -178.5 ppm (hept.d) J_{ab} = 10.74 Hz

ϕ_c = 62.0 ppm (t.hept) $J_{ac} = J_{bc}$ = 5.88 Hz

MS: m/e (int) ion

CI 237 (24.2) and 235 (77.1) M-F, 219 (100) M-Cl, 197 (23.8) $C_4F_6{}^{35}Cl$, 131 (5.1) C_3F_5, 87 (3.7) and 85 (11.8) CF_2Cl.

EI 219 (37.0) M-Cl, 151 (3.8) C_3F_6, 149 (1.3)and 147 (4.6) C_3F_4Cl, 131 (15.9) C_3F_5, 100 (11.6) C_2F_4, 87 (21.6) and 85 (68.0) CF_2Cl, 69 (100) CF_3.

IR: (cm^{-1})

1300(sh), 1280(vs), 1195(s), 1162(s), 1070(w), 1042(m), 988(s) 916(m), 863(s), 751(m), 722(ms).

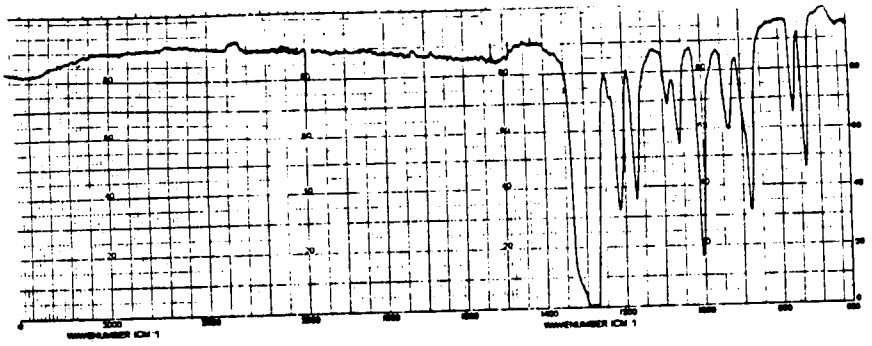
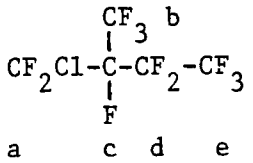


TABLE B-8

1-Chloro-F-2-methylbutane (XIX)



^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -60.6 ppm

ϕ_b = -71.4 ppm

ϕ_c = -177.0 ppm

ϕ_d = -117.5 ppm

ϕ_e = -80.8 ppm

MS: m/e (int) ion

CI 287 (15.6) and 285 (49.1) M-F, 269 (100) M-Cl

EI 269 (26.0) M-Cl, 199 (1.8) and 197(6.2) C_4F_6Cl, 181 (14.5) C_4F_7, 137 (2.7) and 135 (8.5) C_2F_4Cl, 131 (22.1) C_3F_5, 119 (42.0) C_2F_5, 87 (20.7) and 85 (61.2) CF_2Cl, 69 (100) CF_3.

IR: (cm^{-1})

1330(m), 1270(sh), 1240(vs), 1200(s), 1170(m), 1140(m), 1090(m), 1020(m), 950(m), 925(m), 900(m), 870(m), 835(m), 795(m), 740(m), 720(m).

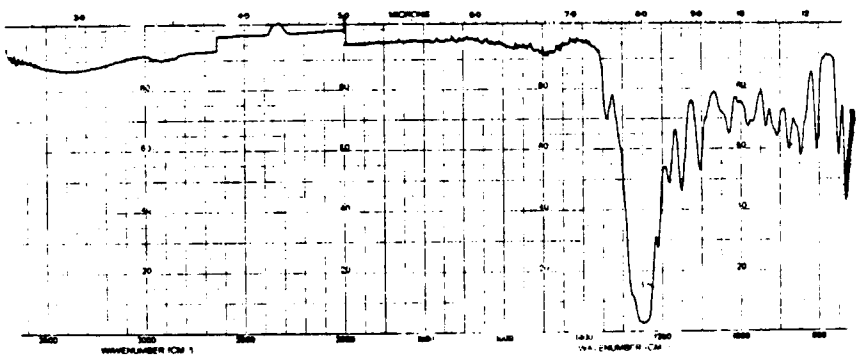


TABLE B-9

1-Chloro-F-3-methylbutane (XX)

^{19}F NMR: (ϕ_{CFCL_3} = 0 ppm)

$$\begin{array}{l} \quad\quad CF_3 \\ \quad\quad | \\ CF_3\text{-}CF\text{-}CF_2\text{-}CF_2Cl \\ \quad a \quad b \quad c \quad d \end{array}$$

ϕ_a = -72.8 ppm

ϕ_b = -185.7 ppm

ϕ_c = -113.2 ppm

ϕ_d = -68.3 ppm

MS: m/e (int) ion

CI 287 (10.3) and 287 (32.1) M-F, 269 (63.4) M-Cl

EI 269 (18.7) M-Cl, 199 (2.0) and 197 (7.3) C_4F_6Cl, 181 (11.0) C_4F_7, 137 (5.8) and 135 (18.7) C_2F_4Cl, 131 (19.2) C_3F_5, 119 (20.9) C_2F_5, 100 (11.1) C_2F_4, 87 (18.5) and 85 (56.7) CF_2Cl, 69 (100) CF_3.

IR: (cm^{-1})

1300(sh), 1260(vs), 1250(vs), 1225(s), 1180(s), 1145(m), 1100(s), 975(s), 855(m), 795(s), 740(m), 710(m)

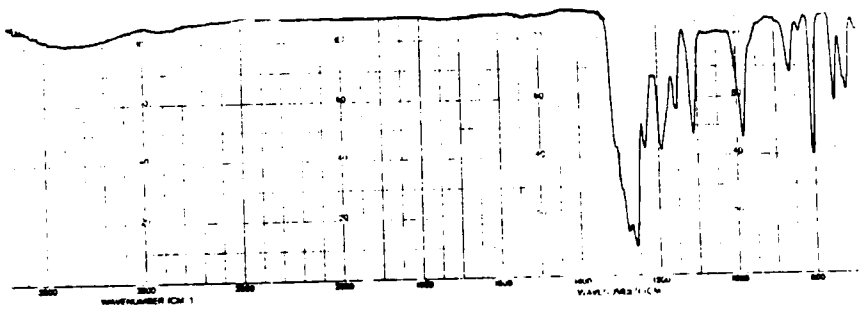


TABLE B-10

2-Chloro-F-butane (XXII)

^{19}F NMR: (ϕ_{CFCL_3} = 0 ppm)

$CF_3CFClCF_2CF_3$
a b c d

ϕ_a = -78.1 ppm (q.t)

ϕ_b = -139.2 ppm (t.q) J_{ac} = 10.99 Hz

ϕ_c = -121.1 ppm (q.q) J_{bd} = 9.77 Hz

ϕ_d = -79.6 ppm (q.d) J_{ad} = 3.66 Hz

MS: m/e (int) ion

CI 237 (23.1) and 235 (75.3) M-F, 219 (100) M-Cl, 131 (6.1) C_3F_5, 119 (7.9) C_2F_5, 69 (41.8) CF_3.

EI 219 (7.9) M-Cl, 149 (2.2) and 147 (7.2) C_3F_4Cl, 137 (4.3) and 135 (14.0) C_2F_4Cl, 131 (9.5) C_3F_5, 119 (13.2) C_2F_5, 100 (10) C_2F_4, 69 (100) CF_3.

TABLE B-11

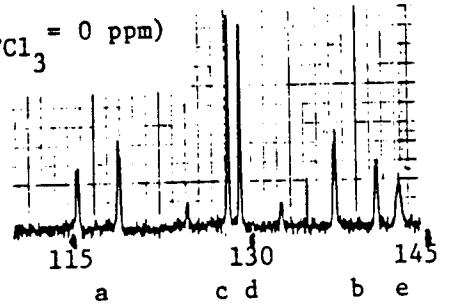
Tentative NMR assignments for chloro-F-pentanes

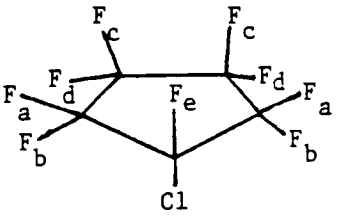
^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)	
	CF_3-CF_2-CFCl-CF_2-CF_3 (XXIII)
	a b c
ϕ_a = -79.0 ppm (d)	
ϕ_b = -120.1 ppm (s)	J_{ac} = 9.2 Hz
ϕ_c = -137.0 ppm (m)	
	CF_3-CFCl-CF_2-CF_2-CF_3 (XXIV)
	a b c d e
ϕ_a = -77.8 ppm (d.t)	
ϕ_b = -138.7 ppm (m)	J_{ac} = 9.2 Hz
ϕ_c = -117.6 ppm (m)	J_{ab} = 12.2 Hz
ϕ_d = -124.3 ppm (m)	J_{ce} = 4.5 Hz
ϕ_e = -81.3 ppm (t)	
	CF_2Cl-CF_2-CF_2-CF_2-CF_3 (XXV)
	a b c d e
ϕ_a = -68.6 ppm (t)	
ϕ_b = -120.8 ppm (m)	J_{ac} = 12.2 Hz
ϕ_c = -122.6 ppm (m)	J_{ce} = 12.2 Hz
ϕ_d = -126.7 ppm (m)	
ϕ_e = -81.2 ppm (t)	

TABLE B-12

Chloro-F-cyclopentane (XXVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)





ϕ_a = -118.0 ppm
ϕ_b = -136.5 ppm
AB pattern J_{ab} = 262.5 Hz

ϕ_c = -126.5 ppm
ϕ_d = -129.0 ppm
AB pattern J_{cd} = 253.3 Hz

ϕ_e = -139.8 ppm

MS: m/e (int) ion

CI 199 (31) and 197 (100) C_4F_6Cl, 149 (40) and 147 (74) C_3F_4Cl, 131 (56) C_3F_5.

EI 199 (1) and 197 (6.6) C_4F_6Cl, 181 (1.2) C_4F_6, 149 (22) and 147 (54) C_3F_4Cl, 131 (100) C_3F_5, 118 (3) and 116 (12) C_2F_3Cl, 100 (22) C_2F_4.

IR: (cm^{-1})

1310(s), 1275(m), 1240(s), 1220(vs), 1120(m), 1065(w), 1020(m), 970(s), 920(w), 870(s), 740(w).

