THE SYNTHESIS AND CHARACTERIZATION OF FLUORO DERIVATIVES OF CHLOROPENTAFLUOROBENZENE AND BROMOPENTAFLUOROBENZENE

A DISSERTATION
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JOSHUA AYOOLA OBALEYE, B.S.

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DEDICATED

TO

MY FATHER

AND

MY MOTHER

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CHAPTER I

INTRODUCTION

Perfluoroalkyl derivatives of iodine trifluoride were first prepared by Schmeisser and Scharf (1) in 1959 using a perfluoroalkyl iodide and either chlorine trifluoride or elemental fluorine. In 1966, Parsons (2) synthesized the perfluoroalkyliodine(III) difluorides according to the following:

$$3R_fI + 2ClF_3 \longrightarrow 3R_fIF_2 + Cl_2 \qquad (A)$$

(where R_f = perfluoroalkyl group).

In 1968, Rondestvedt (3) used n-perfluorobutyl iodide and perfluoroethyl iodide as substrates and chlorine trifluoride and bromine pentafluoride as fluorinating agents. His results were as follows:

$$C_4F_9I + 2ClF_3 \xrightarrow[C_6F_{14}]{-80^{\circ}} C_4F_9IF_4 + Cl_2 + F_2 \qquad (B)$$

$$3C_2F_5I + 2BrF_5 \xrightarrow{\Delta} C_2F_5IF_2 + 2C_2F_5IF_4 + Br_2 \qquad (C)$$

$$3C_4F_9I + 2BrF_5 \xrightarrow[C_6F_{14}]{0^{\circ}} C_4F_9IF_2 + 2C_4F_9IF_4 + Br_2 \qquad (D)$$

He found iodine pentafluoride to be an ineffective fluorinating agent. Perfluoroalkyliodine(III) difluoride was explained to be moderately stable at room temperature and above.

Its stability was found to increase with chain length. According to Rondestvedt, samples of pentafluoroethyliodine(III) difluoride were unstable and several percent decomposed per day at room temperature. The corresponding tetrafluorides were found by him to be much less stable, perhaps by an order of magnitude. Pentafluoroethyliodine(V) tetrafluoride was about 50% destroyed in 24 hours at room temperature, with weight loss and solid formation. About 5% of perfluorobutyliodine(V) tetrafluoride was degraded in a day.

A year later, Rondestvedt (4) again provided experimental evidence for the formation of perfluoroalkyliodine(III) difluorides and perfluoroalkyliodine(V) tetrafluorides which were new classes of organic polyvalent iodine. He prepared them by fluorination of a perfluoroalkyl iodide with chlorine trifluoride, bromine trifluoride, bromine pentafluoride or elemental fluorine. He found that the pure difluorides formed from excess perfluoroalkyl iodide with chlorine trifluoride, bromine trifluoride or bromine pentafluoride in slight excess. He also devised safe conditions for synthesis. He discovered that the reaction product from perfluorobutyl iodide and fluorine was the new perfluorobutyliodine(III) difluoride contaminated with varying amounts of perfluorobutyliodine(V) tetrafluoride and a solid believed to be bis(perfluorobutyl)iodonium hexafluoroiodide.

In 1970, pentafluorophenyliodine(III) difluoride was prepared by Schmeisser, Dahmen and Sartori (5) by reaction of iodopentafluorobenzene with elemental fluorine. Pentafluorophenyliodine(III) difluoride was hydrolyzed to give a colorless product assumed to be iodosopentafluorobenzene. Both the difluoride and its hydrolysis product were poorly characterized. According to Schmeisser _et_ _al._, the hydrolysis product decomposed at -5°C so that absolute analysis was very difficult.

More interest continued to develop for these unusual compounds. Three other chemists from the University of Glasgow, Chambers, Oates and Winfield (6) decided to further the uncompleted work of Schmeisser _et_ _al_. (5). In 1972, they communicated their work on the preparation of trifluoromethyliodine(V) tetrafluoride by the oxidation of trifluoromethyl iodide with chlorine trifluoride. They also prepared pentafluorophenyliodine(V) tetrafluoride in a similar way. They were unable to see the parent ion of trifluoromethyliodine(V) tetrafluoride in the mass spectrum but they did see fragmentation patterns. They did observe the molecular ion peak for pentafluorophenyliodine(V) tetrafluoride. They also found that trifluoromethyliodine(V) tetrafluoride decomposed after one hour, the detectable products being tetrafluoromethane, iodotrifluoromethane and iodine. The stability of perfluoroalkyliodine(V) tetrafluoride compounds with respect to decomposition increased in the order $CF_3 < (CF_3)_2CF < C_6F_5$ and pentafluorophenyliodine(V) tetrafluoride was found to be stable indefinitely at 20°C. They were unsuccessful in their attempt to isolate trifluoromethyliodine(III) difluoride from the products of a reaction between trifluoromethyl and chlorine trifluoride. According to them, trifluoromethyliodine(III) difluoride and pentafluorophenyliodine(III) difluoride were less stable than the analogous iodine(V) compounds, in contrast to the previous work of Rondestvedt (4).

In 1972, Oates and Winfield (7) reported replacement of fluorine in iodine pentafluoride using trimethylmethoxosilane and related compounds, a route which had been widely used to prepare aryloxo- and alkoso- derivatives of covalent fluorides (8 - 11). The alkoxoiodine(V) tetrafluorides, IF_4OR ($R = CH_3$ or CH_3CH_2), were successfully formed from reactions between iodine pentafluoride and trimethylalkoxosilane (1:1 mole ratio) at 20°C in vacuum. The other product was fluorotrimethylsilane. Oates and Winfield (7) were unsuccessful in their attempt to prepare phenoxoiodine(V) tetrafluoride as the phenoxo group was apparently fluorinated by iodine pentafluoride. It was also observed that methoxoiodine(V) tetrafluoride showed similar behavior towards benzene. According to their results, when an excess of iodine pentafluoride was present, difluorodimethylsilane and iodine were formed in addition to alkoxoiodine(V) tetrafluoride and fluorotrimethylsilane. Silicon-carbon bonds in fluorotrimethylsilane were readily cleaved by iodine pentafluoride at 20°C, although no reaction occurred between methoxoiodine(V) tetrafluoride and fluorotrimethylsilane. Consequently, careful control of the reaction stoichiometry was found necessary to isolate pure alkoxoiodine(V) tetrafluoride.

In 1973, Baumanns, Deneken, Naumann and Schmeisser (12) formed trifluoromethyliodine(III) difluoride by the direct fluorination of trifluoromethyl iodide at -78°C; but were unsuccessful in isolating a stable trifluoromethyliodine(III) difluoride as was Chambers, *et al.* (6).

In the same year, Oates and Winfield (13) oxidized trifluoromethyl iodide with chlorine trifluoride in perfluorohexane at -78°C to give trifluoromethyliodine(V) tetrafluoride in addition to trifluoromethyliodine(III) difluoride. They found that trifluoromethyliodine(V) tetrafluoride decomposed at 20°C but was more stable than trifluoromethyliodine(III) difluoride.

Berry, Oates and Winfield (14) synthesized pentafluorophenyliodine(V) tetrafluoride. This was done by oxidizing iodopentafluorobenzene with chlorine trifluoride.

In 1975, Naumann, Deneken and Renk (15) prepared some derivatives of trifluoromethyliodine(III) difluoride and trifluoromethyliodine(V) tetrafluoride. Naumann continued the work with Baumanns (16) in 1976. He also worked on this project with Heinsen and Lehman (17). Naumann *et al.* (18) discussed their work on the preparation of perfluoroalkyliodine(III) difluorides, RIF_2 ($R = CF_3$, C_2F_5 and C_3F_7) by the direct fluorination of perfluoroalkyliodides. They also produced pentafluoroalkyliodine(V) tetrafluoride.

No aromatic interhalogen compounds containing either chlorine or bromine have been synthesized. It should be possible to prepare stable compounds which contain either chlorine or bromine. This is the subject of this dissertation.

CHAPTER II

EXPERIMENTAL

Chloropentafluorobenzene, bromopentafluorobenzene and pentafluorobenzene were purchased from PCR, Incorporated. Elemental fluorine, chlorine trifluoride and bromine trifluoride were bought from Air Products, Incorporated. Elemental fluorine was passed through a -78°C trap or through a tower filled with sodium fluoride pellets for removal of traces of hydrogen fluoride before use. Chlorine trifluoride and bromine trifluoride were used as received.

A. Gas Chromatograph

The liquid products, at 25°C, were analyzed using a Varian 90P-3 gas chromatograph fitted with a 3/8 inch x 20 foot column packed with 30% SE-30 on Chromosorb P. The retention times of the chlorine containing products were determined at the following conditions: column temperature 187°C and a helium flow rate of 52 cc/min.; while that of the bromine containing products were determined at the following conditions: column temperature 187°C and a helium rate of 100 cc/min. Trapping of the appropriate peak from the gas chromatograph was done with the aid of a U-tube held at -78°C.

B. Elemental Analyses

Elemental analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee, and by the Midwest Microlab, Ltd., Indianapolis, Indiana.

C. Infrared Spectra

Infrared spectra were recorded with a Perkin-Elmer model 225 infrared spectrophotometer using a 0.1 mm liquid cell fitted with sodium chloride or polyethylene windows.

D. Fluorine Nuclear Magnetic Resonance

Fluorine nuclear magnetic resonance spectra were obtained with a Varian EM-390 spectrometer using fluorotrichloromethane as an internal reference.

E. Mass Spectra

The mass spectra were obtained with a Consolidated Electrodynamics Corporation (CEC) model 21-104 single-focus mass spectrometer with an electron multiplier detector. The operating conditions were as follows: Inlet system temperature 170°C; Source temperature 250°C; Ionizing voltage 70, 12, 10, 8 eV; Anode current 10 μA; Accelerating voltage 3500 volts-nominal; Magnet current 7.3A: Slit width 4 mil; Electrostatic scanning rate Position 9 and Recording chart rate 0.25 in/sec. Generally, two microliters of the samples were injected into the liquid inlet system.

F. Micro Boiling Points

The equipment and techniques used are described elsewhere (20).

G. Monel Pressure Reactor

The reactor used for the pressure fluorinations was Monel, Hoke 69 H 1695, W.P. 5000 PSI; volume 0.392 liter.

After each reaction, the mixture was allowed to come to room temperature and the bulk of the liquid transferred from the Monel reactor into a brown glass bottle for low temperature storage (10°C).

H. Manifolds

Two manifolds were constructed. One of these was made of pyrex glass according to Figure 1. This was used for loading the Monel reactor with substrates.

The second manifold constructed of Monel was used to pressurize the reaction mixture.

After the construction of the line was complete, the reservoirs and all measuring equipment were calibrated with nitrogen. A glass flask container filled with alumina was connected to the line, to trap excess fluorinating agent and other gaseous products.

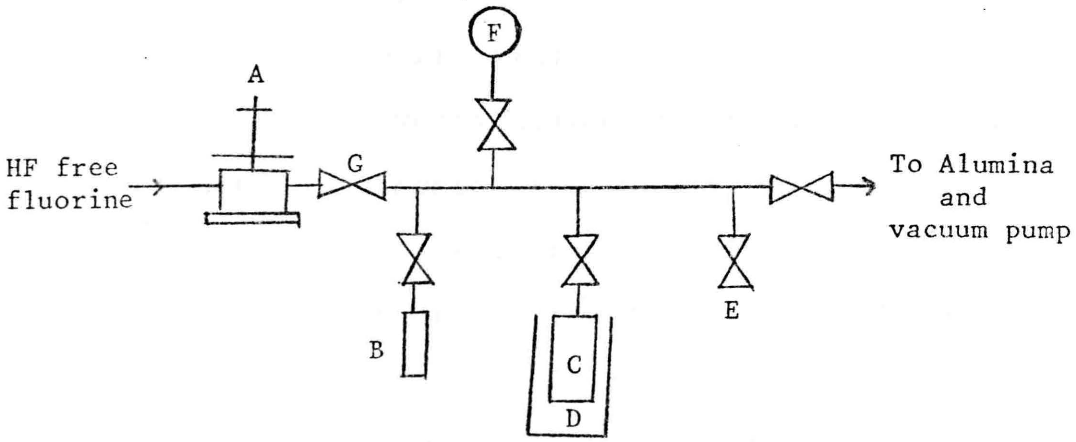


Figure 1. Line Diagram of Apparatus

A. Pressure regulator

B. Substrate metering tube

C. Monel pressure reactor

D. Dewar containing liquid nitrogen

E. Connection point for sample bottle

F. 0-1500 mm pressure gauge for fluorine service

G. Valve

I. Preparation of Pentafluorophenylchlorine(III) Difluoride

1. Reactions of Chloropentafluorobenzene with Fluorine (see Table 1) (21)

Early in the investigation, a series of experiments were carried out to determine the optimum fluorinating conditions based on percent yield of pentafluorophenylchlorine-(III) difluoride. Maintaining the fluorine to chloropentalfluorobenzene mole ration at 1.0, reactions were conducted at -78, 0, 10, 117, 128 and 220°C following techniques similar to those described below. The optimum reaction temperature was considered to be 117°C. During the course of this investigation the following procedures were carried out on a routine basis. A manifold was used to condense 2.02 ± 0.01g (10.0 mmoles) of chloropentafluorobenzene into a previously evacuated and cooled (-78°C) Monel pressure reactor. Liquid nitrogen was used to reduce the temperature of the reactor to -196°C and 10.0 mmoles of elemental fluorine were allowed to flow into the reactor from a fluorine metering tank. Dry helium gas was added to bring the pressure to 4 atm. The reactor was closed and placed in an oven maintained at 117°C for 18 hours. It was reconnected to the mainfold, cooled to -196°C, and evacuated. The products, liquid at 25°C, were analyzed by gas chromatography.