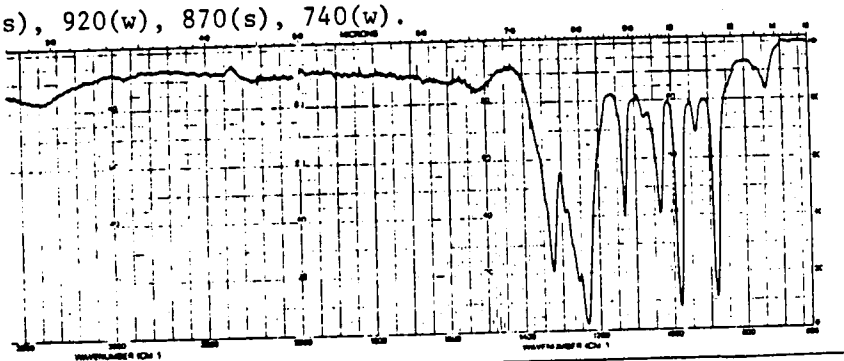


TABLE B-13

1,2-Difluoro-1-chloro-2-methylpropane (XXVIII) and
1,2-Difluoro-3-chloro-2-methylpropane (XXIX)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -244 ppm (m.t)

ϕ_b = -185 ppm (m)

$FCH_2-\overset{\overset{CH_3\ e}{|}}{C}F-CH_2Cl$ (XXVII)
a c b d

J_{ab} = 9 Hz

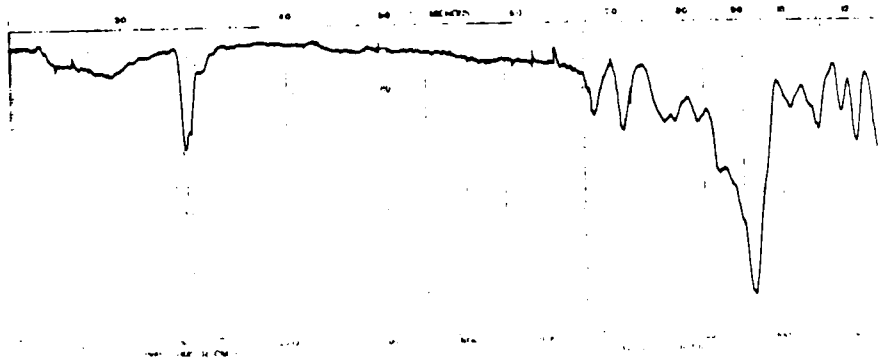
^1H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_c = 4.45 ppm (d.d) J_{ac} = 47 Hz

δ_d = 3.65 ppm (d.m) $J_{bc} = J_{bd} = J_{be}$ = 19 Hz

δ_e = 1.45 ppm (d.d) $J_{ad} = J_{ae}$ = 2 Hz

IR: contains impurities



^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -144 ppm (m.d)

ϕ_b = -187 ppm (m)

$(CH_3)_2CF-CHFCl$ (XXIX)
d b c a

J_{ab} = 9 Hz

TABLE B-13 (Continued)

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_c = 5.95 ppm (d.d) J_{ac} = 56 Hz

δ_d = 1.45 ppm (m.d) J_{bd} = 19 Hz

J_{bc} = 9 Hz

J_{ad} = 2 Hz

IR: contains impurities

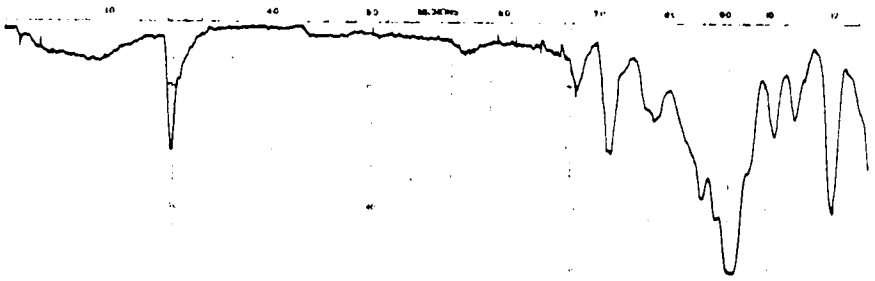


TABLE B-14

2-Chloro-F-3-methylbutane (XXX)

^{19}F NMR: (Φ_{CFCl_3} = 0 ppm)

Φ_a = -70.7 ppm

Φ_b = -176.0 ppm

Φ_c = -135.3 ppm

Φ_d = -77.8 ppm

$$\underset{a}{CF_3}-\underset{b}{\underset{|}{\overset{CF_3}{CF}}}-\underset{c}{CFCl}-\underset{d}{CF_3}$$

TABLE B-15

1,3-Dichloro-F-2-methylpropane (XXXII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -60.1 ppm (d.q)

ϕ_b = -71.4 ppm (d.p)

ϕ_c = -167.2 ppm (q.p)

$CF_2Cl\text{-}\overset{\overset{CF_3\ b}{|}}{CF}\text{-}CF_2Cl$

a c a

J_{ab} = 9.8 Hz

$J_{ac} = J_{bc}$ = 4.9 Hz

MS: m/e (int) ion

CI 255 (1.0) and 253 (23.7) and 251 (36.4) M-F, 237 (34.0) and 235 (100) M-Cl, 149 (2.0) and 147 (6.6) C_3F_4Cl, 87 (15.8) and 85 (48.6) CF_2Cl, 69 (5.6) CF_3.

EI 237 (4.1) and 235 (14.1) M-Cl, 149 (1.8) and 147 (6.1) C_3F_4Cl, 131 (8.6) C_3F_3, 100 (6.7) C_2F_4, 93 (5.8) C_3F_3, 87 (33.1) and 85 (100) CF_2Cl, 81 (1.1) C_2F_3, 69 (48.7) CF_3.

IR: (cm^{-1})

1285(vs), 1255(vs), 1230(vs), 1185(sh), 1170(s), 1150(sh), 1090(s), 1040(s), 930(m), 910(m), 855(s), 830(s) 775(m), 740(m).

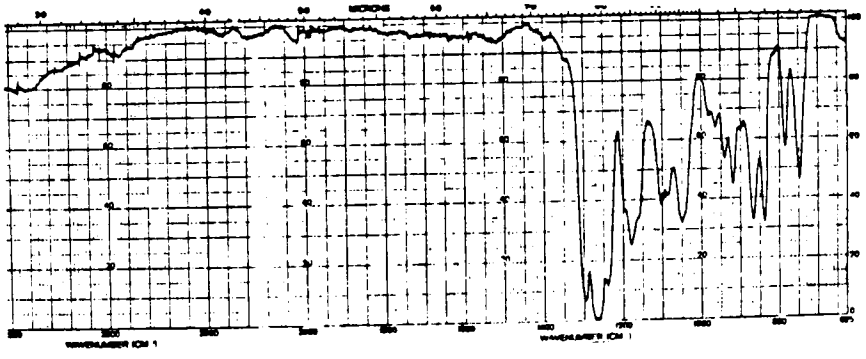
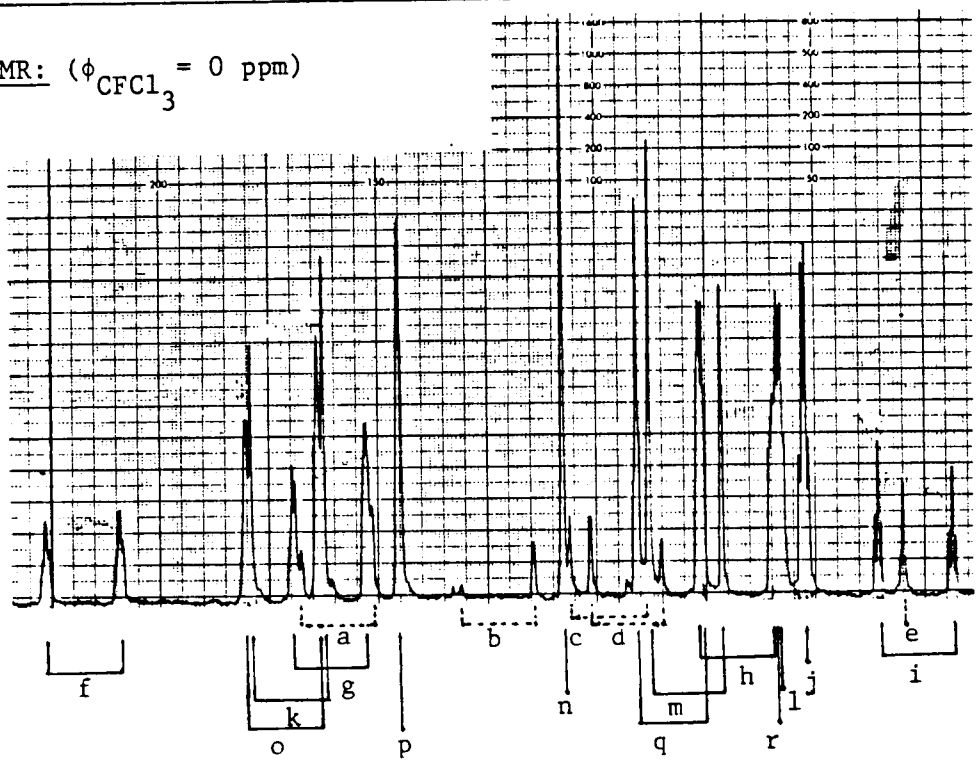


TABLE B-16

NMR assignments of dichloro-F-cyclopentanes

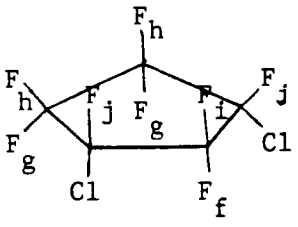
^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)



XXXVI

$\phi_a - \phi_e$ *

XXXV



ϕ_f = -104.9 ppm
ϕ_i = -138.6 ppm
AB J_{fi} = 257 Hz

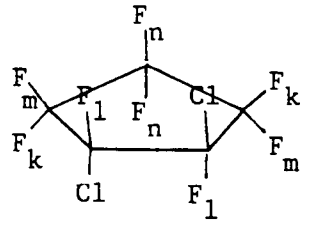
ϕ_g = -114.5 ppm
ϕ_h = -131.1 ppm
AB J_{gh} = 255 Hz

ϕ_j = -134.0 ppm (q)

* cis-1,2-dichloro-F-pentane: Table B-17.