2. Reactions of Chloropentafluorobenzene with Chlorine Trifluoride (see Table 2)

Series of experiments were carried out just as in the case of cluorine in order to determine the optimum fluorinating conditions based on percent yield of pentafluorophenylchlorine(III) difluoride. Samples of 2.02 ± 0.01g (10.0 mmoles) of chloropentafluorobenzene in a Monel reactor attached to the vacuum line were held at -78°C. The reactor temperature was reduced to -196°C and gaseous chlorine trifluoride (10.0 mmoles) were added. Enough dry helium gas was allowed to flow into the reactor to bring the pressure to 4 atm. The reactor was closed and kept at either -78, 0, 10, -17, 128 or 220°C for 18 hours. It was then reconnected to the vacuum line, cooled to -196°C, and evacuated. The products, liquid at 25°C, were analyzed by gas chromatography.

3. Reactions of Pentafluorobenzene with Chlorine Trifluoride (see Table 3)

A mixture of 1.68 ± 0.01g (10.0 mmoles) of pentafluorobenzene and 10.0 mmoles of chlorine trifluoride were allowed to react by following the same method and conditions described under paragraph 2. Enough helium was added prior to reaction to bring the pressure to 4 atm. Reaction temperatures were as follows: -78, 0, 10, 117, 128 and 220°C. The products, liquid at 25°C were analyzed by gas chromatography.

TABLE 1
REACTION CONDITIONS AND YIELDS FOR REACTING CHLOROPENTAFLUOROBENZENE WITH FLUORINE

Temperature (°C)	Total Pressure at -196° C (atm)	Mole Ratio F_2/C_6F_5Cl	Time (hour)	%C_6F_5Cl unreacted[a]	%Yield $C_6F_5ClF_2$[a]	%Yield $C_6F_5ClF_4$[a]	%Yield $(C_6F_5ClF)_2$[a]	%Yield Unidentified Products[a]
-78	4	1.0	18	87(86-87)*	8(7-8)*	3(2-3)*		2(1-2)*
0	4	1.0	18	85(83-86)	9(9)	3(1-4)		3(3)
10	4	1.0	18	68(68)	16(16)	6(6)	2(2)	8(8)
117	4	1.0	18	46(45-46)	44(43-44)		3(2-3)	7(6-7)
128	4	1.0	18	30(29-30)	32(31-32)	5(4-5)	20(18-21)	13(12-14)
220	4	1.0	18	50(50)	20(18-22)	10(8-12)	9(8-9)	11(10-11)
-78	4	2.0	18	87(87)	4(4)	6(6)	1(1)	2(2)
0	4	2.0	18	89(87-89)	5(5)	5(3-5)		1(1)
10	4	2.0	18	63(62-65)	20(19-23)	8(6-8)	4(3-4)	5(4-5)
117	4	2.0	18	33(33)	34(33-34)	12(11-12)	10(9-10)	11(10-11)
128	4	2.0	18	10(9-10)	30(29-30)	11(10-11)	18(17-18)	31(30-31)
220	4	2.0	18	82(82)	9(8-10)	3(3)	5(3-5)	1(1)

a average of three results

* range of values

TABLE 2

REACTION CONDITIONS AND YIELDS FOR REACTING CHLOROPENTAFLUOROBENZENE WITH CHLORINE TRIFLUORIDE

Temperature (°C)	Total Pressure at -196°C (atm)	Mole Ratio ClF_3/C_6F_5Cl	Time (hour)	%C_6F_5Cl unreacted[a]	%Yield $C_6F_5ClF_2$[a]	%Yield $C_6F_5ClF_4$[a]	%Yield $(C_6F_5ClF)_2$[a]	%Yield $C_6F_6Cl(ClF_2)$[a]	%Yield Unidentified Products[a]
-78	4	1.0	18	6(5-7)*	13(12-14)*	6(5-7)*	10(9-11)*	39(38-40)*	26(25-27)*
0	4	1.0	18	5(5)	13(12-13)	6(5-6)	9(9)	39(38-39)	28(28)
10	4	1.0	18		16(16)	7(6-8)	17(16-18)	30(29-31)	30(29-31)
117	4	1.0	18		22(22)		17(16-17)	32(31-32)	29(29)
128	4	1.0	18	5(4-5)	19(18-19)	10(8-11)		35(33-36)	31(30-31)
220	4	1.0	18	8(8)	7(7)	11(11)	8(7-8)	21(20-21)	45(44-45)
-78	4	2.0	18		8(7-9)	10(9-11)	4(3-5)	22(21-23)	56(55-57)
0	4	2.0	18		9(8-9)	11(10-12)		25(24-25)	55(54-56)
10	4	2.0	18		17(17)	10(10)		23(22-23)	50(49-50)
117	4	2.0	18		21(20-21)	12(11-12)	6(6)	28(28)	33(32-33)
128	4	2.0	18		21(20-21)	12(12)		28(27-28)	39(38-39)
220	4	2.0	18	1(1)	13(12-13)	10(10)		15(15)	61(60-61)

a average of three results

* range of values

TABLE 3

REACTION CONDITIONS AND YIELDS FOR REACTING PENTAFLUOROBENZENE WITH CHLORINE TRIFLUORIDE

Temperature (°C)	Total Pressure at -196°C (atm)	Mole Ratio ClF_3/C_6F_5H	Time (hour)	%C_6F_5H unreacted[a]	%Yield $C_6F_5ClF_2$[a]	%Yield $C_6F_5ClF_4$[a]	%Yield Unidentified Products[a]
-78	4	1.0	18	11(10-11)	15(14-15)		74(73-74)
0	4	1.0	18	11(9-11)	15(15)		74(72-74)
10	4	1.0	18	8(8)	12(12)	7(7)	73(73)
117	4	1.0	18		13(12-13)	10(9-10)	77(76-77)
128	4	1.0	18	40(39-40)	25(23-25)		35(33-35)
220	4	1.0	18	38(37-38)	5(5)	6(6)	51(50-51)
-78	4	2.0	18	17(16-17)	4(4)	10(9-10)	69(69)
0	4	2.0	18	18(18)	5(4-5)	10(10)	67(66-67)
10	4	2.0	18	10(10)		8(8)	82(82)
117	4	2.0	18	10(10)		12(12)	78(78)
128	4	2.0	18			11(10-12)	89(88-90)
220	4	2.0	18			12(11-12)	88(87-88)

[a] average of three results
* range of values

J. Preparation of Pentafluorophenylchlorine(V) Tetrafluoride

1. Reactions of Chloropentafluorobenzene with Fluorine (see Table 1)

A series of experiments were done just as for the pentafluorophenylchlorine(III) difluoride in order to determine the optimum fluorinating conditions based on percent yield of pentafluorophenylchlorine(V) tetrafluoride. Reactions were carried out under conditions similar to paragraph I1. A mixture of 2.02 ± 0.01g (10.0 mmoles) of chloropentafluorobenzene and 20.0 mmoles of fluorine were allowed to react in a previously evacuated and cooled ($-78^{\circ}C$) Monel reactor for 18 hours. Enough helium was added prior to reaction to bring the pressure to 4 atm . Reaction temperatures were as follows: $-78^{\circ}C$, $0^{\circ}C$, $10^{\circ}C$, $117^{\circ}C$, $128^{\circ}C$ and $220^{\circ}C$. The products, liquid at $25^{\circ}C$, were analyzed by gas chromatography.

2. Reactions of Chloropentafluorobenzene with Chlorine Trifluoride (see Table 2)

Reactions were carried out under conditions similar to paragraph I2. Each reaction was carried out in a Monel cylinder by condensing a mixture of chloropentafluorobenzene (2.02 ± 0.01g, 10.0 mmoles) and chlorine trifluoride (10.0

mmoles) and allowing them to react at either -78, 0, 10, 117, 128 or 220°C for 18 hours. Helium gas was added prior to reaction to bring the reactor pressure to 4 atm. A control experiment was done without helium. Little or no effect was observed in the absence of helium. The reaction products were white solid compounds and a pale yellow liquid. The products, liquid at 25°C, were analyzed by gas chromatography.

3. Reactions of Pentafluorobenzene with Chlorine Trifluoride (see Table 3)

Reactions were carried out under conditions similar to paragraph I2. Samples of 1.68 ± 0.01g (10.0 mmoles) of pentafluorobenzene were placed in a Monel cylinder and 20.0 mmoles of chlorine trifluoride was condensed into the cooled (-78°C) reactor. The mixture was allowed to react at either -78, 0, 10, 117, 128, or 220°C for 18 hours. Helium gas was added prior to reaction to bring the reactor pressure to 4 atm. The pale yellow liquid products were analyzed by gas chromatograpy.

K. Preparation of Pentafluorophenylbromine(III) Difluoride

1. Reactions of Bromopentafluorobenzene with Fluorine (see Table 4) (29)

Reactions were carried out under conditions similar to paragraph J2. A mixture of 2.47 ± 0.01g (10.0 mmoles) of bromopentafluorobenzene and 10.0 mmoles of fluorine were allowed to react in a previously evacuated and cooled (-78°C) Monel reactor for 18 hours. Helium gas was added prior to reaction to bring the pressure to 4 atm. Reaction temperatures were as follows: -78°C, 0°C, 10°C, 117°C, 128°C and 220°C. The products, liquid at 25°C, were analyzed by gas chromatography.

2. Reactions of Bromopentafluorobenzene with Bromine Trifluoride (see Table 5)

Series of experiments were also performed in an effort to determine the optimum fluorinating conditions based on percent yield of pentafluorophenylbromine(III) difluoride). A small Teflon beaker was placed on a balance, and liquid bromine trifluoride (1.37 ± 0.01g, 10.0 mmoles) was drained into it from the storage bottle. Meanwhile, samples of 2.47 ± 0.01 g (10.0 mmoles) of bromopentafluorobenzene were condensed into a previously evacuated and cooled (-78°C) Monel reactor. Bromine trifluoride was added all at once. The reactor was attached to the vacuum line, degassed and then kept at either -78, 0, 10, 117, 128 or 220°C for 18 hours. Helium gas was added prior to reaction to bring the reactor pressure to 4 atm. The reactor was cooled with liquid nitrogen and evacuated to remove gaseous products. The products, liquid at 25°C, were analyzed by gas chromatography.

TABLE 4
REACTION CONDITIONS AND YIELDS FOR REACTING BROMOPENTAFLUOROBENZENE WITH FLUORINE

Temperature (°C)	Total Pressure at -196°C (atm)	Mole Ratio F_2/C_6F_5Br	Time (hour)	%C_6F_5Br unreacted[a]	%Yield $C_6F_5BrF_2$[a]	%Yield $C_6F_5BrF_4$[a]	%Yield $(C_6F_5BrF)_2$[a]	%Yield Unidentified Products
-78	4	1.0	18	51(51)*	17(17)*	5(5)*	4(4)*	23(23)*
0	4	1.0	18	44(44)	19(19)	5(5)	3(3)	29(29)
10	4	1.0	18	37(36-37)	25(24-25)	7(6-7)	7(7)	24(23-24)
117	4	1.0	18	38(37-39)	38(37-39)	11(10-12)	1(0-1)	12(11-13)
128	4	1.0	18	34(33-35)	42(41-42)		9(8-9)	15(14-16)
220	4	1.0	18	50(49-50)	33(32-33)	7(6-8)	3(2-3)	7(6-7)
-78	4	2.0	18	46(45-46)	14(13-15)	8(7-9)	1(0-1)	31(30-32)
0	4	2.0	18	47(46-47)	14(14)	4(4)		35(34-35)
10	4	2.0	18	40(40)	22(22)	9(9)		29(29)
117	4	2.0	18	42(41-42)	40(40-41)	11(10-12)	3(2-4)	4(3-4)
128	4	2.0	18	26(25-26)	40(40)	24(23-24)		10(10)
220	4	2.0	18	5(4-5)	39(38-39)	15(14-15)		41(40-41)

a average of three results

* range of values

TABLE 5

REACTION CONDITIONS AND YIELDS FOR REACTING BROMOPENTAFLUOROBENZENE WITH BROMINE TRIFLUORIDE

Temperature (°C)	Total Pressure at -196 °C (atm)	Mole Ratio BrF_3/C_6F_5Br	Time (hour)	%C_6F_5Br unreacted[a]	%Yield $C_6F_5BrF_2$[a]	%Yield $C_6F_5BrF_4$[a]	%Yield $(C_6F_5BrF)_2$[a]	%Yield Unidentified Products[a]
-78	4	1.0	18	96(95-97)*	2(1-2)*		1(1)*	1(0-1)*
0	4	1.0	18	95(94-96)	2(1-2)		1(0-1)	2(1-2)
10	4	1.0	18	53(53)	19(18-19)	8(7-8)	5(5)	15(14-15)
117	4	1.0	18	22(22)	18(18)	9(9)		51(51)
128	4	1.0	18		20(20)	9(9)	10(10)	61(61)
220	4	1.0	18	5(3-6)		6(4-7)		89(87-90)
-78	4	2.0	18	89(89)	5(5)	1(1)	2(2)	3(3)
0	4	2.0	18	71(70-72)	9(8-10)	6(5-7)	2(1-3)	12(11-13)
10	4	2.0	18	30(29-31)		10(10)		60(59-61)
117	4	2.0	18			10(9-10)	5(4-5)	85(84-85)
128	4	2.0	18		11(11)	12(11-12)	8(8)	69(69)
220	4	2.0	18	5(5)	7(6-7)	6(5-6)	3(3)	79(79)

a average of three results

* range of values

TABLE 6

REACTION CONDITIONS AND YIELDS FOR REACTING PENTAFLUOROBENZENE WITH BROMINE TRIFLUORIDE

Temperature (°C)	Total Pressure at -196°C (atm)	Mole Ratio BrF_3/C_6F_5H	Time (hour)	%C_6F_5H unreacted[a]	%Yield $C_6F_5BrF_2$[a]	%Yield $C_6F_5BrF_4$[a]	%Yield $(C_6F_5BrF)_2$[a]	%Yield Unidentified Products[a]
-78	4	1.0	18	80(79-81)*	5(4-6)*	--	7(6-7)*	8(7-8)*
0	4	1.0	18	75(75)	8(8)	2(2)	6(6)	9(9)
10	4	1.0	18	71(70-71)	10(9-11)	2(1-2)	6(5-6)	11(10-12)
117	4	1.0	18	20(19-20)	13(12-13)			67(66-67)
128	4	1.0	18	30(30)	13(12-13)	4(4)	3(3)	50(49-50)
220	4	1.0	18	32(32)	12(12)	3(2-3)		53(52-53)
-78	4	2.0	18	81(81)	4(3-4)	4(4)	2(1-2)	9(8-9)
0	4	2.0	18	83(81-83)			5(4-6)	12(12)
10	4	2.0	18	32(31-32)	6(5-6)	5(4-5)	1(0-1)	56(55-56)
117	4	2.0	18	10(10)	10(10)	9(9)		71(71)
128	4	2.0	18	4(3-4)	12(11-12)	14(13-14)		70(70)
220	4	2.0	18		7(7)	10(9-11)	5(5)	78(77-79)

a average of three results

* range of values

3. Reactions of Pentafluorobenzene with Bromine Trifluoride (see Table 6)

Reaction procedures and conditions were similar to those described in paragraph K2 above. Bromine trifluoride (1.37 ± 0.01g, 10.0 mmoles) and pentafluorobenzene (1.68 ± 0.01g, 10.0 mmoles) were allowed to react at either -78, 0, 10, 117, 128 or 220 °C for 18 hours. Helium gas was added prior to reaction to bring the reactor pressure to 4 atm. The products, liquid at 25 °C, were analyzed by gas chromatography.