TABLE B-16 (Continued)

XXXIII

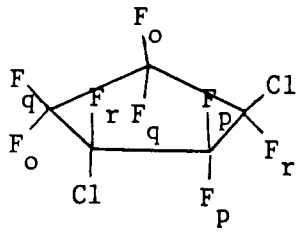


ϕ_k = -112.8 ppm
ϕ_m = -129.1 ppm
AB
J_{km} = 243 Hz

ϕ_l = -132.9 ppm (m)

ϕ_n = -124.0 ppm (m)

XXXIV



ϕ_0 = -112.6 ppm
ϕ_q = -128.4 ppm
AB
J_{oq} = 245 Hz

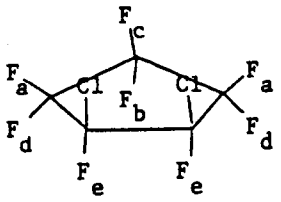
ϕ_p = -117.4 ppm (m)

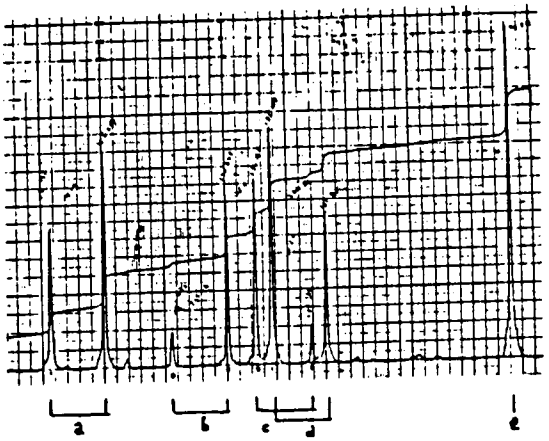
ϕ_r = -132.7 ppm (m)

TABLE B-17

Cis-1,2-Dichloro-F-cyclopentane (XXXVI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)





ϕ_e = -137.8 ppm (s)

ϕ_a = -114.8 ppm
ϕ_d = -126.3 ppm
AB pattern J_{ad} = 241.1 Hz

ϕ_b = -121.7 ppm
ϕ_c = -125.1 ppm
AB pattern J_{bc} = 250.4 Hz

MS: m/e (int) ion

CI 267 (5.4)and 265 (37) and 263 (63) M-F, 249 (4.1) and 247 (14) C_5F_8Cl, 149 (24) and 147 (75) C_3F_4Cl, 93 (11) C_3F_3, 81 (26) C_2F_3, 69 (55) CF_3.

EI 149 (32) and 147 (100) C_3F_4Cl, 118 (3.6) and 116 (12) C_2F_3Cl, 69 (14) CF_3.

IR: (cm^{-1})

1330(m), 1300(m), 1240(s), 1210(s), 1100(m), 1040(s), 1000(s), 910(s), 860(s), 820(w).

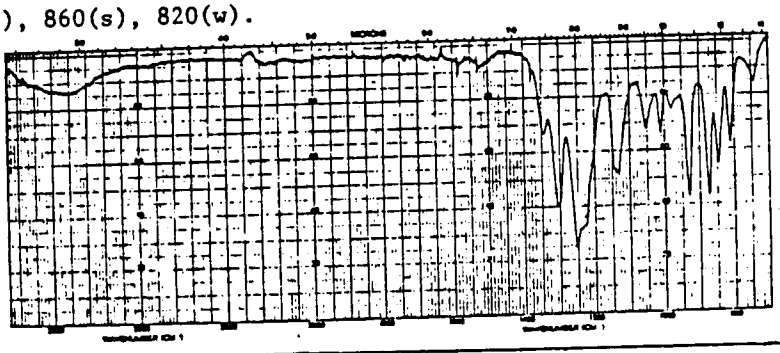


TABLE B-18

Tentative NMR assignments of dichloro-F-pentanes

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)	$CF_3CFClCFClCF_2CF_3$ (XLII) a b c d e
ϕ_a = -75 ppm (d.d)	
ϕ_b = -131 ppm (m)	J_{ab} = 6 Hz
ϕ_c = -130 ppm (m)	$J_{ac} = J_{bc}$ = 12 Hz
ϕ_d = -120 ppm (m)	
ϕ_e = -79 ppm (d)	
ϕ_a = -77 ppm (t.d)	$CF_3CFClCF_2CFClCF_3$ (XLIII) a b c b a
ϕ_b = -134 ppm (m)	
ϕ_c = -112 ppm (m)	J_{ab} = 8 Hz J_{ac} = 16 Hz
ϕ_a = -64 ppm (d.m)	$CF_2ClCF_2CFClCF_2CF_3$ (XL) a b c d e
ϕ_b = -115 ppm (m)	
ϕ_c = -135 ppm (m)	$J_{ac} = J_{ce}$ = 12 Hz
ϕ_d = -124 ppm (m)	
ϕ_e = -79 ppm (d)	
ϕ_a = -68 ppm (t)	$CF_2ClCF_2CF_2CFClCF_3$ (XLI) a b c d e
ϕ_b = -119 ppm (m)	
ϕ_c = -118 ppm (m)	J_{ac} = 14 Hz
ϕ_d = -137 ppm (m)	J_{ce} = 11 Hz
ϕ_e = -81 ppm (t)	

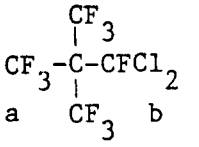
TABLE B-19

1,1-Dichloro-F-neopentane (XLIV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -62.99 ppm (d)

ϕ_b = -57.86 ppm (dect)



J_{ab} = 12.2 Hz

MS: m/e (int) ion

CI 305 (2.3) and 303 (8.1) and 301 (27.2) M-F, 287 (41) and 285 (100) M-Cl, 69 (43.4) CF_3

EI 199 (12.8) and 197 (31.5) C_4F_6Cl, 181 (45.8) C_4F_7, 103 (5.2) and 101 (14.7) $CFCl_2$, 69 (100) CF_3, 68 (6.6) and 66 (18.2) CFCl.

IR: (cm^{-1})

1300(sh), 1270(vs), 1255(vs), 1220(sh), 1185(m), 990 (m), 840(w), 825(w), 785(w), 750(sh), 730(m), 710(sh).

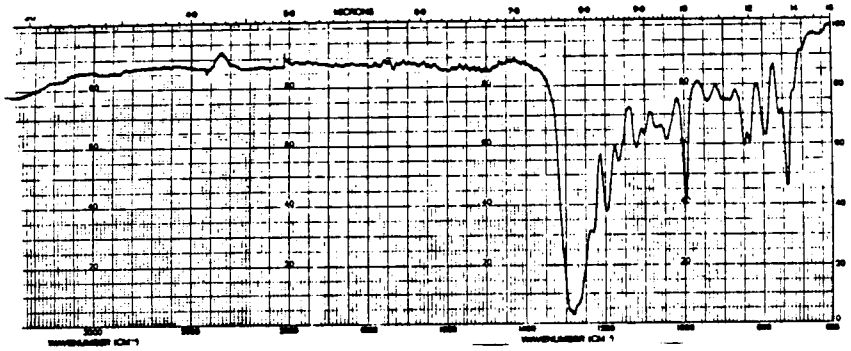
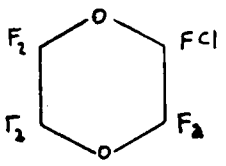
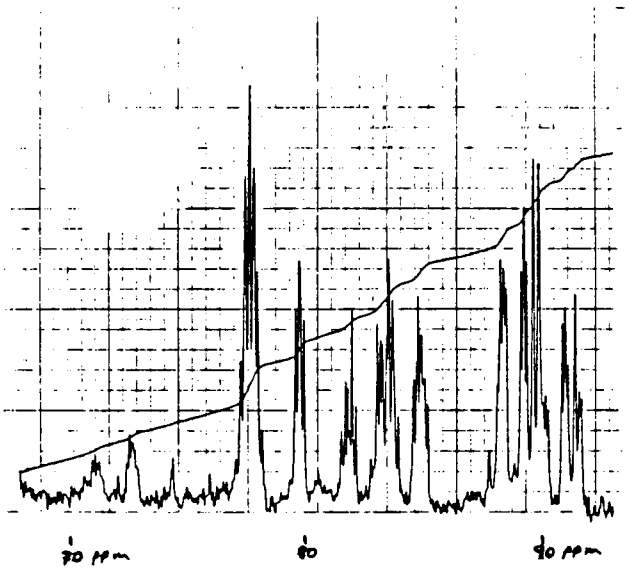


TABLE B-20

2-Chloro-F-1,4-dioxane (XLVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)





MS: m/e (int) ion

CI 213 (99) M-Cl

EI 231 (2.3) and 229 (6.8) M-F, 213 (9.7) M-Cl, 118 (9.5) and 116 (25.5) C_2F_3Cl, 100 (100) C_2F_4.

IR: (cm^{-1})

1315(w), 1280(m), 1225(s), 1175(m), 1115(m), 1100(m), 1085(m), 1040(w) 1020(w), 845(w).

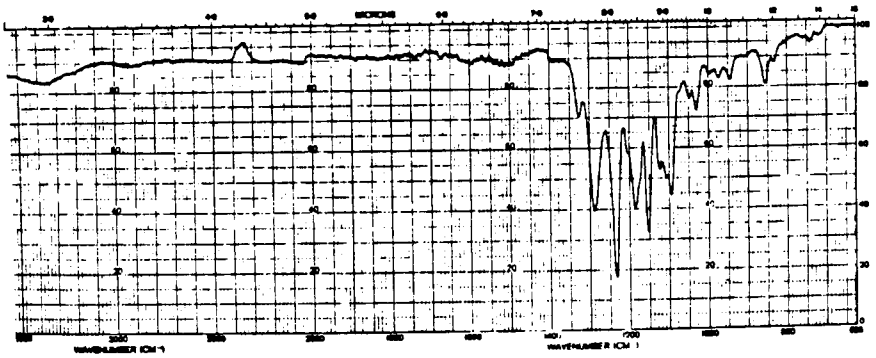
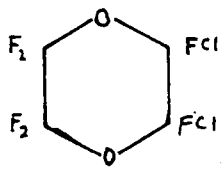
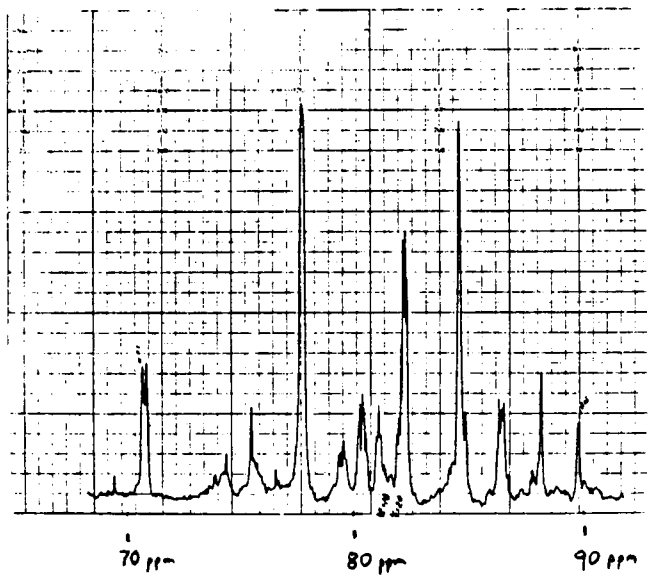


TABLE B-21

2,3-Dichloro-F-1,4-dioxane (XLVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)





MS: m/e (int) ion

CI 249 (0.6) and 247 (4.0) and 245 (6.2) M-F, 231 (12.1) and 229 (22.3) M-Cl, 194 (100) $C_4F_6O_2$.