L. Preparation of Pentafluorophenylbromine(V) Tetrafluoride

1. Reactions of Bromopentafluorobenzene with Fluorine (see Table 4) (30)

Reaction procedures and conditions were the same as those in paragraph I1. A mixture of 2.47 ± 0.01g (10.0 mmoles) of bromopentafluorobenzene and 20.0 mmoles of fluorine were admitted to a Monel reactor. Helium gas was allowed to flow into the reactor to bring the pressure to 4 atm. The mixture was allowed to react at either -78, 0, 10, 117, 128 or 220 °C for 18 hours. A pale brown liquid formed. The products, liquid at 25 °C, were analyzed by gas chromatography.

2. Reactions of Bromopentafluorobenzene with Bromine Trifluoride (see Table 5)

The reaction procedure and conditions were similarly carried out just as described under paragraph K2. A mixture of 2.47 ± 0.01g (10.0 mmoles) of bromopentafluorobenzene and 20.0 mmoles of bromine trifluoride were allowed to react at either -78, 0, 10, 117, 128 or 220°C for 18 hours. Helium gas was added prior to reaction to bring the reactor pressure to 4 atm. The products, liquid at 25°C, were analyzed by gas chromatography.

3. Reactions of Pentafluorobenzene with Bromine Trifluoride (see Table 6)

In a manner analogous to paragraph K2, pentafluorobenzene (1.68 ± 0.01g, 10.0 mmoles) and bromine trifluoride (2.74 ± 0.01g, 20.0 mmoles) were allowed to react at either -78, 0, 10, 117, 128 or 220°C for 18 hours. The products, liquid at 25°C, were analyzed by gas chromatography.

4. Synthesis of Bromine Pentafluoride to be Used as a Fluorinating Agent

Bromine pentafluoride was not commercially available. Bromine pentafluoride was made by combining bromine trifluoride (4.11 ± 0.01g, 30.0 mmoles) and elemental fluorine (30.0 mmoles) at a temperature of 220°C for 6 hours. In the reaction, bromine trifluoride was converted to the more dense bromine pentafluoride. Purification of this product was not attempted. Bromine pentafluoride was transferred to a Teflon bottle for storage. It was handled as a liquid.

5. Reactions of Bromopentafluorobenzene with Bromine Pentafluoride (see Table 7)

Reaction procedures and conditions were very similar to paragraph K2. Bromopentafluorobenzene (2.47 ± 0.01g, 10.0 mmoles) and bromine pentafluoride (1.75 ± 0.01g, 10.0 mmoles) were allowed to react at either -78, 0, 10, 117, 128, or 220°C for 18 hours, to give a brown colored, viscous liquid. Helium gas was added prior to reaction to bring the reactor pressure to 4 atm. The products, liquid at 25°C, were analyzed by gas chromatography.

6. Reactions of Pentafluorobenzene with Bromine Pentafluoride (see Table 8)

Reaction procedure and conditions were very similar to paragraph K2. Pentafluorobenzene (1.68 ± 0.01g, 10.0 mmoles) and bromine pentafluoride (1.75 ± 0.01g, 10.0 mmoles) were mixed and allowed to react at either -78, 0, 10, 117, 128 or 220°C for 18 hours. Helium gas was added prior to reaction to bring the reactor pressure to 4 atm. The reaction gave hydrogen fluoride as the sole volatile product and a red-brown liquid. The products, liquid at 25°C, were analyzed by gas chromatography.

M. Preparation of 1,2-Difluoro-1,2-bis(pentafluorophenyl) Dichlorane

1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane was formed as a by-product during the synthesis of

TABLE 7
REACTION CONDITIONS AND YIELDS FOR REACTING BROMOPENTAFLUOROBENZENE WITH BROMINE PENTAFLUORIDE

Temperature (^oC)	Total Pressure at -196 ^oC (atm)	Mole Ratio BrF_5/C_6F_5Br	Time (hour)	%C_6F_5Br unreacted^a	%Yield $C_6F_5BrF_2$^{a}	%Yield $C_6F_5BrF_4$^{a}	%Yield $(C_6F_5BrF)_2$^{a}	%Yield Unidentified Products
-78	4	1.0	18	70(70-71)*		5(4-5)*		25(24-25)*
0	4	1.0	18	63(63)	4(4)	5(5)	1(1)	27(27)
10	4	1.0	18	20(20)	2(1-2)	13(13)		65(64-65)
117	4	1.0	18	2(1-3)	4(3-4)	14(13-15)	3(2-3)	77(77)
128	4	1.0	18		11(11)	20(19-20)		69(68-69)
220	4	1.0	18		11(10-11)	19(18-20)	3(2-4)	67(66-68)
-78	4	2.0	18	51(51)	4(4)	5(5)	2(2)	38(38)
0	4	2.0	18	42(40-42)	3(2-4)	3(2-3)		52(50-52)
10	4	2.0	18		13(12-13)	10(9-10)		77(76-77)
117	4	2.0	18	5(4-6)	10(9-11)	16(15-17)	1(0-1)	68(67-69)
128	4	2.0	18		8(8)	17(17)		75(75)
220	4	2.0	18		11(10-12)	17(16-17)	4(3-4)	68(67-69)

a average of three results
* range of values

TABLE 8
REACTION CONDITIONS AND YIELDS FOR REACTING PENTAFLUOROBENZENE WITH BROMINE PENTAFLUORIDE

Temperature (°C)	Total Pressure at -196 °C (atm)	Mole Ratio BrF_5/C_6F_5H	Time (hour)	%C_6F_5H unreacted^a	%Yield $C_6F_5BrF_2$^{a}	%Yield $C_6F_5BrF_4$^{a}	%Yield $(C_6F_5BrF)_2$^{a}	%Yield Unidentified Products^a
-78	4	1.0	18	65 (65)*	1 (0-2)*	3 (2-4)*	1 (1)*	30 (29-30)*
0	4	1.0	18	52 (50-52)	8 (6-8)	14 (13-15)	3 (2-4)	23 (23)
10	4	1.0	18	51 (50-51)	8 (8)	15 (15)	2 (2)	24 (24)
117	4	1.0	18	31 (30-32)	6 (5-7)	19 (18-19)		44 (43-44)
128	4	1.0	18		7 (6-7)	22 (21-22)		71 (70-71)
220	4	1.0	18	3 (3)		15 (14-15)		82 (81-82)
-78	4	2.0	18	40 (39-40)			4 (3-4)	56 (55-56)
0	4	2.0	18	30 (29-30)	5 (5)	14 (13-14)		51 (51)
10	4	2.0	18	24 (24)		13 (13)	1 (1)	62 (62)
117	4	2.0	18	10 (10)	7 (6-7)	17 (17)		66 (65-66)
128	4	2.0	18	15 (14-15)	9 (8-10)	17 (16-18)		59 (58-60)
220	4	2.0	18	15 (14-15)		3 (2-3)		82 (82)

a average of three results
* range of values

pentafluorophenylchlorine(III) difluoride by reaction of chloropentafluorobenzene with fluorine. Other preparative methods described above produce the dichlorane in extremely small yields.

A series of experiments were performed analogous to those of the pentafluorophenylchlorine(III) difluoride in order to determine the optimum fluorinating conditions based on percent yield of 1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane. The best molar ratio and optimum temperature were found to be 1.0 and 128°C, respectively. The reactor was charged to a pressure of 4 atm. prior to reaction. The products, liquid at 25°C. were analyzed by gas chromatography.

N. Preparation of 1,2-Difluoro-1,2-bis(pentafluorophenyl) Dibromane

1,2-difluoro-1,2-bis(pentafluorophenyl) dibromane was also formed as a by-product during the synthesis of pentafluorophenylbromine(III) difluoride by the oxidation of bromopentafluorobenzene at 128°C with elemental fluorine.

Bromopentafluorobenzene (2.47 ± 0.01g, 10.0 mmoles) and fluorine (10.0 mmoles) were allowed to react at 128°C for 18 hours.

O. Preparation of 5-Chloro-1-(difluorochloro) -2,3,4,5,6, 6-hexafluoro-1,3- Cyclohexadiene

5-Chloro-1-(difluorochloro)-2,3,4,5,6,6-hexafluoro-1,3-cyclohexadiene was formed as a by-product during the synthesis of pentafluorophenylchlorine(III) difluoride at -78°C using chloropentafluorobenzene and chlorine trifluoride as starting compounds.

Chloropentafluorobenzene (2.02 ± 0.01g, 10.0 mmoles) and chlorine trifluoride (10.0 mmoles) were allowed to react at -78°C for 18 hours. Reaction procedures and conditions were very similar to those in paragraph I2.

CHAPTER III

RESULTS AND DISCUSSIONS

A. Analysis of the Three Preparations (I1, I2, I3) in which Pentafluorophenylchlorine(III) Difluoride was the Product of Interest (See Tables 1, 2, 3)

The liquid products were purified by gas chromatography. Pentafluorophenylchlorine(III) difluoride (retention time 13.2 min.) was isolated by trapping the appropriate peak from the gas chromatograph.

Pentafluorophenyl chlorine(III) difluoride was a colorless liquid (boiling point 96-98°C) which fumed when exposed to air. It did not decolorize a 0.1 M potassium permanganate solution. The composition was established by elemental analysis. Anal. calcd. for pentafluorophenylchlorine(III) difluoride: C, 29.96; F, 55.29; Cl, 14.74. Found: C, 29.79; F, 55.07; Cl, 14.90. The atom ratios agree well with the empirical formula $C_6F_5ClF_2$. However, the sum of percentages is less than 100%. The discrepancy may result from the well-known difficulty of decomposing perfluorinated compounds by standard microanalytical procedures (4). However, since the atom ratios are satisfactory, it may also result from inclusion of some oxygen from the glass vessel or from traces of moisture.

The ^{19}F nuclear magnetic resonance spectrum at 25°C consists of a doublet at 141.63, a triplet at 157.05, a triplet at 162.25 and a singlet at -132.67 ppm ($CFCl_3$). This spectrum is consistent to that of a compound with a pentafluorophenyl group. The -132 67 ppm is far downfield in the region where one would expect to find the absorption from fluorine which is bonded to electronegative elements. Chlorine trifluoride showed a similar signal at -116 ppm (22).

The liquid phase infrared spectrum contains absorption bands at 1540 (s), 1501 (s), 1376 (m), 1352 (m), 1310 (w), 1159 (m), 1100 (s), 998 (s), 980 (s), 861 (s), 801 (w), 741 (m), 703 (s), 640 (vs), 621 (vs), 553 (vs), 530 (s), 502 (w), 459 (s), 425 (s), 395 (m), 370 (m), 334 (m), 315 (vs), 301 (m), 278 (m), 242 (vw), and 220 (vw) cm^{-1}. This infrared spectrum showed the presence of the pentafluorophenyl group (23) and the observed absorption bands at 741, 703 and 530 cm^{-1} were similar to those of chlorine trifluoride 742, 702 and 538 cm^{-1} respectively (24).

Molecular ions at m/e 240 and 242, accompanied by supporting fragmentation patterns, were present in the mass spectrum along with the isotopic ratio of approximately 3:1 as expected for the ^{35}Cl and ^{37}Cl. The mass spectrum of pentafluorophenylchlorine(III) difluoride consists of peaks assigned to $C_6F_5ClF_2^+$ (13), $C_6F_5ClF^+$ (0.71), $C_6F_5Cl^+$ (26), $C_6F_4Cl^+$ (0.92), $C_6F_6^+$ (6.7), $C_6F_5^+$ (29), $C_6F_4^+$ (0.72), $C_5F_3^+$ (100), ClF_2^+ (1·1), ClF^+ (0.7) and Cl^+ (0.2). In the cleavage scheme (Figure 2), the masses given refer to the ^{35}Cl isotope, and the peak +2 for ^{37}Cl was noted in every case.

An intense peak observed at m/e 186, is due to the possible ejection of the chlorine monofluoride radical from the molecular ion. The carbon-fluorine bond is stablized due to the aromaticity of the compound. Some fragmentation of the ring is observed due to its polyfluorination. A prominent peak was observed at m/e 167 which may be due to loss of chlorine difluoride radical. The extremely intense base peak, observed at m/e 117, was a result of $C_5F_3^+$ (25, 26). According to Beynon, Saunders and Williams (26), $C_5F_3^+$ had been found to be an abundant ion in the spectra of many aromatic fluorinated compounds. Loss of the trifluoromethyl radical from $C_6F_6^+$ may have accounted for $C_5F_3^+$ formation. It could also be due to loss of chlorine monofluoride radical from m/e 202. The peak at m/e 240 showed a very weak metastable peak at m* = obs., 144·0, calc., 144·2 from the process: $240^+ \longrightarrow 186^+ + ClF^o$. There are metastable ions corresponding to formation of m/e 202.

$240^{+} \longrightarrow 202^{+} + F^{o}$ (m*, obs., 170·0, calc., 170·0) and

$221^{+} \longrightarrow 202^{+} + F^{o}$ (m*, obs., 184·5, calc., 184·6), followed by further breakdown of the 202^{+} ion:

$202^{+} \longrightarrow 183^{+} + F^{o}$ (m*, obs., 165·6, calc., 165·8).

Fluorine attached to chlorine in pentafluorophenylchlorine(III) difluoride was readily liberated by hydrolysis (Reaction E). The difluoride was hydrolyzed to produce the chlorosopentafluorobenzene, which oxidized the iodide ion to iodine (Reaction F). The iodine was titrated using sodium thiosulfate (Reaction G). Pentafluorophenylchlorine(III) difluoride oxidized two equivalents of a potassium iodide solution. Since hydrogen fluoride is the only compound which etches glass, the etching of the glass vessel was proof of the hydrogen fluoride product.

$$C_6F_5ClF_2 + H_2O \longrightarrow C_6F_5ClO + 2HF \qquad (E)$$

$$C_6F_5ClO + 2I^- \xrightarrow{2H^+} C_6F_5Cl + I_2 + H_2O \qquad (F)$$

$$I_2 + 2\ S_2O_3^{=} \longrightarrow 2I^- + S_4O_6^{=} \qquad (G)$$

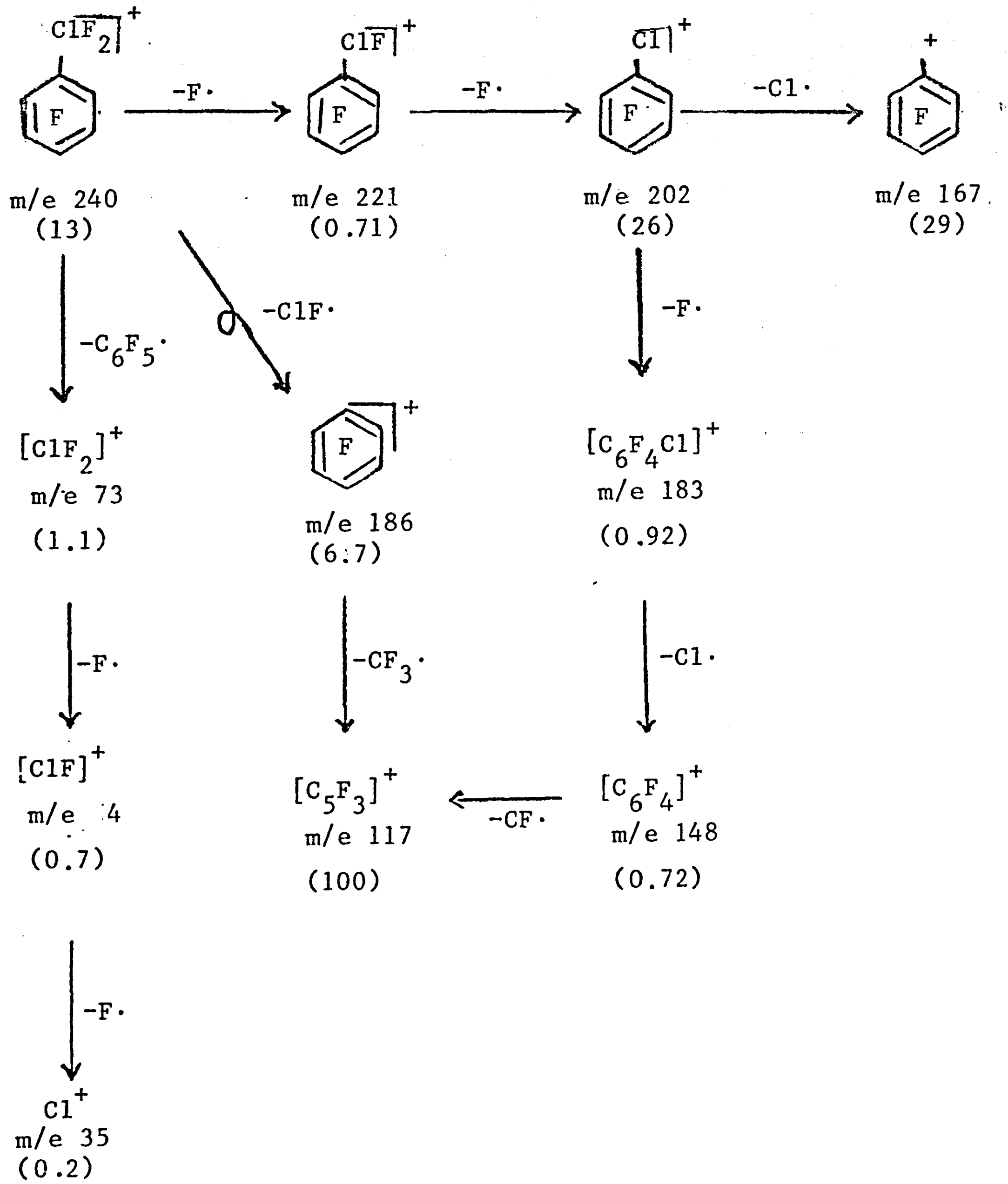


Figure 2. Cleavage Scheme of Pentafluorophenylchlorine(III) Difluoride as Observed from Mass Spectrum

B. Analysis of the Three Preparations (J1, J2, J3) in which Pentafluorophenylchlorine(V) Tetrafluoride was the Product of Interest (See Tables 1, 2, 3)

The pale yellow liquid products were purified by gas chromatography. Pentafluorophenylchlorine(V) tetrafluoride (retention time 7.9 min) was isolated by trapping the appropriate peak from the gas chromatograph.

Pentafluorophenylchlorine(V) tetrafluoride was a colorless liquid (boiling point 40-42°C) which fumed when exposed to moist air. Elemental analyses were extremely erratic, reflecting either the inability to purify this compound, or difficulty of decomposing perfluorinated compounds by standard microanalytical procedures or more probably, the instability of the compound itself.

The ^{19}F nuclear magnetic resonance spectrum consists of a doublet at 141.95, a triplet at 157.53, a triplet at 162.71 and a singlet at -153.80 ppm ($CFCl_3$). This spectrum is consistent to that of a compound with a pentafluorophenyl group. The -153.80 ppm is far downfield in the region where one would expect to find the absorption from fluorine which is bonded to electronegative elements. Chlorine pentafluoride showed a similar signal at -247 ppm (27).

The liquid phase infrared spectrum contains absorption bands at 1501 (s), 1380 (w), 1330 (w), 1152 (w), 1094 (s), 1008 (s), 981 (vs), 863 (s), 739 (m), 678 (w), 646 (m), 640 (vs), 619 (vs), 553 (vs), 528 (s), 502 (m), 458 (s), 423 (w), 400 (w), 395 (w), 375 (w), 332 (w), 301 (m), 278 (w), 242 (vw) and 220 (vw) cm^{-1}. This infrared spectrum showed the presence of the pentafluorophenyl group (23) and the observed absorption bands at 981, 739, and 301 cm^{-1} were similar to those of chlorine pentafluoride 981, 732, and 301 cm^{-1} respectively (28).

Molecular ions at m/e 278 and 280, accompanied by supporting fragmentation patterns, were present in the mass spectrum along with the isotopic ratio of approximately 3:1 as expected for ^{35}Cl and ^{37}Cl. The mass spectrum of pentafluorophenylchlorine(V) tetrafluoride consists of peaks assigned to $C_6F_5ClF_4^+$ (15), $C_6F_5ClF_3^+$ (14), $C_6F_5ClF_2^+$ (9 4), $C_6F_5ClF^+$ (19), $C_6F_5Cl^+$ (100), $C_6F_4Cl^+$ (39), $C_6F_6^+$ (18), $C_6F_5^+$ (50), $C_6F_4^+$ (9.6), ClF_4^+ (13), ClF_3^+ (6.9), ClF_2^+ (3.1), $C_5F_3^+$ (63), ClF^+ (11) and Cl^+ (3.5). In the cleavage scheme (Figure 3), the masses given refer to the ^{35}Cl isotope; the peak +2 for ^{37}Cl was noted in every case.

An intense peak observed at m/e 186, just as in the difluoride, is due to the possible ejection of the chlorine trifluoride radical from the m/e 278 with rearrangement. Alternatively, expulsion of the chlorine monofluoride radical from m/e 240 with rearrangement may also account for this. The base peak observed at m/e 202 is a result of loss of tetrafluoride radical from the molecular ion. There are two metastable ions corresponding to further breakdown of m/e 202:

$202^{+} \longrightarrow 167^{+} + Cl^{o}$ (m*, obs., 138.1, calc., 138.1) and

$202+ \longrightarrow 183^{+} + F^{o}$ (m*, obs., 165.7, calc., 165.8).

The peak observed at m/e 278 showed a weak metastable peak at m* = obs., 241.2, calc., 241.3 from the process: $278^{+} \longrightarrow 259^{+} + F^{o}$. Formation of $C_5F_3^{+}$, a commonly abundant ion in many aromatic fluorinated compounds, is from the following two processes which are supported by the presence of metastable ions:

$186^{+} \longrightarrow 117^{+} + CF_3^{o}$ (m*, obs., 73.6, calc., 73.6)

and

$148^{+} \longrightarrow 117^{+} + CF^{o}$ (m*, obs., 92.4, calc., 92.5)

Fluorine attached to chlorine in pentafluorophenylchlorine(V) tetrafluoride was readily liberated by hydrolysis (Reaction H). The tetrafluoride was hydrolyzed to produce the chloroxypentafluorobenzene which oxidized the iodide ion to iodine (Reaction I). The iodine was titrated using sodium thiosulfate (Reaction J). Pentafluorophenylchlorine(V) tetrafluoride oxidized four equivalents of potassium iodide solution.

$$C_6F_5ClF_4 + 2H_2O \longrightarrow C_6F_5ClO_2 + 4HF \qquad (H)$$

$$C_6F_5ClO_2 + 4I^- \xrightarrow{4H^+} C_6F_5Cl + 2I_2 + 2H_2O \qquad (I)$$

$$I_2 + 2S_2O_3^= \longrightarrow 2I^- + S_4O_6^= \qquad (J)$$

C. Analysis of the Three Preparations (K1, K2, K3) in which Pentafluorophenylbromine(III) difluoride was the Product of Interest (See Tables 4, 5, 6)

The liquid products were purified by gas chromatography. Pentafluorophenylbromine(III) difluoride (retention time 8.3 min.) was isolated by trapping the appropriate peak from the gas chromatograph.

Pentafluorophenylbromine(III) difluoride was a colorless liquid (boiling point 109-111°C) which fumed when exposed to moist air. It did not decolorize a 0.1M potassium permanganate solution. The composition was established by elemental analysis. Anal. calcd. for pentafluorophenylbromine(III) difluoride: C, 25.29; F, 46.47; Br, 28.04. Found: C, 24.89; F, 46.54; Br, 28.86. The atom ratios agree reasonably well with the empirical formula $C_6F_5BrF_2$.

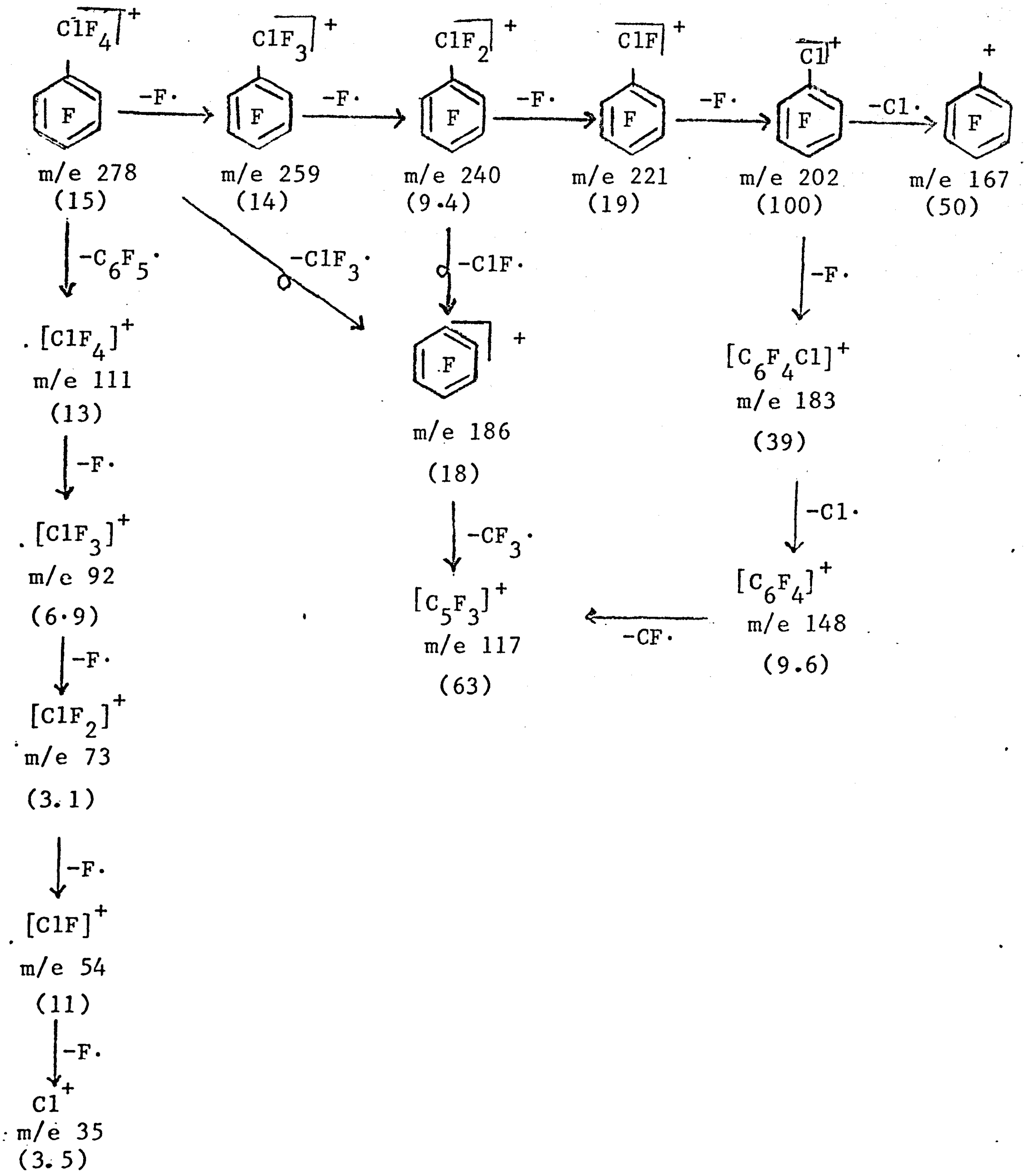


Figure 3. Cleavage Scheme of Pentafluorophenylchlorine(V) Tetrafluorde as Observed from Mass Spectrum

The ^{19}F nuclear magnetic resonance spectrum at 25°C consists of a doublet at 132.40, a triplet at 154.50, a triplet at 160.50 and a singlet at 63.13 ppm ($CFCl_3$). This spectrum is consistent with that of a compound with a pentafluorophenyl group. The 63.13 ppm is in the region where one would expect to find the absorption from fluorine which is bonded to electronegative elements. Bromine trifluoride showed a similar signal at 23.00 ppm (22).