EI 231 (5.1) and 229 (8.5) M-Cl, 194 (32.6) $C_4F_6O_2$, 100 (100) C_2F_4.

IR: (cm^{-1})

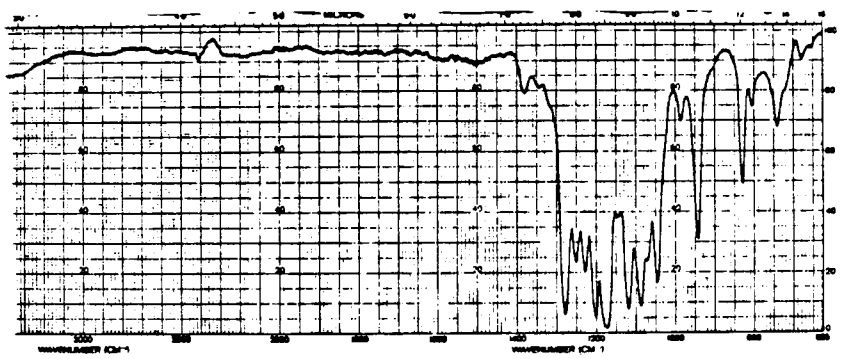


TABLE B-22

F-Bis-(2-chloroethyl)-ether (L)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

$CF_2ClCF_2OCF_2CF_2CF_2Cl$
a b b a

ϕ_a = -74.4 ppm (s)

ϕ_b = -87.7 ppm (s)

MS: m/e (int) ion

CI 272 (0.4) and 270 (3.6) and 268 (4.7) M-F, 153 (0.7) and 151 (1.2) C_2F_4ClO, 137 (6.3) and 135 (26.5) C_2F_4Cl. 97 (11.2) C_2F_3O, 87 (31.2) and 85 (100) CF_2Cl.

EI 203 (3.4) and 201 (11.6) M-CF_2Cl, 137 (31.0) and 135 (100) C_2F_4Cl, 119 43.1) C_2F_5 100 (9.7) C_2F_4, 87 (13.8) and 85 (42.7) CF_2Cl.

IR: (cm^{-1})

1355(w), 1320(w), 1290(w), 1215(vs), 1185(vs). 1155(vs), 1135(m), 995(m), 975(m), 775(w), 750(w).

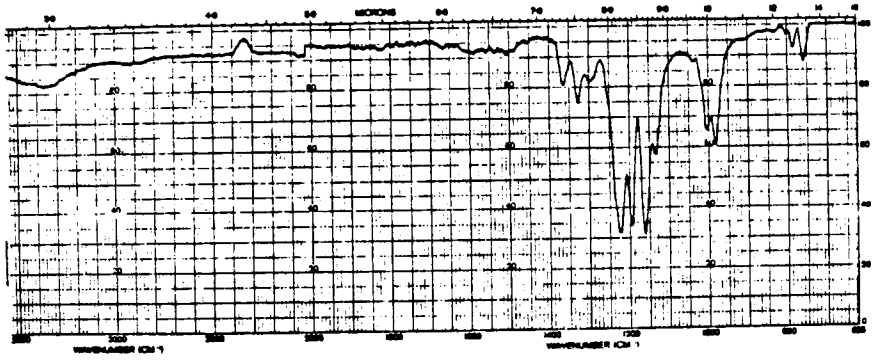


TABLE B-23

2,3,3-Trifluoro-2-methylbutane (LI)

^{19}F NMR: (ϕ_{CFCL_3} = 0 ppm)

CH_3-CF_2-$CF(CH_3)_2$
a b c d

ϕ_b = -105.7 ppm (q)

ϕ_c = -154.2 ppm (hept) J_{ab} = 18.3 Hz J_{bc} = 1.2 Hz

^1H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_a = 1.65 ppm (t.d) J_{ac} = 2.0 Hz

δ_d = 1.74 ppm (d.t) J_{cd} = 21.4 Hz

MS: m/e (int) ion

CI 143 (10.5) $M+CH_5$, 125 (17.0) M, 107 (100) M-F, 89 (24.6) $C_5H_{10}F$, 87 (13.7) C_5H_8F.

EI 111 (3.6) $C_4H_6F_3$, 95 (8.3) $C_4H_9F_2$, 93 (16.2) $C_4H_7F_2$, 69 (15.3) C_5H_9, 65 (51.9) $C_2H_3F_2$, 61 (100) C_3H_6F, 47 (15.6) C_2H_4F, 43 (17.5) C_3H_7, 41 (19.2) C_3H_5.

IR: (cm^{-1})

3000(m), 2980(w), 1880(vw), 1485(w), 1390(m), 1260(m), 1170(vs), 1100(w), 1030(w), 940(m), 850(w) 740(w).

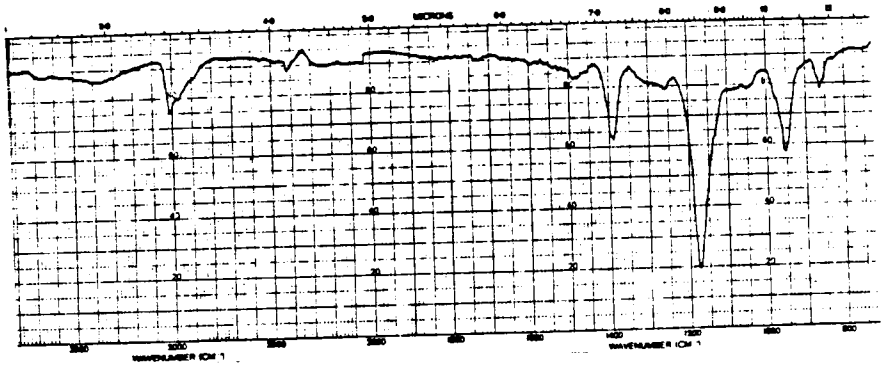


TABLE B-24

3,3-Difluoro-2-methylbutane (LII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

$CH_3-CF_2-CH(CH_3)_2$
a b c d

ϕ_b = -98.0 ppm (q.d)

^1H NMR: (δ_{CHCl_3} =7.25 ppm)

δ_a = 1.51 ppm (t) J_{ab} = 18.8 Hz

δ_c = 1.6-2.1 ppm (m) J_{bc} = 12.8 Hz

δ_d = 1.0 ppm (d) J_{cd} = 6.8 Hz

MS: m/e (int) ion

CI 125 (0.6) $M+CH_5$, 107 (0.7) M-H, 89 (100) M-F, 69 (2.1) C_5H_9.

EI 93 (13.5) $C_4H_7F_2$, 78 (2.0) $C_3H_4F_2$, 77 (7.6) $C_3H_3F_2$, 69 (18.4) C_5H_9, 65 (69.7) $C_2H_3F_2$, 47 (8.2) C_2H_4F, 43 (100) C_3H_7.

IR: (cm^{-1})

2980(s), 2900(m), 1480(m), 1390(s), 1360(w), 1260(s), 1200(sh), 1160(vs), 1110(s), 1050(m), 920(s), 880(w), 730(w).

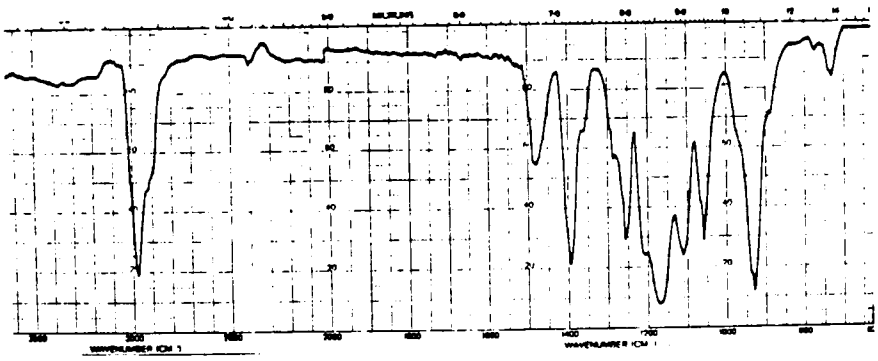


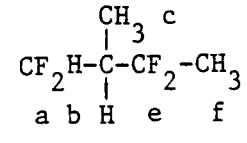
TABLE B-25

1,1,3,3-Tetrafluoro-2-methylbutane (LII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -123.8 ppm (d.d.m)

ϕ_e = -92.1 ppm (d.m)



J_{ee} = 200 Hz J_{ae} = 10 Hz

^{1}H NMR: (δ_{CHCl_3}=7.25 ppm)

δ_b = 5.9 ppm (t.d) J_{ab} = 53 Hz

δ_c = 1.06 ppm (m.d) J_{cd} = 7 Hz

δ_d = 1.50 ppm (p.m) J_{ad} = J_{de} = J_{ef} = 18 Hz

δ_f = 1.57 ppm (m.t) J_{bd} = 3 Hz

J_{ac} = J_{ce} = 14 Hz

MS: m/e (int) ion

CI 144 (22.6) M, 125 (100) M-F.

EI 129 (2.4) $C_4F_4H_5$, 79 (100) $C_3F_2H_5$, 77 (10.3) $C_3F_2H_3$, 65 (74.1) $C_2F_2H_3$, 51 (26.3) CF_2H.

IR: (cm^{-1})

2900(m), 1475(w), 1400(m), 1335(w), 1255(m), 1175(s), 1125(s), 1080(s), 1005(w), 940(w).

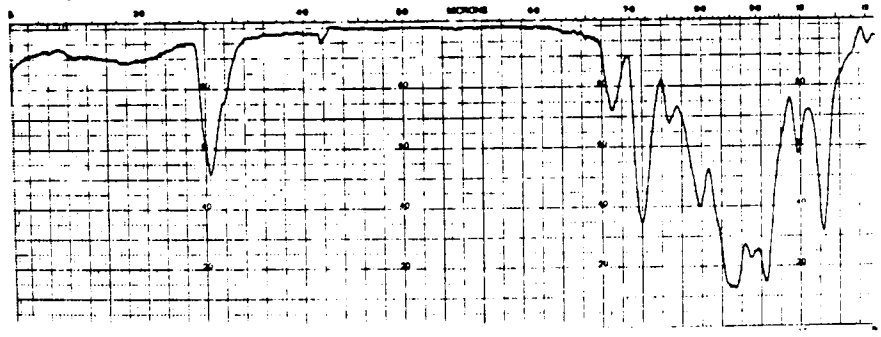


TABLE B-26

2,3-Difluoro-2-methylbutane (LIV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

CH_3-CHF-CF(CH_3)$_2$
a b c d e

ϕ_c = -151.6 ppm (d.d.hept)

ϕ_d = -184.3 ppm (m.d.d.q) J_{bc} = 47.6 Hz J_{cd} = 9.8 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_a = 1.32 ppm (d.d.d) J_{ac} = 23.2 Hz J_{ab} = 6.6 Hz

δ_b = 4.47 ppm (d.d.q) J_{bd} = 12.7 Hz J_{ad} = 1.0 Hz

δ_e = 1.74 ppm (d.d) J_{ce} = 2.0 Hz J_{de} = 21.5 Hz

MS: m/e (int) ion

CI 107 (2.1) M-H, 89 (100) M-F, 69 (9.6) C_5H_9, 61 (1.7) C_3H_6F.