The liquid phase infrared spectrum contains absorption bands at 1594 (s), 1500 (s), 1429 (m), 1361 (w), 1330 (w), 1100 (s), 1005 (s), 985 (s), 830 (s), 815 (m), 706 (s), 653 (vs), 638 (vs), 603 (vs), 540 (w), 500 (m), 461 (vs), 438 (w), 417 (s), 360 (vs), 337 (s), 319 (m), 288 (s), 257 (m) and 224 (w) cm^{-1}. This infrared spectrum showed the presence of the pentafluorophenyl group (23) and the observed absorption bands at 603, 540, 360, and 337 cm^{-1} were similar to those of bromine trifluoride 604, 547, 359 and 342 cm^{-1}, respectively (24).

Molecular ions at m/e 284 and 286, accompanied by supporting fragmentation patterns, were present in the mass spectrum along with the isotopic ratio of approximately 1:1 as expected for ^{79}Br and ^{81}Br. The mass spectrum of pentafluorophenylbromine(III) difluoride consists of peaks assigned to $C_6F_5BrF_2^+$ (2·8), $C_6F_5BrF^+$ (0·96), $C_6F_5Br^+$ (14), $C_6F_4Br^+$ (1·9), $C_6F_6^+$ (29), $C_6F_5^+$ (31), $C_6F_4^+$ (12), $C_5F_3^+$ (100), BrF_2^+ (2.6), BrF^+ (8·3) and Br^+ (4). In the cleavage scheme (Figure 4), the masses given refer to the ^{79}Br, the peak +2 for ^{81}Br was noted in every case.

Cleavage patterns were similar to those of pentafluorophenylchlorine(III) difluoride. The extremely intense base peak, observed at m/e 117 was a result of $C_5F_3^+$ with a little contribution from BrF_2^+. $C_5F_3^+$ is formed from the following two processes:

$$186^+ \longrightarrow 117^+ + CF_3^o \text{ (m* = obs., 73.5, calc., 73.6)}$$

and

$$148+ \longrightarrow 117^+ + CF^o \text{ (m* = obs., 92·5, calc., 92·5)}$$

The breakdown of the molecular ion was due to the processes $284^+ \longrightarrow 265^+ + F^o$, $284^+ \longrightarrow 186^+ + BrF^o$ and $284^+ \longrightarrow 117^+ + C_6F_5^o$. The former two processes were supported by the metastable peak at m* = obs., 247·2, calc., 247·3 and at m* = obs., 121·8, calc., 121·8, respectively. The metastable peak at m* = obs., 113·4, calc., 113·4 was due to the loss of a bromine radical from m/e 246. Loss of the fluorine radical from m/e 117 was also supported by the presence of the metastable ion at m* = obs., 82.0, calc., 82.1.

Fluorine attached to bromine in pentafluorophenylbromine(III) difluoride was readily liberated by hydrolysis (Reaction K). The difluoride was hydrolyzed to produce the bromosopentafluorobenzene which oxidized the iodide ion to iodine (Reaction L). The iodine was titrated using sodium thiosulfate (Reaction M). Pentafluorophenylbromine(III) difluoride oxidized two equivalents of a potassium iodide solution.

$$C_6F_5BrF_2 + H_2O \longrightarrow C_6F_5BrO + 2HF \qquad (K)$$

$$C_6F_5BrO + 2I^- \xrightarrow{2H^+} C_6F_5Br + I_2 + H_2O \qquad (L)$$

$$I_2 + 2S_2O_3^= \longrightarrow 2I^- + S_4O_6^= \qquad (M)$$

D. Analysis of the Five Preparations (L1, L2, L3, L5, L6) in which Pentafluorophenylbromine(V) Tetrafluoride was the Product of Interest (See Tables 4, 5, 6, 7, 8)

The liquid product was purified by gas chromatography. Pentafluorophenylbromine(V) tetrafluoride (retention time 7.5 min.) was isolated by trapping the appropriate peak from the gas chromatograph.

Pentafluorophenylbromine(V) tetrafluoride was a colorless, moisture-sensitive liquid (boiling point 87-89°C) which fumed when exposed to moist air. It did not decolorize a 0.1M potassium permanganate solution.

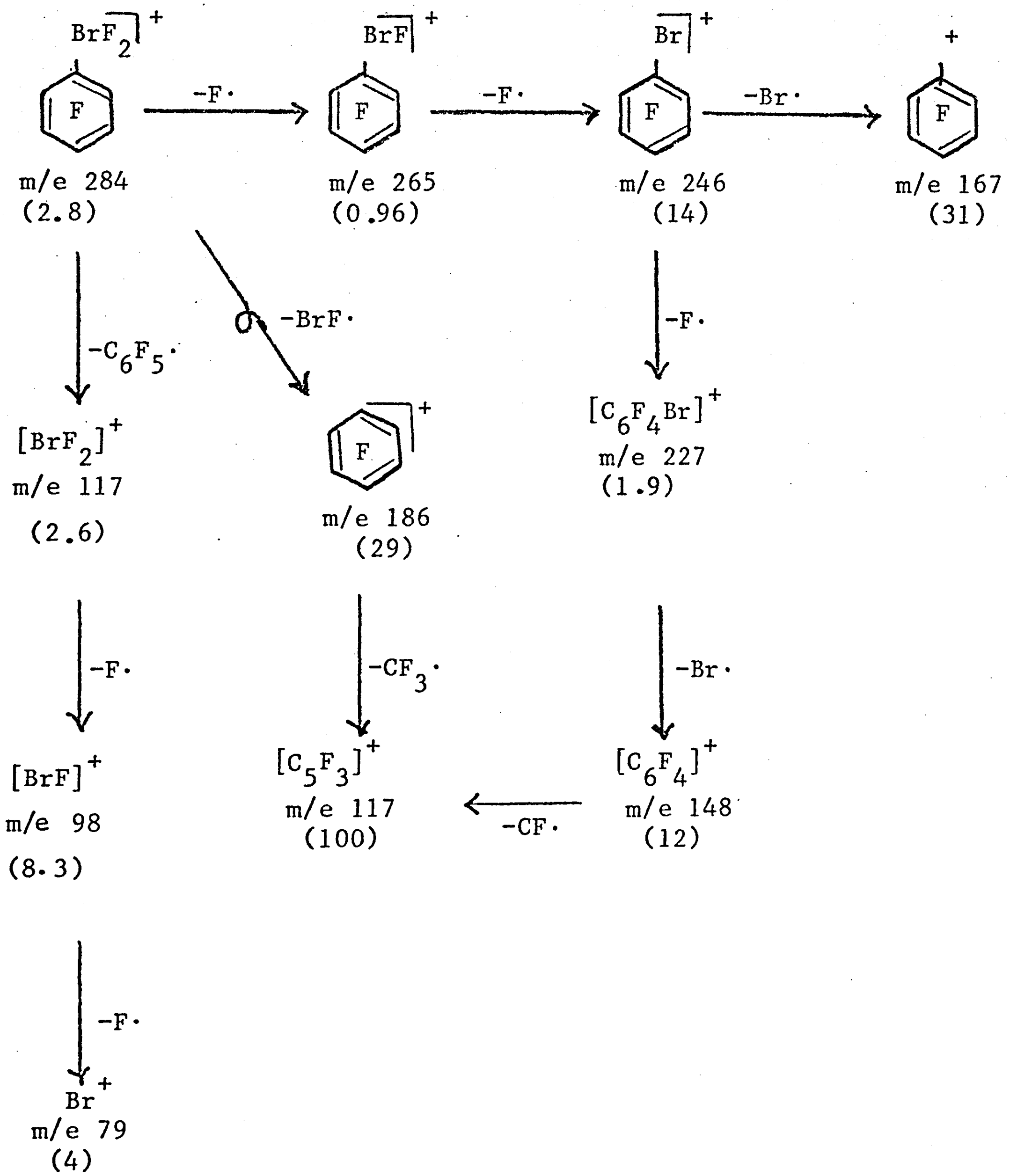


Figure 4. Cleavage Scheme of Pentafluorophenylbromine(III) Difluoride as Observed from Mass Spectrum

The ^{19}F nuclear magnetic resonance spectrum at 25°C consists of a doublet at 132.70, a triplet at 154.98, a triplet at 160.96 and a singlet at -140.33 ppm ($CFCl_3$). This spectrum is consistent with that of a compound with a pentafluorophenyl group. The -140.33 ppm is far downfield in the region where one would expect to find the absorption from fluorine which is bonded to electronegative elements. Bromine pentafluoride shows a similar signal at -142 ppm (22).

The liquid phase infrared spectrum contains absorption bands at 1595 (s), 1570 (w), 1512 (s), 1425 (m), 1361 (m), 1332 (m), 1268 (w), 1154 (m), 1101 (s), 1006 (s), 980 (s), 831 (s), 783 (m), 742 (m), 690 (w), 648 (m), 603 (vs), 554 (vs), 510 (s), 435 (s), 415 (w), 365 (w), 321 (w), 303 (s), 279 (m), 242 (w) and 219 (w) cm^{-1}. This infrared spectrum showed the presence of the pentafluorophenyl group (23) and the observed absorption bands at 690, 648, 415 and 365 cm^{-1} were similar to those of bromine pentafluoride 683, 644, 415 and 369 cm^{-1}, respectively (28).

Molecular ions at m/e 322 and 324, accompanied by supporting fragmentation patterns, were present in the mass spectrum along with the isotopic ratio of approximately 1:1 as expected for the ^{79}Br and ^{81}Br. The mass spectrum of pentafluorophenylbromine(V) tetrafluoride consists of peaks assigned to $C_6F_5BrF_4^+$ (13), $C_6F_5BrF_3^+$ (12), $C_6F_5BrF_2^+$ (6.7), $C_6F_5BrF^+$ (25), $C_6F_5Br^+$ (89), $C_6F_4Br^+$ (25), $C_6F_6^+$ (33), $C_6F_5^+$ (91), $C_6F_4^+$ (16), BrF_4^+ (3.1), BrF_3^+ (9.8), BrF_2^+ (15), $C_5F_3^+$ (100), BrF^+ (46) and Br^+ (10). In the cleavage scheme (Figure 5), the masses given refer to the ^{79}Br isotope; the peak +2 for ^{81}Br was noted in every case.

An intense peak observed at m/e 186 is due to the possible ejection of the bromine trifluoride radical from the m/e 322 with rearrangement, supported by the metastable peak at m* = obs., 107.5, calc., 107.4. Alternatively, expulsion of the bromine monofluoride radical from m/e 284 with rearrangement could account for this. This was supported by the metastable peak at m* = obs., 122.0, calc., 121.8. The extremely intense peak observed at m/e 246 is a result of the loss of the tetrafluoride radical from the molecular ion. A metastable ion was observed at m* = obs., 113.4; (calc., 113.4) due to loss of a bromine radical from m/e 246. The base peak, observed at m/e 117, was a result of $C_5F_3^+$, a commonly abundant ion in the spectra of many aromatic fluorinated compound (25, 26). Formation of $C_5F_3^+$ was from the following two processes which are supported by the presence of metastable ions:

$$227^{+} \longrightarrow 148^{+} + Br^{o} \quad (m^{*} = \text{obs., } 96.6, \text{ calc., } 96.5)$$

and

$$148^{+} \longrightarrow 117^{+} + CF^{o} \quad (m^{*} = \text{obs., } 92.7, \text{ calc., } 92.5)$$

Loss of the pentafluorophenyl radical from the molecular ion was also supported by the metastable peak at m* = obs., 74.5; calc., 74.6.

Fluorine attached to bromine in pentafluorophenylbromine(V) tetrafluoride was readily liberated by hydrolysis (Reaction N). The tetrafluoride was hydrolyzed to produce the bromoxypentafluorobenzene which oxidized the iodide ion to iodine (Reaction O). The iodine was titrated using sodium thiosulfate (Reaction P). Pentafluorophenylbromine(V) tetrafluoride oxidized four equivalents of potassium iodide.

$$C_6F_5BrF_4 + 2H_2O \longrightarrow C_6F_5BrO_2 + 4HF \qquad (N)$$

$$C_6F_5BrO_2 + 4I^- \xrightarrow{4H^+} C_6F_5Br + 2I_2 + 2H_2O \qquad (O)$$

$$I_2 + 2S_2O_3 \longrightarrow 2I^- + S_4O_6^{=} \qquad (P)$$

E. Analysis of 1,2 Difluoro-1,2-bis (pentafluorophenyl) Dichlorane

The products from preparation (M) were purified by distillation and gas chromatography. The fraction that boiled above 118°C was collected. 1,2-difluoro-1,2-bis (pentafluorophenyl) dichlorane (retention time 22.8 min.) was isolated from the distilled fraction by trapping the appropriate peak from the gas chromatograph.