EI 93 (13.0) $C_4H_7F_2$, 79 (25.6) $C_3H_5F_2$, 61 (100) C_3H_6F,
60 (17.7) C_3H_5F, 47 (14.4) C_2H_4F.

IR: (cm^{-1})

3000(s), 2950(m), 1465(m), 1385(s), 1170(s), 1120(s), 1085(s), 960(m), 865(m), 740(w).

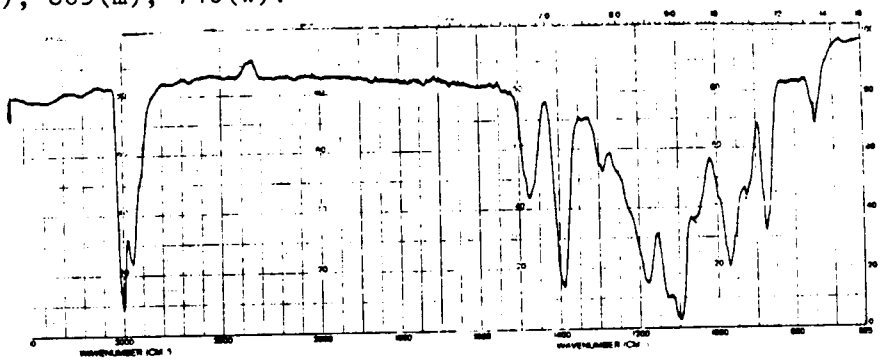


TABLE B-27

1,3,3-Trifluoro-2-methylbutane (LV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

CH_3-CF_2-$CH(CH_3)(CH_2F)$
a b c d e f

ϕ_b = -95.5 ppm (d.m)

ϕ_f = -226.8 ppm (t.d) J_{ef} = 47.3 Hz J_{cf} = 21.4 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_a = 1.60 ppm (t) J_{ab} = 19.1 Hz

δ_c = 1.5-2.0 ppm (m) J_{ce} = 6.8 Hz

δ_d = 1.10 ppm (d) J_{cd} = 6.0 Hz

δ_e = 4.50 ppm (d.m)

MS: m/e (int) ion

CI 143 (12.9) M+CH_5, 125 (60.4) M-H, 107 (100) M-F,
89 (54.6) $C_5H_{10}F$, 87 (63.1) C_5H_8F.

EI 93 (10.4) $C_4H_7F_2$, 78 (25.6) $C_3H_4F_2$, 77 (23.2) $C_3H_3F_2$,
69 (86.4) C_5H_9, 65 (100) $C_2H_3F_2$. 61 (18.4) C_3H_6F.

IR: (cm^{-1})

2990(m), 2940(sh), 1750(w), 1470(m), 1400(s), 1300(sh), 1250(s)
1215(s), 1170(s), 1110(vs), 1040(s). 990(m), 930(s), 870(sh),
740(w).

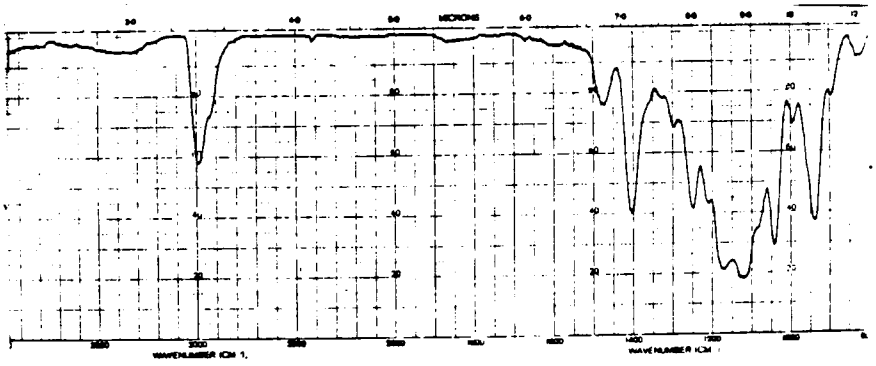


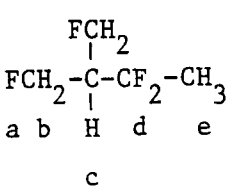
TABLE B-28

1,3,3-trifluoro-2-fluoromethylbutane (LVI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -231 1 ppm (t.d)

ϕ_d = -99.8 ppm (q.d)



^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_b = 4.65 ppm (d.d)

δ_c = 2.20 ppm (m)

δ_e = 1.64 ppm (t)

J_{ab} = 46.8 Hz

J_{ac} = 21.4 Hz

J_{de} = 21.0 Hz

J_{cd} = 11.0 Hz

J_{bc} = 5.4 Hz

IR: Contains impurities

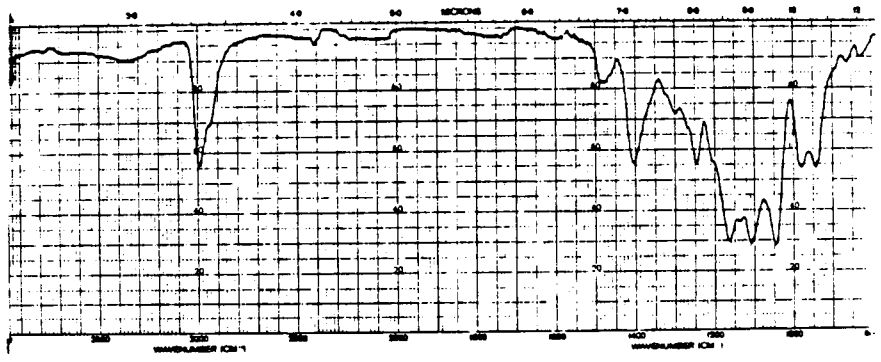


TABLE B-29

1,2,3,3-Tetrafluoro-2-methylbutane (LVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -220 ppm (t.d)

ϕ_c = -140 ppm (m)

ϕ_e = -92 ppm (m)

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_b = 4.60 ppm (d.d.m)

δ_d = 1.44 ppm (d)

δ_f = 1.60 ppm (t)

$J_{ac} = J_{ce}$ = 9-10 Hz

J_{ab} = 46.1 Hz

J_{cd} = 24.4 Hz

J_{ef} = 18.6 Hz

$J_{ac} = J_{bd} = J_{bc}$ = 7-8 Hz

IR: Contains impurities

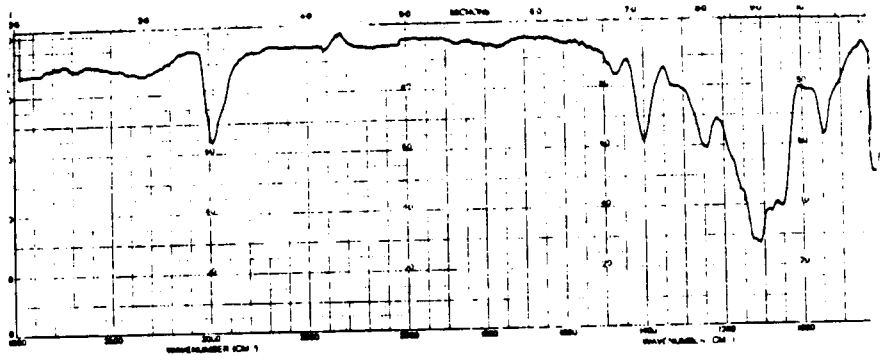
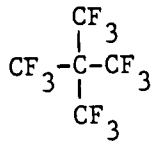


TABLE B-30

F-neopentane (LX)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -65.42 ppm (s)



MS: m/e (int) ion

CI 269 (100) M-F, 69 (62.1) CF_3.

EI 200 (7.3) C_4F_8, 150 (42) C_3F_6, 69 (100) CF_3.

IR: (cm^{-1})

1320(vs) 1300(vs), 1000 (s), 745(m).

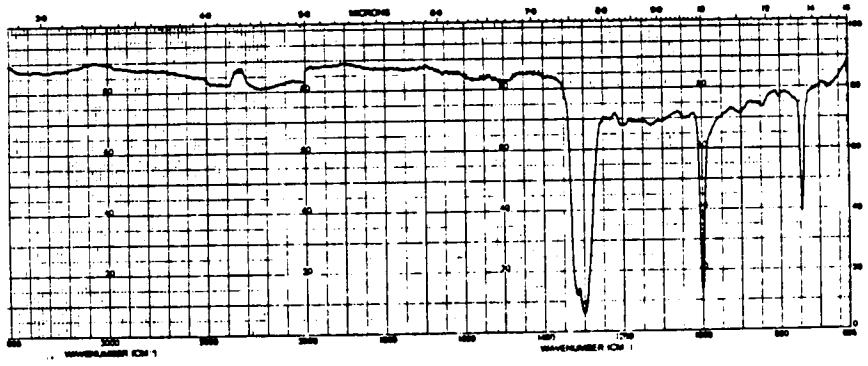


TABLE B-31

1-Hydryl-F-neopentane (LXI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -65.4 ppm (t.d)

ϕ_b = -125.7 ppm (d.m)

J_{ab} = 10.5 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_c = 6.26 ppm (t.m)

J_{bc} = 53.0 Hz

J_{ac} = 1.0 Hz

MS: m/e (int) ion

EI 251 (0.4) M-F, 200 (2.9) C_4F_8, 181 (77.2) C_4F_7, 163 (5.0) C_4F_6H, 131 (2.9) C_3F_5, 113 (18) C_3F_4H, 93 (9.8) C_3F_3, 75 (3.9) C_3F_2H, 69 (100) CF_3, 51 (91.6) CF_2H.

IR: (cm^{-1})

3000(vw), 1400(w), 1363(m), 1302(sh), 1275(vs), 1250(sh), 1215(m), 1183(w), 1138(vw), 1109(w), 1066(m), 985(s), 743(m), 727(m), 670(m).

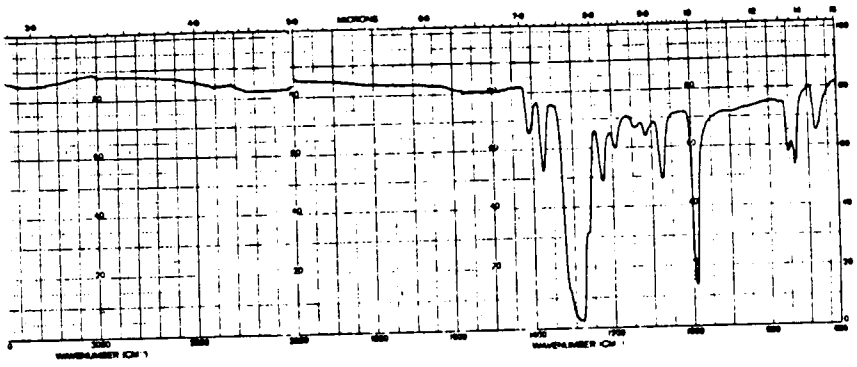


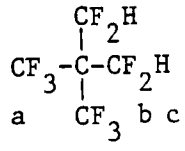
TABLE B-32

1,3-Dihydryl-F-neopentane (LXII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -64.6 ppm (p.t)

ϕ_b = -127.3 ppm (d.m)



J_{ab} = 11.0 Hz J_{ac} = 0.8 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_c = 6.21 ppm (t.m) J_{bc} = 54.5 Hz

MS: m/e (int) ion

EI 181 (8.9) C_4F_7, 163 (100) C_4F_6H, 113 (36) C_3F_4H, 95(15.6) $C_3F_3H_2$, 93 (9.0) C_3F_3, 75 (13.3) $C_3F_2H_2$, 69 (50.6) CF_3, 51 (76.0) CF_2H, 31 (2.8) CF.

IR: (cm^{-1})

3005(vw), 1390(sh), 1370(m), 1305(sh), 1285(s), 1264(vs), 1210(w), 1180(m), 1160(w), 1090(w), 1075-1056-1040(m), 981(s), 765(w) 740-725-710(w), 670(w).

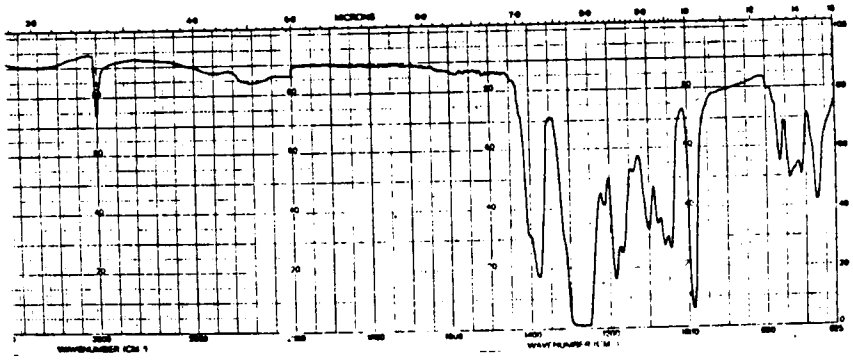
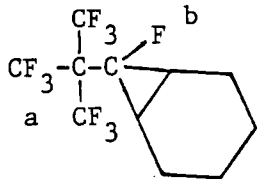


TABLE B-33

7-Fluoro-7-(nonafluoro-tert-butyl)-norcarane (LXIII)



^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -65.2 ppm (d)

ϕ_b = not observed (m)

J_{ab} = 12.5 Hz

^{1}H NMR: ($_{CHCl_3}$ = 0 ppm)

$_c$ = 1.5 ppm (broad m)

MS: m/e (int) ion

CI 332 (0.5) M, 313 (3.1) M-F.

IR: (cm^{-1})

2950(m), 2930(sh), 2887(w), 2860(w), 1320(s), 1287(vs), 1273(s), 1260(sh), 1250(s), 1204(w),1107(w), 1000(m), 980(s), 938(w), 890(w), 725(m).

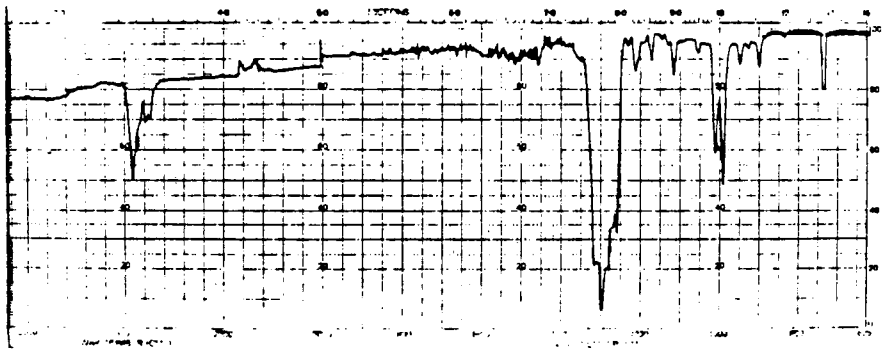
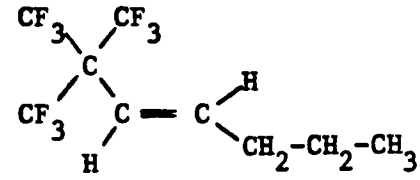


TABLE B-34

Trans-2,2-bis-(trifluoromethyl)-1,1,1-trifluoro-3-heptene (LXIV)



^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -66.5 ppm

J_{HF} = 1.3 Hz

MS: m/e (int) ion

CI 289 (100) M+H, 269 (63.1) M-F, 249 (14.9) $C_9F_7H_8$.

EI 288 (9.7) M, 269 (4.7) M-F, 69 (100) CF_3 and C_5H_9, 42 (84) C_3H_6.

IR: (cm^{-1})

3030(vw), 2977(m), 2940(m), 2930(sh), 2890(w), 2860(w), 1668(w), 1465(w), 1290(vs), 1268(vs), 1250(sh), 1210(w) 1178(w), 1140(m), 1118(s), 980(s), 730(m).

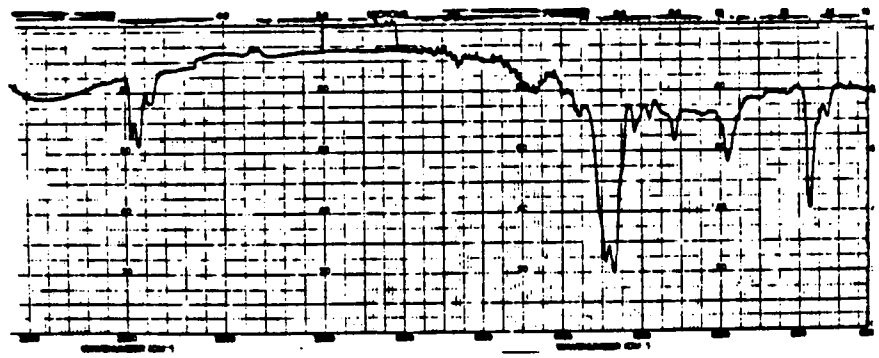


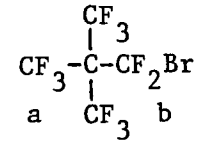
TABLE B-35

F-neopentyl bromide (LXVI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -63.84 ppm (t)

ϕ_b = -47.94 ppm (dect)



J_{ab} = 1o.5 Hz

MS: m/e (int) ion

CI 331 (10.5) and 329 (10.8) M-F, 269 (100) M-Br, 181 (21.6) C_4F_7.

EI 269 (51.9) M-Br, 243 (2.0) and 241 (2.1) C_4F_6Br, 181 (30) C_4F_7, 131 (42.9) and 129 (40.7) CF_2Br, 93 (13.4) C_3F_3, 81 (3.8) and 79 (3.2) Br, 69 (100) CF_3.

IR: (cm^{-1})

1290(vs), 1280(vs), 1225(m), 1040(w), 995(s), 840(m), 760(w), 735(m).

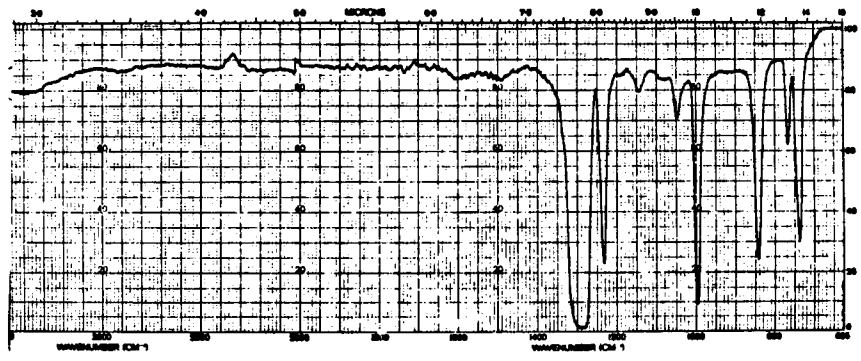


TABLE B-36

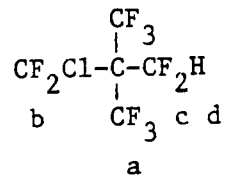
1-Chloro-3-hydryl-F-neopentane (LXVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -63.85 ppm (p)

ϕ_b = -52.44 ppm (m)

ϕ_c = -125.51 ppm (d.m)



J_{FF} = 9.8 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_d = 6.28 ppm (t)

J_{cd} = 50.9 Hz

MS: m/e (int) ion

CI 267 (51.7) and 265 (53.2) M-F, 251 (100) M-Cl,

EI 199 (12.6) and 197 (5.0) C_4F_6Cl, 181 (52.8) C_4F_7, 163 (100) C_4F_6H, 149 (8.3) and 147 (2.9) C_3F_4Cl, 113 (24.7) C_3F_4H, 87 (64.3) and 85 (26.8) CF_2Cl, 69 (79.7) CF_3. 51 (21.5) CF_2H.

IR: (cm^{-1})

3000(w), 1405(w), 1375(w), 1285(vs), 1260(vs), 1190(w), 990(m), 870(w), 830(w) 770(w).

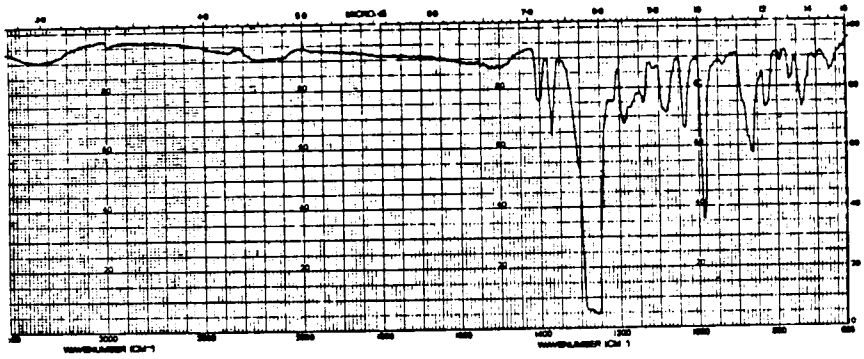


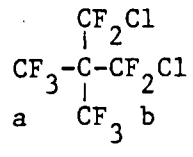
TABLE B-37

1,3-Dichloro-F-neopentane (LXVIII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -62.95 ppm (p)

ϕ_b = -51.05 ppm (hept)



J_{ab} = 10.5 Hz

MS: m/e (int) ion

CI 305 (1.5) and 303 (5.0) and 301 (16.3) M-F, 287 (6.3) and 285 (19.7) M-Cl.