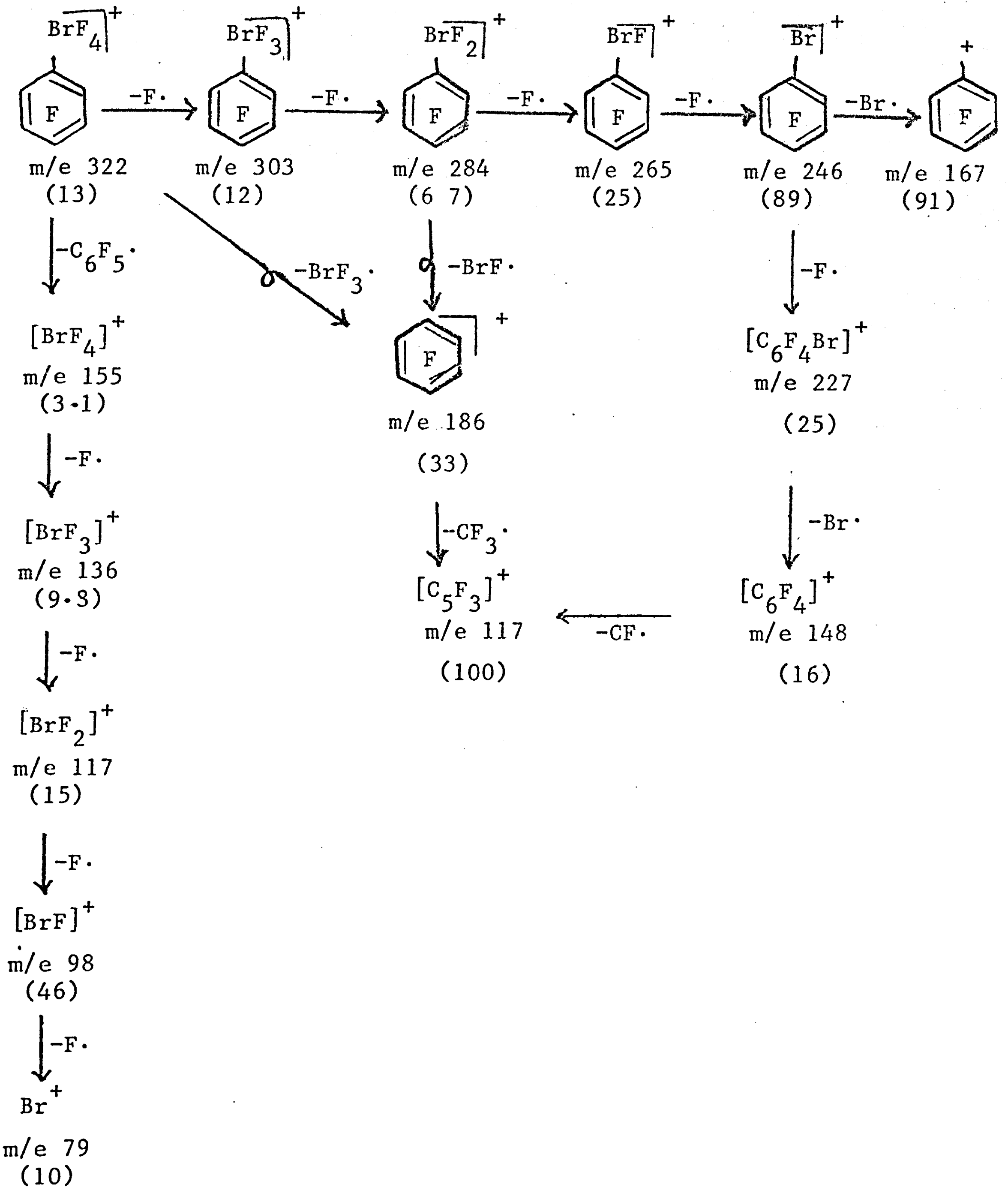


Figure 5. Cleavage Scheme of Pentafluorophenylbromine(V) Tetrafluoride as Observed from Mass Spectrum

1,2-Difluoro-1,2—bis(pentafluorophenyl) dichlorane was a colorless liquid (boiling point 121-123°C). It did not decolorize a 0 1M potassium permanganate solution. It changed to pale yellow when exposed to air for several hours. It also polymerized to form a thick yellowish semi-solid when heated. The composition was established by elemental analysis. Anal. calcd. for 1,2-Difluoro-1,2-bis(pentafluorophenyl) dichlorane C, 32.53; F, 51.47; Cl, 16.00. Found: C, 29.87; F, 49.79; Cl, 15.89. Despite the methods used in purifying this compound, the elemental analysis was not as good as expected. This may be due to the well-known difficulty of decomposing perfluorinated compounds by standard microanalytical procedures (4). The atom ratios agree well enough with the empirical formula $C_6F_5Cl(F)Cl(F)C_6F_5$.

The ^{19}F nuclear magnetic resonance spectrum at 25°C consists of a doublet at 140.39, a triplet at 156.58, a triplet at 161.88 and a singlet at -138.35 ppm ($CFCl_3$). This spectrum is consistent with that of a compound with a pentafluorophenyl group. The -138.35 ppm is far downfield in the region where one would expect to find the absorption of fluorine which is bonded to electronegative elements. Chlorine trifluoride showed a similar signal at -116 ppm (22).

The liquid phase infrared spectrum contains absorption bands at 1538 (s), 1501 (s), 1380 (w), 1330 (w), 1152 (w), 1094 (s), 1008 (s), 981 (vs), 863 (s), 730 (m), 764 (w), 694 (s), 660 (m), 621 (vs), 555 (s), 531 (s), 466 (m), 459 (s), 427 (w), 395 (m), 370 (m), 334 (m), 316 (vs), 301 (w) and 274 (m) cm^{-1}. This infrared spectrum showed the presence of the pentafluorophenyl group (23) and the observed absorption bands at 730, 694 and 531 cm^{-1} were similar to those of chlorine trifluoride 742, 702 and 538 cm^{-1}, respectively (24).

Molecular ions at m/e 442 and 444 accompanied by supporting fragmentation patterns, were present in the mass spectrum. The mass spectrum of 1,2 difluoro-1,2 bis (pentafluorophenyl) dichlorane consists of peaks $C_6F_5Cl(F)Cl(F)C_6F_5^+$ (0.59), $C_6F_5Cl(F)Cl(F)^+$ (5.15), $C_6F_5ClF_3^+$ (5.54), $C_6F_5ClF_2^+$ (1.98), $C_6F_5ClF^+$ (90.18), $C_6F_5Cl^+$ (100), $C_6F_6^+$ (50.92), $C_6F_4Cl^+$ (8.51), $C_4F_5Cl^+$ (6.93), $C_5F_4Cl^+$ (24.14), $C_6F_5^+$ (45.40), $C_5F_5^+$ (8.51), $C_6F_4^+$ (6.93), $C_3F_4Cl^+$ (7.52), $C_5F_2Cl^+$ (39.26), $C_5F_3^+$ (93.25), $C_3F_2Cl^+$ (12.27), $CFCl_2^+$ (28.89), $C_5F_2^+$ (25.93), $C_3F_3^+$ (31.66), CF_2Cl^+ (22.76), C_5F^+ (19.20), $C_3F_2^+$ (8.51), CF_3^+ (31.27), C_3F^+ (5.74), C_2F^+ (31.66) and Cl^+ (0.99).

In the clevage scheme (Figure 6), the masses given refer to the ^{35}Cl isotope; the peak +2 for ^{37}Cl was noted in every case.

The base peak at m/e 202 was from the processes $275^{+} \longrightarrow 202^{+} + ClF_2^{o}$ and $221^{+} \longrightarrow 202^{+} + F^{o}$. The latter process was supported by the metastable peak at m* = obs., 184.3; calc., 184.6. An intense peak at m/e 221 may be due to elimination of the same m/e 221 from the molecular ion. There was a metastable peak at m* = obs., 177.2, calc., 177.6 corresponding to formation of m/e 221 from further breakdown of the 275^{+} ion, i.e. $275^{+} \longrightarrow 221^{+} + ClF^{o}$. The direct loss of a chlorine radical from the base peak was confirmed by the presence of a weak metastable ion at m* = obs., 138.1; calc., 138.1. Loss of a chlorine monofluoride radical from the base peak was also supported by the metastable peak at m* = obs., 144.3; calc., 144.8. Common to both the previously discussed compounds and 1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane was a large peak at 117 mass units corresponding to the ion ($C_5F_3^{+}$), a species also very prevalent in the spectra of pentafluorophenyl halides (31).

Fluorine attached to chlorine in 1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane was readily liberated by hydrolysis. The compound was hydrolyzed to produce the chloroxypentafluorobenzene which oxidized the iodide ion to iodine. The iodine was titrated using sodium

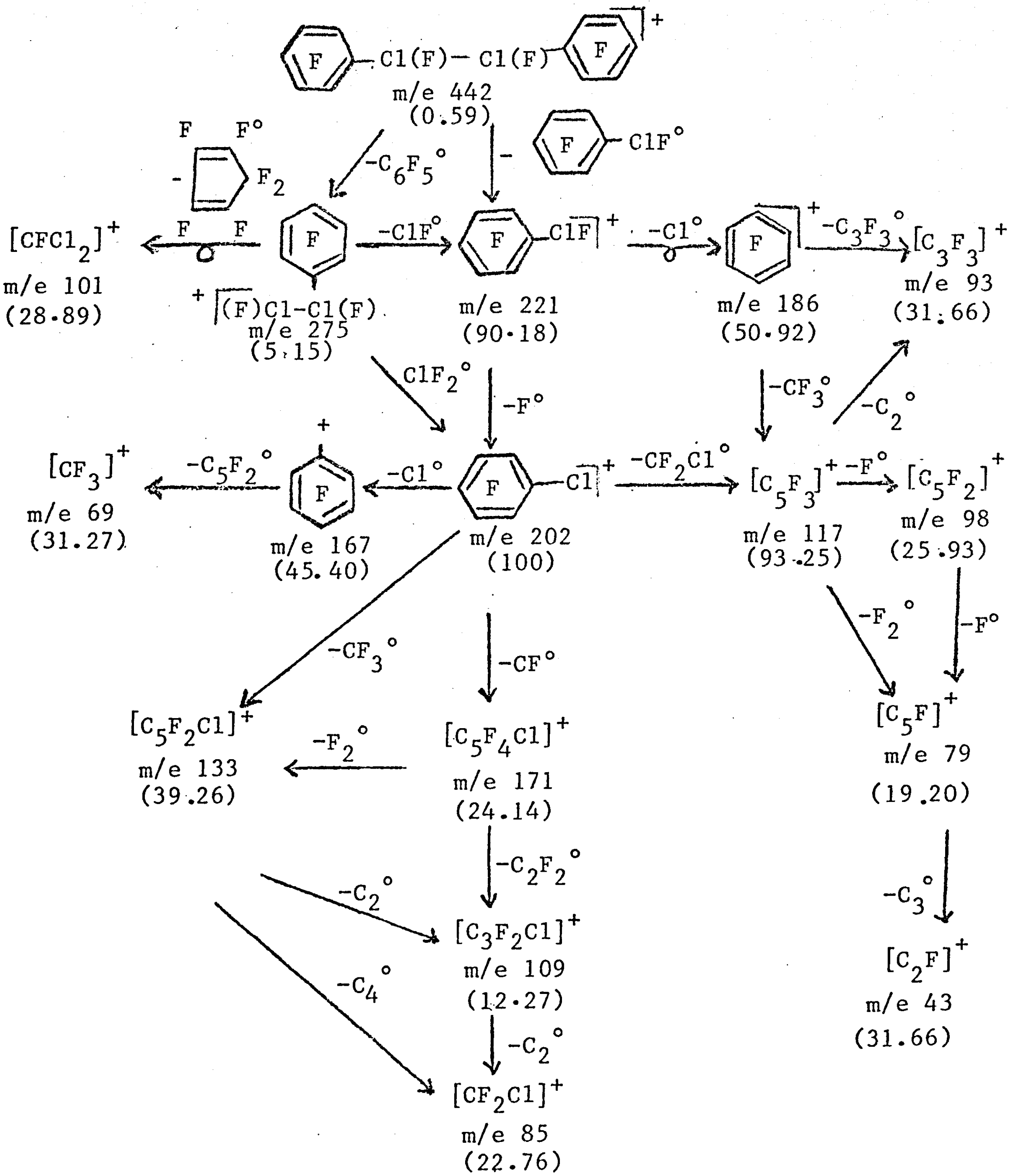


Figure 6. Cleavage Scheme of 1,2-Difluoro-1,2-bis (pentafluorophenyl) Dichlorane as Observed from Mass Spectrum

thiosulfate. 1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane oxidized four equivalents of 0.1M potassium iodide.

F. Analysis of 1,2-Difluoro-1,2-bis (pentafluorophenyl) Dibromane

The liquid products from preparation (N) were purified by gas chromatography. 1,2-Difluoro-1,2-bis (pentafluorophenyl) dibromane (retention time 17.9 min.) was isolated by trapping the appropriate peak from the gas chromatograph.

1,2-difluoro-1,2-bis(pentafluorophenyl) dibromane was a colorless liquid (boiling point 139-141°C). As a result of the small yield of this compound, it was characterized only by mass spectroscopy.