EI 287 (0.5) and 287 (1.5) M-Cl, 199 (8.3) and 197 (25.2) C_4F_6Cl, 181 (47.5) C_4F_7, 87 (13.5) and 85 (41.7) CF_2Cl, 69 (100) CF_3

IR: (cm^{-1})

1280(vs), 1265(vs), 1190(w), 990(m), 900(w), 865(w), 840(w), 780(w), 730(w).

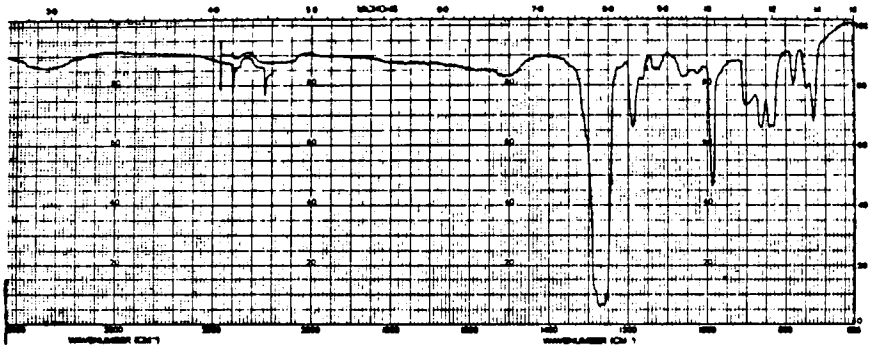


TABLE B-38

1-Bromo-3-hydryl-F-neopentane (LXIX)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

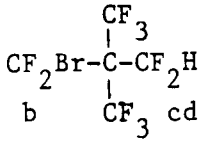
ϕ_a = -63.45 ppm (p)

ϕ_b = -47.95 ppm (m)

ϕ_c = -125.36 ppm (d.m)

^{1}H NMR: (δ_{CHCl_3} = 7.25ppm)

δ_d = 6.29 ppm (t)



$J_{ab} = J_{ac}$ = 9.8 Hz

J_{cd} = 51.0 Hz

MS: m/e (int) ion

CI 313 (18.7) and 311 (19.1) M-F, 251 (100) M-Br.

EI 181 (52.0) C_4F_7, 163 (83.1) C_4F_6H, 113 (34.4) C_3F_4H, 131 (8.1) and 129 (8.7) CF_2Br, 81 (40.3) and (41.1) Br, 69 (100) CF_3, 51 (17.9) CF_2H.

IR: (cm^{-1})

3000(vw), 1405(w), 1375(w), 1285(vs), 1260(vs), 1190(w), 990(m), 840(m), 770(w).

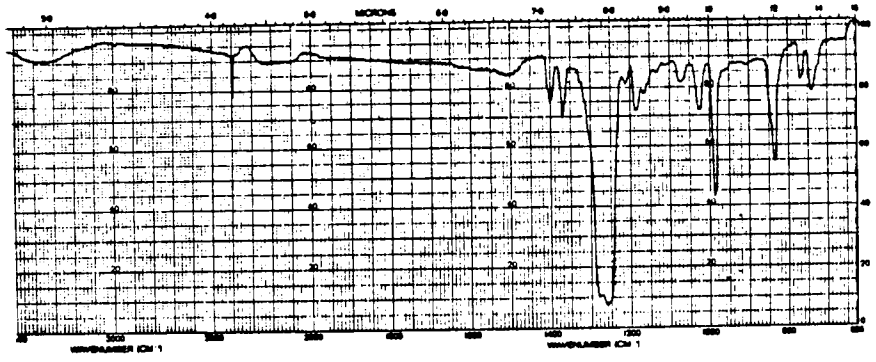


TABLE B-39

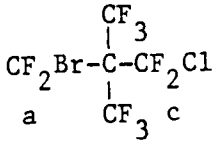
1-Bromo-3-chloro-F-neopentane (LXX)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -47.30 ppm (m)

ϕ_b = -63.35 ppm (p)

ϕ_c = -51.35 ppm (m)



$J_{ab} = J_{bc} = 11.4$ Hz

MS: m/e (int) ion

CI 349 (11.6) and 347 (14.5) and 345 (5.3) M-F,
331 (12.4) and 329 (12.8) M-Cl,
287 (36.2) and 285 (100) M-Br.

EI 199 (17.3) and 197 (5.6) C_4F_6Cl, 181 (34.2) C_4F_7,
131 (5.7) and 129 (6.2) CF_2Br, 87 (17.9) and 85 (45.4) CF_2Cl,
81 (32.1) and 79 (33.5) Br, 69 (100) CF_3.

IR: (cm^{-1})

1275(vs), 1265(vs), 1190(w), 990(m), 890(w), 880(w), 870(w),
835(w), 825(w), 815(w), 750(w), 730(w).

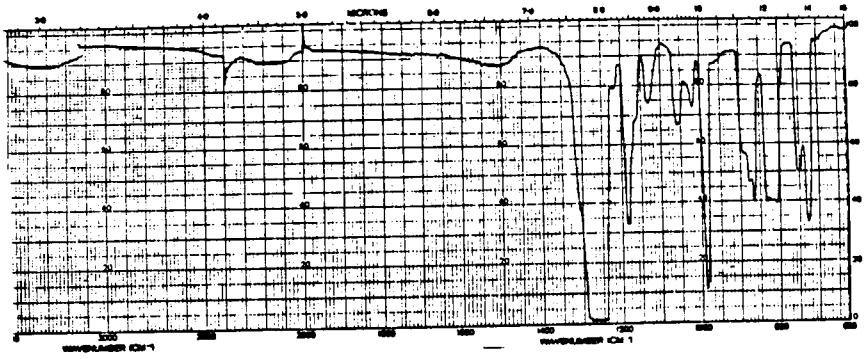


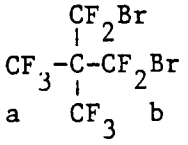
TABLE B-40

1,3-Dibromo-F-neopentane (LXXI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -62.29 ppm (p)

ϕ_b = -46.56 ppm (hept)



J_{ab} = 9.8 Hz

MS: m/e (int) ion

CI 393 (13.1) and 391 (26.8) and 389 (12.9) M-F.
331 (98.5) and 329 (100) M-Br.

EI 331 (4.2) and 329 (4.8) M-Br, 243 (8.3) and 241 (8.9) C_4F_6Br, 181 (29.6) C_4F_7, 131 (142) and 129 (15.1) CF_2Br, 81 (68.5) and 79 (70.2) Br, 69 (100) CF_3.

IR: (cm^{-1})

1280(vs), 1260(vs), 1190(w), 990(m), 860(w), 840(m), 810(w), 795(m), 745(w), 730(m).

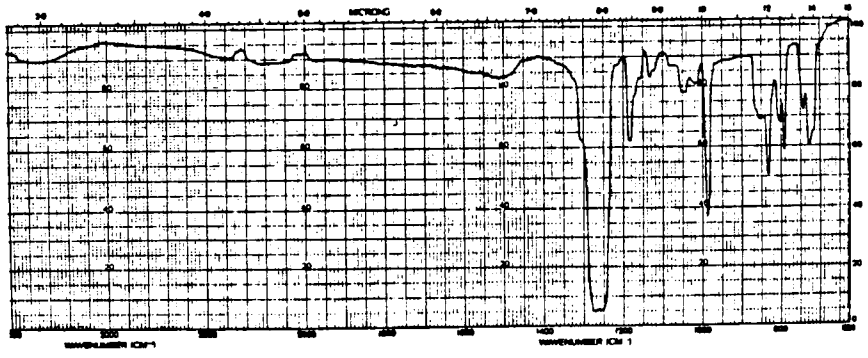


TABLE B-41

1-Bromo-F-2,5-dioxahexane (LXXIII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

$CF_3OCF_2CF_2OCF_2Br$
a b c d

ϕ_a = -55.75 ppm (t)

ϕ_b = 91.06 ppm (q)

ϕ_c = -90.13 ppm (t)

ϕ_d = -19.19 ppm (t)

J_{ab} = 8.79 Hz

J_{bc} < 1 Hz

J_{cd} = 10.74 Hz

MS: m/e (int) ion

CI 313 (66) and 311 (65) M-F, 247 (10) and 245 (11) C_3F_6OBr, 185 (100) C_3F_7O, 109 (30) and 107 (32) COBr.

EI 251 (1.5) M-Br, 235 (0.2) C_4F_9O, 185 (18) C_3F_7O, 131 (23) and 129 (23) CF_2Br, 119 (100) C_2F_5, 69 (80) CF_3.

IR: (cm^{-1})

1290(vs), 1245(vs), 1215(vs), 1160(s), 1130(vs), 1070(m), 1030(m), 905(m), 845(w), 810(m), 750(m), 685(w).

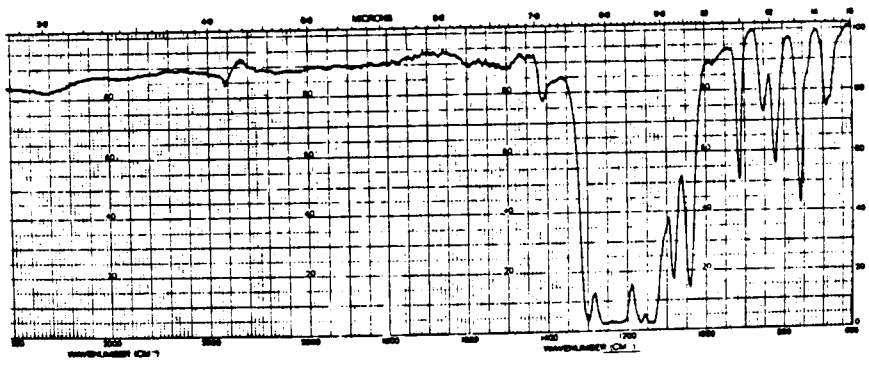


TABLE B-42

1-Chloro-F-2,5-dioxahexane (LXXIV)

$CF_3OCF_2CF_2OCF_2Cl$
a b c d

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -55.74 ppm (t)

ϕ_b = -91.06 ppm (q) J_{ab} = 8.79 Hz

ϕ_c = -90.52 ppm (t) J_{bc} < 1 Hz

ϕ_d = -27.46 ppm (t) J_{cd} = 10.74 Hz

MS: m/e (int) ion

CI 269 (17.8) and 267 (72.6) M-F, 85 (32.6) CF_3O, 69 (10.1) CF_3, 65 (34) and 63 (100) COCl.