Molecular ions at m/e 530 and 532, accompanied by supporting fragmentation patterns, were present in the mass spectrum. The mass spectrum of 1,2-difluoro-1,2-bis(pentafluorophenyl) dibromane consists of peaks $C_6F_5Br(F)Br(F)C_6F_5^+$ (0.47), $C_6F_5Br(F)Br(F)^+$ (0.90), $C_6F_5Br(F)Br^+$ (4.24), $C_6F_5BrF^+$ (12.72), $C_6F_5Br^+$ (12.77), $C_5F_4Br^+$ (5.66), $C_6F_6^+$ (36.76), $Br\text{-}BrF^+$(1.89), $C_6F_5^+$ (18.38), $C_5F_5^+$ (5.18), $C_6F_4^+$ (8.72), $C_5F_4^+$ (15.46), $C_6F_3^+$ (3.77) $C_4F_4^+$ (7.45), $C_5F_3^+$ (100), $C_4F_3^+$ (7.16), $C_5F_2^+$ (47.60), $C_3F_3^+$ (68.19), $C_4F_2^+$ (24.88), C_5F^+ (49.01), Br^+ (7.12),

$C_3F_2^+$ (30.40), CF_3^+ (55.47) and C_3F^+ (20.78). In the cleavage scheme (Figure 7), the masses given refer to the ^{79}Br isotope; the peak +2 for ^{81}Br was noted in every case.

The peak at m/e 265 was from the processes $530^+ \longrightarrow 265^+ + C_6F_5BrF^o$ and $363^+ \longrightarrow 265^+ + BrF^o$. Both processes were supported by the metastable peaks at m* = obs., 132.6; calc., 132.5 and m* = obs., 193.8; calc., 193.5, respectively. Loss of a fluorine radical from m/e 265 was confirmed by the presence of a metastable ion at m* = obs., 228.4; calc., 228.4. The base peak at m/e 117 was a result of the ion $(C_5F_3)^+$. There was a metastable peak at m* = obs., 100.9; (calc., 100.7) which supports the formation of $C_5F_3^+$ through elimination of a fluorine radical from m/e 136. Another process that may account for $C_5F_3^+$ formation is $186^+ \longrightarrow 117^+ + CF_3^o$. As previously mentioned, $C_5F_3^+$ is very prevalent in the spectra of pentafluorophenyl halides (31).

G. Analysis of 5-Chloro-1-(difluorochloro)-2,3,4,5,6,6-hexafluoro-1,3-Cyclohexadiene

The liquid products from preparation (O) were purified by gas chromatography. 5-Chloro-1-(difluorochloro)-2,3,4,5,6,6-hexafluoro-1,3-cyclohexadiene (retention time 15.6 min.) was isolated by trapping the appropriate peak from the gas chromatograph.

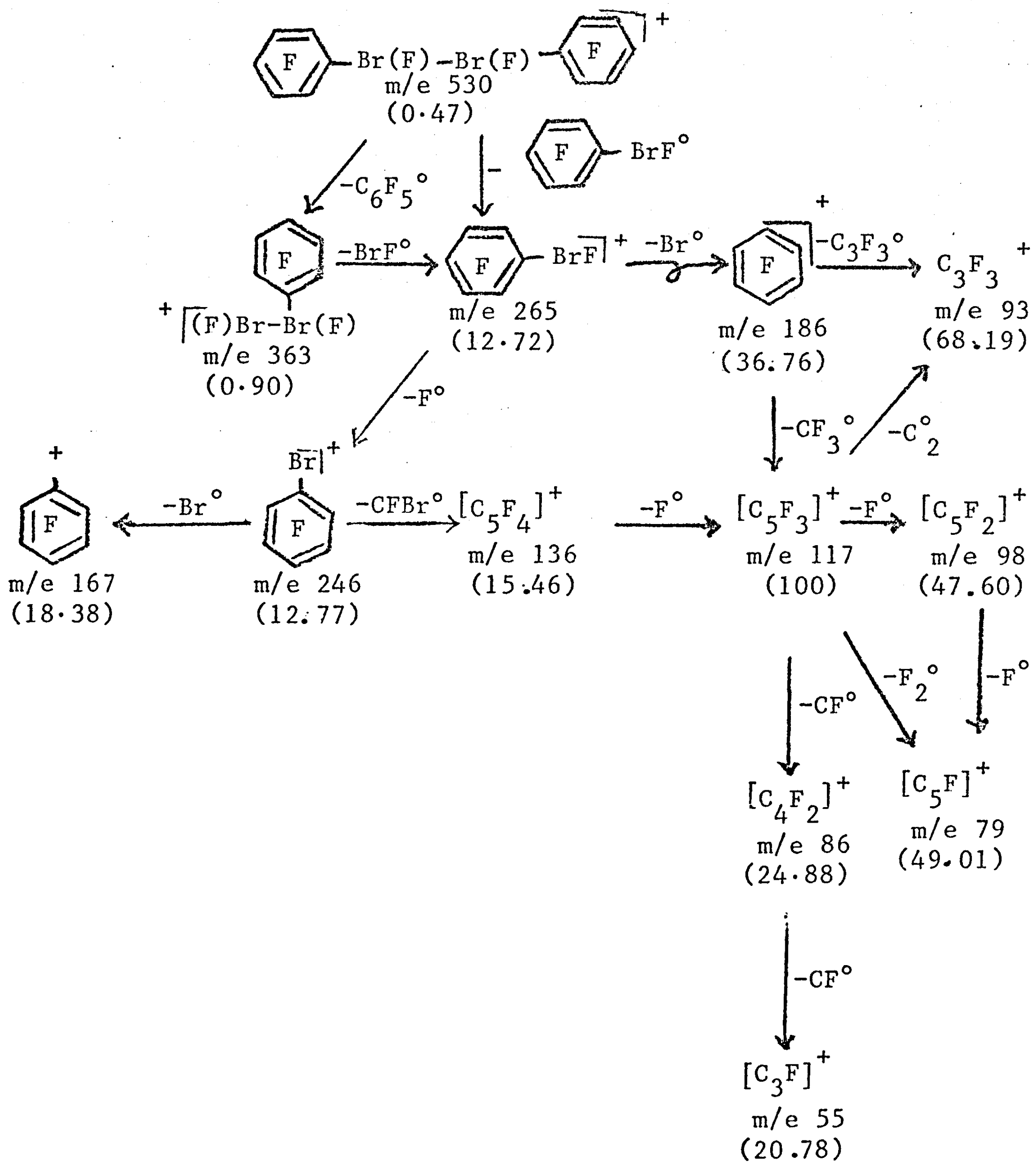


Figure 7. Cleavage Scheme of 1,2-Difluoro-1,2 bis-(pentafluorophenyl) Dibromane as Observed from Mass Spectrum

5-Chloro-1-(difluorochloro)-2,3,4,5,6,6-hexafluoro-1,3-cyclohexadiene was a colorless, moisture-sensitive liquid (boiling point 113-115°C) which fumed when exposed to moist air. The composition was established by elemental analysis. Anal. calcd. for 5-chloro-1-(difluorochloro)-2,3,4,5,6,6-hexafluoro-1,3-cyclohexadiene C, 24.41; F, 51.52; Cl, 24.07. Found: C, 24.55; F, 51.33; Cl, 24.11. The atom ratios agree very well with the empirical formula $C_6F_6Cl(ClF_2)$.

The ^{19}F nuclear magnetic resonance spectrum at 25°C consists of peaks in the following region: 104.35, 110.60, 113.61, 118.49, 120.68, 123.12, 124.41, 128.58, 131.67, 132.61, 134.50, 142.00, 142.66, 149.80, 152.70, 155.34 and 157.50 ppm ($CFCl_3$). This spectrum was complex and could not be fully interpreted. Perfluorocyclohexadienes are known to have very complicated ^{19}F resonance spectra due to the presence of strongly coupled, chemically equivalent fluorine nuclei (32).

The liquid phase infrared spectrum (1700-460 cm^{-1}) contains absorption bands at 1735 (s), 1687 (s), 1356 (vs), 1319 (w), 1270 (s), 1231 (s), 1193 (vs), 1140 (vs), 1113 (m), 1061 (m), 1038 (vs), 983 (s), 940 (vs), 900 (m), 845 (vs), 819 (s), 804 (s), 792 (m), 768 (m), 639 (vw), 610 (w) and

475 (m) cm^{-1}. This infrared spectrum also showed the presence of the cyclohexadiene ring structure. The two bands at 1735 and 1687 cm^{-1} are significant bands for a 1,3-diene. They arise from splittings due to conjugation.

Molecular ions at m/e 294 and 296 accompanied by supporting fragmentation patterns, were present in the mass spectrum. The mass spectrum of 5-Chloro-1-(difluorochloro)-2,3,4,5,6,6-hexafluoro-1,3-cyclohexadiene consists of peaks $C_6F_6Cl(ClF_2)^{+\cdot}$ (0.10), $C_6F_5Cl(ClF_2)^+$ (3.70), $C_6F_6ClF_2^+$ (6.21), $C_5F_6Cl^+$ (8.70), $C_6F_7^+$ (7.45), $C_4F_5Cl^+$ (33.54), $C_5F_4Cl^+$ (18.01), $C_4F_6^+$ (24.84), $C_4F_4Cl^+$ (19.88) $C_5F_5^+$ (49.07), $C_3F_4Cl^+$ (20.50), $C_4F_4^+$ (29.81), $C_5F_3^+$ (51.55), $C_3F_2Cl^+$ (66.46), $C_3F_3^+$ (100), $CClF_2^+$ (67.08), $C_3F_2^+$ (49.07), ClF_2^+ (4.00), CF_3^+ (99.38), C_3F^+ (23.60), Cl^+ (16.15) and CF^+ (98.76). This spectrum is as expected of this compound.

H. Pentafluorophenyl Ring

"The pentafluorophenyl ring is a unique substituent that imparts improved stability to many compounds. It has an inductive electronegative effect that is much stronger than phenyl but weaker than trifluoromethyl (σ_1 = C_6F_5 0.25, CF_3 0.39, C_6H_5 0.08). However, the π system of the pentafluorophenyl ring is probably severely distorted relative to phenyl and many of the interesting properties of pentafluorophenyl compounds could result from a combination of the inductive effects of five fluorines coupled with strong fluorine - π interactions." (33)

I. Direct Fluorination

In this work, it was determined that the reaction products from chloropentafluorobenzene and fluorine were pentafluorophenylchlorine(III) difluoride, pentafluorophenylchlorine(V) tetrafluoride and 1,2-difluoro-1,2-bis (pentafluorophenyl) dichlorane (equation Q), all new compounds.

$$C_6F_5Cl + F_2 \longrightarrow C_6F_5ClF_2,\ C_6F_5ClF_4,\ C_6F_5Cl(F)Cl(F)C_6F_5 \qquad (Q)$$

Since the reaction gave the desired difluoride and tetrafluoride, an intensive study of these compounds was begun.

The products from the reaction of bromopentafluorobenzene and fluorine were pentafluorophenylbromine(III) difluoride, pentafluorophenylbromine(V) tetrafluoride and 1,2-difluoro-1,2-bis(pentafluorophenyl) dibromane (equation R):

$$C_6F_5Br + F_2 \longrightarrow C_6F_5BrF_2,\ C_6F_5BrF_4,\ C_6F_5Br(F)Br(F)C_6F_5. \qquad (R)$$

The dissociation energy of fluorine is very low (approximately 37 kcal/mole); and so it is likely that the fluorination process proceeds by a radical mechanism (34).

The suggested mechanism for the reaction $C_6F_5X + F_2 \longrightarrow C_6F_5XF_2$ is as follows:

$$\begin{array}{lcl}
F_2 & \rightleftharpoons & 2F\cdot \\
C_6F_5X + F\cdot & \longrightarrow & C_6F_5\dot{X}F \\
2C_6F_5\dot{X}F & \longrightarrow & (C_6F_5XF)_2 \\
2C_6F_5\dot{X}F & \longrightarrow & C_6F_5XF_2 + C_6F_5X \\
C_6F_5\dot{X}F + F\cdot & \longrightarrow & C_6F_5XF_2
\end{array}$$

(Where X is Cl or Br)

In the above mechanism and all mechanisms that follow, it is understood that the reactions:

$$C_6F_5\dot{X}F + F\cdot \longrightarrow C_6F_5XF_2$$

and

$$C_6F_5\dot{X}F_3 + F\cdot \longrightarrow C_6F_5XF_4$$

will not be important unless their rate constants are several orders of magnitude greater than for the other reactions. It follows that production of the tetrafluorides would depend upon the yield of difluoride produced. The mechanism for the reaction $C_6F_5X + 2F_2 \longrightarrow C_6F_5XF_4$ might be as follows:

$$\begin{array}{lcl}
F_2 & \rightleftharpoons & 2F\cdot \\
C_6F_5X + F\cdot & \longrightarrow & C_6F_5\dot{X}F \\
2C_6F_5\dot{X}F & \longrightarrow & (C_6F_5XF)_2
\end{array}$$

$$2C_6F_5\dot{X}F \longrightarrow C_6F_5XF_2 + C_6F_5X$$

$$C_6F_5\dot{X}F + F\cdot \longrightarrow C_6F_5XF_2$$

$$C_6F_5XF_2 + F\cdot \longrightarrow C_6F_5\dot{X}F_3$$

$$2C_6F_5\dot{X}F_3 \longrightarrow (C_6F_5XF_3)_2$$

$$2C_6F_5\dot{X}F_3 \longrightarrow C_6F_5XF_4 + C_6F_5XF_2$$

$$C_6F_5\dot{X}F_3 + F\cdot \longrightarrow C_6F_5XF_4$$

The synthesis of 1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane and 1,2-difluoro-1,2-bis(pentafluorophenyl) dibromane $\{2C_6F_5X + F_2 \longrightarrow C_6F_5X(F)X(F)C_6F_5\}$ may be explained by the dimerization of the free radical ($C_6F_5\dot{X}F$) as shown below:

$$F_2 \rightleftharpoons 2F\cdot$$

$$C_6F_5X + F\cdot \longrightarrow C_6F_5\dot{X}F$$

$$2C_6F_5\dot{X}F \longrightarrow C_6F_5X(F)X(F)C_6F_5$$

Direct fluorination gave good yields of the difluoride. The amount of pentafluorophenylchlorine(III) difluoride produced by reacting chloropentafluorobenzene with fluorine ranged from 0 to 44%; while that of the corresponding tetrafluoride ranged from 0 to 12%. The yields of 1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane ranged from 0 to 20%. Elemental fluorine oxidized neat bromopentafluorobenzene even at low temperature and low mole ratio. The amount of pentafluorophenylbromine(III) difluoride produced by reacting bromopentafluorobenzene with fluorine ranged from 3 to 42%; while that of the corresponding tetrafluoride ranged from 0 to 24%. The yield of 1,2-difluoro-1,2-bis(pentafluorophenyl) dibromane ranged from 0 to 9%.