EI 135 (.3) C_2F_5O, 119 (2.4) C_2F_5, 103 (0.4) and 101 (0.6) CF_2ClO, 87 (0.6) and 85 (1.2) CF_2Cl, 69 (3.0) CF_3

IR: (cm^{-1})

1395 (s), 1250(vs), 1205(vs), 1165(vs), 1140(vs), 1105(s), 1050(m), 905(w), 850(w), 815(w), 770(w), 685(w).

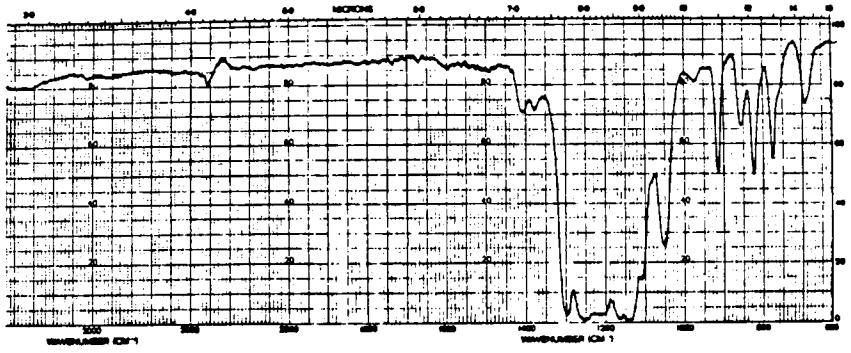


TABLE B-43

1-Hydryl-F-2,5-dioxahexane (LXXV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

$CF_3OCF_2CF_2OCF_2H$
a b c d e

ϕ_a = -59.23 ppm (t)

ϕ_b = -93.63 ppm (q) J_{ab} = 9.4 Hz

ϕ_c = -92.47 ppm (t) $J_{bc} < 1$ Hz

ϕ_d = -88.36 ppm (d.t) J_{cd} = 4.5 Hz

^1H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_e = 6.26 ppm (t) J_{de} = 68.9 Hz

MS: m/e (int) ion

CI 233 (100) M-F, 213 (30) $C_4F_7O_2$, 185 (17) C_3F_7O, 163 (25) $C_3F_5O_2$, 67 (62.9) CHF_2O, 51 (17.6) CHF_2.

EI 213 (7.9) $C_4F_7O_2$, 135 (23.5) C_2F_5O, 119 (83.9) C_2F_5, 117 (16.9) C_2F_4HO, 100 (12.1) C_2F_4, 69 (100) CF_3, 51 (74.5) CHF_2.

IR: (cm^{-1})

3028(vw), 1400(w), 1370(w), 1295(s), 1250(s), 1192(m), 1179(sh) 1159(s), 1125(s), 1040(m), 910(m), 853(w), 818(m), 700(w).

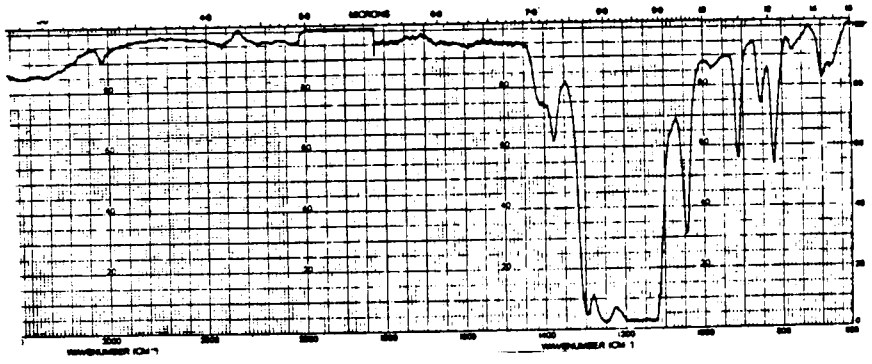
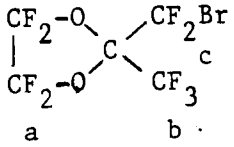


TABLE B-44

F-2-Bromomethyl-2-methyl-1,3-dioxolane (LXXVI)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)



ϕ_a = -81.40 ppm (s)

ϕ_b = -78.76 ppm (t)

ϕ_c = -63.71 ppm (q)

J_{bc} = 7.8 Hz

MS: m/e (int) ion

CI 325 (8.3) and 323 (8.7) M-F, 263 (100) M-Br.

EI 225 (9.3) $C_5F_7O_2$, 131 (23.7) and 129 (22.4) CF_2Br, 128 (28.4) C_3F_4O, 116 (13.6) C_2F_4O, 100 (8.5) C_2F_4, 81 (30.1) and 79 (30.9) Br, 69 (100) CF_3.

IR: (cm^{-1})

1400(w), 1310(m), 1230(vs), 1170(vs), 1135(s), 1030(m), 915(m), 840(m), 720(w).

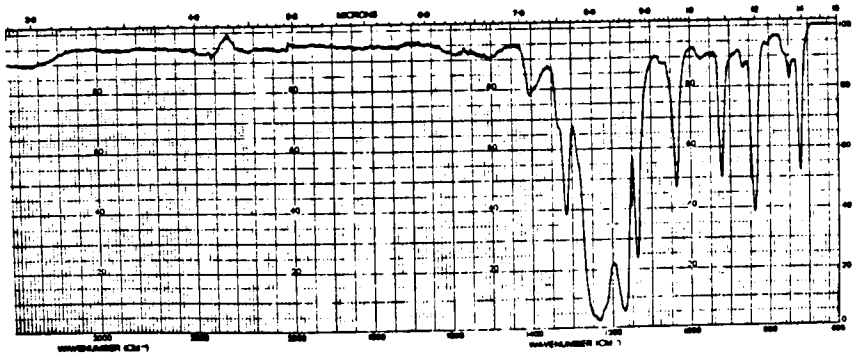
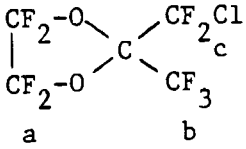


TABLE B-45

F-2-Chloromethyl-2-methyl-1,3-dioxolane (LXXVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)



ϕ_a = -81.78 ppm (s)

ϕ_b = -79.43 ppm (t)

ϕ_c = -68.54 ppm (q)

J_{bc} = 7.8 Hz

MS: m/e (int) ion

CI 281 (29.7) and 279 (51.3) M-F, 263 (100) M-Cl.

EI 213 (8.3) $C_4F_7O_2$, 147 (10.4) C_3F_5O, 131 (8.5) C_3F_7, 116 (6.7) C_2F_4O, 100 (5.3) C_2F_4, 87 (28.2) and 85 (16.3) CF_2Cl, 69 (100) CF_3.

IR: (cm^{-1})

1400(w), 1320(m), 1240(vs), 1170(vs), 1140(s), 1050(m), 940(m), 875(w), 860(w), 840(w), 730(w).

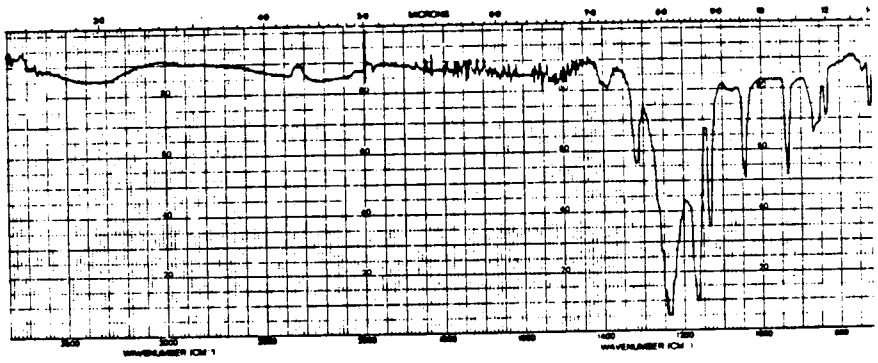
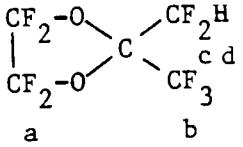


TABLE B-46

F-2-Hydrylmethyl-2-methyl-1,3-dioxolane (LXXVIII)



^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = 83.35 ppm (hext)

ϕ_b = -82.35 ppm (t.p.d)

ϕ_c = -138. 01 ppm (d.q.p)

J_{bc} = 7.8 Hz

$J_{ab} = J_{ac}$ = 2 Hz

^{1}H NMR: (δ_{CHCl_3} = 7.25 ppm)

δ_d = 5.96 ppm (t.q)

J_{cd} = 52.2 Hz

J_{bd} = 1 Hz

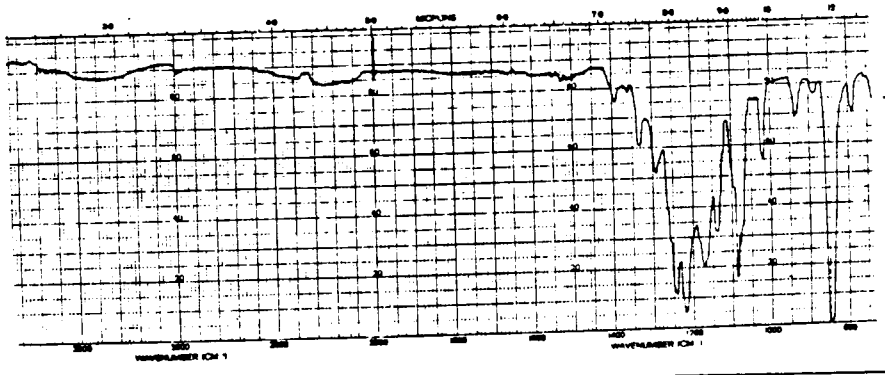
MS: m/e (int) ion

CI 245 (100) M-F, 116 (8.6) C_2F_4O, 69 (20.1) CF_3, 51 (13.2) CF_2.

EI 225 (9.3) $C_5F_7O_2$, 179 (3.0) C_4F_6HO, 128 (13.6) C_3F_4O, 116 (12.1) C_2F_4O, 69 (100) CF_3, 51 (80.4) CF_2H.

IR: (cm^{-1})

3000(vw), 1390(w), 1335(w), 1290(w), 1245(s), 1220(s), 1170(m), 1140(m), 1080(m), 1020(w), 930(w), 890(vw), 850(s), 790(w).



VITA

William Douglas Evans completed his BS degree at Fort Lewis College, Durango, Colorado and his MS degree at the University of Colorado. He accepted a teaching assistantship at the University of Tennessee, Knoxville in 1977 and began his research in the field of fluorine chemistry. He received the Doctor of Philosophy degree with a major in chemistry in December 1983.