J. Chlorine Trifluoride as Fluorinating Agent

Not only elemental fluorine but also the chlorine and bromine fluorides are active fluorinators of the halogens. Chlorine trifluoride, the most active of these, converts chloropentafluorobenzene to the difluoride as shown in the reaction:

$$3C_6F_5Cl + 2ClF_3 \longrightarrow 3C_6F_5ClF_2 + Cl_2$$

according to the following suggested mechanism:

$$ClF_3 \rightleftharpoons ClF + F_2 \quad (35)$$

$$F_2 \rightleftharpoons 2F\cdot$$

$$C_6F_5Cl + F\cdot \longrightarrow C_6F_5\dot{C}lF$$

$$2C_6F_5\dot{C}lF \longrightarrow (C_6F_5ClF)_2$$

$$2C_6F_5\dot{C}lF \longrightarrow C_6F_5ClF_2 + C_6F_5Cl$$

$$C_6F_5\dot{C}lF + F\cdot \longrightarrow C_6F_5ClF_2$$

$$2ClF \rightleftharpoons Cl_2 + F_2 \quad (35)$$

Chlorine trifluoride yielded the tetrafluoride as shown in the reaction:

$$3C_6F_5Cl + 4ClF_3 \longrightarrow 3C_6F_5ClF_4 + 2Cl_2$$

according to the following suggested mechanism:

$$ClF_3 \rightleftharpoons ClF + F_2 \quad (35)$$

$$F_2 \rightleftharpoons 2F\cdot$$

$$C_6F_5Cl + F\cdot \longrightarrow C_6F_5\dot{Cl}F$$

$$2C_6F_5\dot{Cl}F \longrightarrow (C_6F_5ClF)_2$$

$$2C_6F_5\dot{Cl}F \longrightarrow C_6F_5ClF_2 + C_6F_5Cl$$

$$C_6F_5\dot{Cl}F + F\cdot \longrightarrow C_6F_5ClF_2$$

$$C_6F_5ClF_2 + F\cdot \longrightarrow C_6F_5\dot{Cl}F_3$$

$$2C_6F_5\dot{Cl}F_3 \longrightarrow (C_6F_5ClF_3)_2$$

$$2C_6F_5\dot{Cl}F_3 \longrightarrow C_6F_5ClF_4 + C_6F_5ClF_2$$

$$C_6F_5\dot{Cl}F_3 + F\cdot \longrightarrow C_6F_5ClF_4$$

$$2ClF \rightleftharpoons Cl_2 + F_2 \quad (35)$$

The yield of pentafluorophenylchlorine(V) tetrafluoride was not significantly affected by the conditions of the reactions.

The reaction between pentafluorobenzene and chlorine trifluoride was also found to produce difluoride as shown in the reaciton:

$$C_6F_5H + ClF_3 \longrightarrow C_6F_5ClF_2 + HF$$

and tetrafluoride as shown in the reaction:

$$3C_6F_5H + 5ClF_3 \longrightarrow 3C_6F_5ClF_4 + Cl_2 + 3HF$$

according to the following suggested mechanism:

$$\begin{aligned}
C_6F_5H + ClF_3 &\longrightarrow C_6F_5ClF_2 + HF \\
ClF_3 &\rightleftharpoons ClF + F_2 \qquad (35) \\
F_2 &\rightleftharpoons 2F\cdot \\
C_6F_5ClF_2 + F\cdot &\longrightarrow C_6F_5\overset{\bullet}{Cl}F_3 \\
2C_6F_5\overset{\bullet}{Cl}F_3 &\longrightarrow (C_6F_5ClF_3)_2 \\
2C_6F_5\overset{\bullet}{Cl}F_3 &\longrightarrow C_6F_5ClF_4 + C_6F_5ClF_2 \\
C_6F_5\overset{\bullet}{Cl}F_3 + F\cdot &\longrightarrow C_6F_5ClF_4 \\
2ClF &\rightleftharpoons Cl_2 + F_2 \qquad (35)
\end{aligned}$$

The yields of the difluorides ranged from 0 to 25% by using chlorine trifluoride as the fluorinating agent; while that of the corresponding tetrafluorides ranged from 0 to 12%. The amount of unreacted substrates ranged from 0 to 40%. In other words, as much as 20% of the fluorine in chlorine trifluoride appeared in pentafluorophenylchlorine(III) difluoride.

Chlorine trifluoride and chloropentafluorobenzene formed solid compounds in addition to the liquid products. One of these solids obtained in good yield was analyzed and found to be a polymeric form of chlorotrifluoroethylene (Anal. calcd. C, 20.61; F, 48.95; Cl, 30.44. Found: C, 20.27; F, 48.87; Cl, 30.05).

K. Bromine Trifluoride as Fluorinating Agent

Apparently all the fluorine atoms in bromine trifluoride were available for formation of both the pentafluorophenylbromine(III) difluoride as shown in the reaction:

$$3C_6F_5Br + 2BrF_3 \longrightarrow 3C_6F_5BrF_2 + Br_2$$

and pentafluorophenylbromine(V) tetrafluoride as shown in the reaction:

$$3C_6F_5Br + 4BrF_3 \longrightarrow 3C_6F_5BrF_4 + 2Br_2$$

The difluoride might be formed according to the following suggested mechanism:

$$\begin{array}{rcll}
BrF_3 & \rightleftharpoons & BrF + F_2 & (35) \\
F_2 & \rightleftharpoons & 2F\cdot & \\
C_6F_5Br + F\cdot & \longrightarrow & C_6F_5\dot{B}rF & \\
2C_6F_5\dot{B}rF & \longrightarrow & (C_6F_5BrF)_2 & \\
2C_6F_5\dot{B}rF & \longrightarrow & C_6F_5BrF_2 + C_6F_5Br & \\
C_6F_5\dot{B}rF + F\cdot & \longrightarrow & C_6F_5BrF_2 & \\
3BrF & \rightleftharpoons & BrF_3 + Br_2 & (36)
\end{array}$$

Bromine trifluoride yielded the tetrafluoride according to the following suggested mechanism:

$$\begin{array}{rcll}
BrF_3 & \rightleftharpoons & BrF + F_2 & (35) \\
F_2 & \rightleftharpoons & 2F\cdot & \\
C_6F_5Br + F\cdot & \longrightarrow & C_6F_5\dot{B}rF &
\end{array}$$

$$2C_6F_5\dot{\mathrm{Br}}F \longrightarrow (C_6F_5BrF)_2$$

$$2C_6F_5\dot{\mathrm{Br}}F \longrightarrow C_6F_5BrF_2 + C_6F_5Br$$

$$C_6F_5\dot{\mathrm{Br}}F + F\cdot \longrightarrow C_6F_5BrF_2$$

$$C_6F_5BrF_2 + F\cdot \longrightarrow C_6F_5\dot{\mathrm{Br}}F_3$$

$$2C_6F_5\dot{\mathrm{Br}}F_3 \longrightarrow (C_6F_5BrF_3)_2$$

$$2C_6F_5\dot{\mathrm{Br}}F_3 \longrightarrow C_6F_5BrF_4 + C_6F_5BrF_2$$

$$3BrF \rightleftharpoons BrF_3 + Br_2 \qquad (36)$$

The amount of pentafluorophenylbromine(III) difluoride formed by reacting bromopentafluorobenzene with bromine trifluoride ranged from 0 to 20%; while that of the corresponding tetrafluoride ranged from 0 to 12%.

The reaction between pentafluorobenzene and bromine trifluoride was also found to produce difluoride as shown in the reaction:

$$C_6F_5H + BrF_3 \longrightarrow C_6F_5BrF_2 + HF$$

and tetrafluoride as shown in the reaction:

$$3C_6F_5H + 5BrF_3 \longrightarrow 3C_6F_5BrF_4 + Br_2 + 3HF$$

according to the following suggested mechanism:

$$C_6F_5H + BrF_3 \longrightarrow C_6F_5BrF_2 + HF$$

$$BrF_3 \rightleftharpoons BrF + F_2 \qquad (35)$$

$$F_2 \rightleftharpoons 2F\cdot$$

$$C_6F_5BrF_2 + F\cdot \longrightarrow C_6F_5\dot{\mathrm{Br}}F_3$$

$$2C_6F_5\dot{\mathrm{Br}}F_3 \longrightarrow (C_6F_5BrF_3)_2$$

$$2C_6F_5\dot{B}rF_3 \longrightarrow C_6F_5BrF_4 + C_6F_5BrF_2$$

$$C_6F_5\dot{B}rF_3 + F\cdot \longrightarrow C_6F_5BrF_4$$

$$3BrF \rightleftharpoons BrF_3 + Br_2 \qquad (36)$$

The amount of pentafluorophenylbromine(III) difluoride formed by reacting pentafluorobenzene with bromine trifluoride ranged from 0 to 13%; while that of the corresponding tetrafluoride ranged from 0 to 14%.

Therefore, in almost all the reactions conducted in these experiments, the yield of the difluoride and tetrafluoride were found to be very small. This shows that bromine trifluoride as a fluorinating agent, is not as good as fluorine in the production of these products.

L. Bromine Pentafluoride as Fluorinating Agent

The reaction of bromopentafluorobenzene or pentafluorobenzene with bromine pentafluoride produced the tetrafluoride along with a small amount of difluoride as shown in the reaction:

$$3C_6F_5Br + 2BrF_5 \longrightarrow 2C_6F_5BrF_4 + C_6F_5BrF_2 + Br_2$$

according to the following suggested mechanism:

$$BrF_5 \rightleftharpoons BrF_3 + F_2 \qquad (35)$$

$$F_2 \rightleftharpoons 2F\cdot$$

$$C_6F_5Br + F\cdot \longrightarrow C_6F_5\dot{Br}F$$

$$2C_6F_5\dot{Br}F \longrightarrow (C_6F_5BrF)_2$$

$$2C_6F_5\dot{Br}F \longrightarrow C_6F_5BrF_2 + C_6F_5Br$$

$$C_6F_5\dot{Br}F + F\cdot \longrightarrow C_6F_5BrF_2$$

$$C_6F_5BrF_2 + F\cdot \longrightarrow C_6F_5\dot{Br}F_3$$

$$2C_6F_5\dot{Br}F_3 \longrightarrow (C_6F_5BrF_3)_2$$

$$2C_6F_5\dot{Br}F_3 \longrightarrow C_6F_5BrF_4 + C_6F_5BrF_2$$

$$C_6F_5\dot{Br}F_3 + F\cdot \longrightarrow C_6F_5BrF_4$$

$$BrF_3 \rightleftharpoons BrF + F_2 \qquad (35)$$

$$3BrF \rightleftharpoons BrF_3 + Br_2 \qquad (36)$$

The yield of difluoride ranged from 0 to 18%; while that of the tetrafluoride ranged from 2 to 20%.

The reaction between pentafluorobenzene and bromine pentafluoride was also found to produce tetrafluoride as shown in the reaction:

$$C_6F_5H + BrF_5 \longrightarrow C_6F_5BrF_4 + HF$$

according to the following suggested mechanism:

$$BrF_5 \rightleftharpoons BrF_3 + F_2 \qquad (35)$$

$$C_6F_5H + BrF_3 \longrightarrow C_6F_5BrF_2 + HF$$

$$F_2 \rightleftharpoons 2F\cdot$$

$$C_6F_5BrF_2 + F\cdot \longrightarrow C_6F_5\dot{Br}F_3$$

$$2C_6F_5\dot{Br}F_3 \longrightarrow (C_6F_5BrF_3)_2$$

$$\begin{aligned}
2C_6F_5\overset{\bullet}{Br}F_3 &\longrightarrow C_6F_5BrF_4 + C_6F_5BrF_2 \\
C_6F_5\overset{\bullet}{Br}F_3 + F\cdot &\longrightarrow C_6F_5BrF_4 \\
BrF_3 &\rightleftharpoons BrF + F_2 \quad (35) \\
3\overset{\bullet}{Br}F &\rightleftharpoons BrF_3 + Br_2 \quad (36)
\end{aligned}$$

The yield of difluoride ranged from 0 to 9%; while that of the tetrafluoride ranged from 0 to 22%.

M. Influence of Temperature on Percent Yield of Difluorides and Tetrafluorides

The reaction temperature appeared to be a very important factor in the production of either the difluoride or tetrafluoride. Increase in temperature improved the production of fluorine radicals, which interacted with the substrates according to the mechanisms suggested above. The importance of the reaction temperature can be shown in the reaction between chloropentafluorobenzene and elemental fluorine. At the temperature of -78°C it gave a yield of only 8% of pentafluorophenylchlorine(III) difluoride, while at 117°C it gave 44%. At the temperature of -78°C it gave a yield of only 6% of pentafluorophenylchlorine(V) tetrafluoride, while at 117°C it gave 12% (see Table 1).

A temperature of 128°C gave maximum yield of pentafluorophenylbromine(III) difluoride (42%) when bromopentafluorobenzene reacted with fluorine whereas 8% was found at -78°C. A maximum yield (24%) of pentafluorophenylbromine(V) tetrafluoride was observed at 128°C (see Table 4). From the above one can conclude that 117 C was the best temperature for the compounds containing chlorine {pentafluorophenylchlorine(III) difluoride and pentafluorophenylchlorine (V) tetrafluoride} while 128°C proved to be the best for compounds containing bromine {pentafluorophenylbromine(III) difluoride and pentafluorophenylbromine(V) tetrafluoride} .

At -78°C both substrates (chloropentafluorobenzene and bromopentafluorobenzene) are solid. The generally lower yields at -78°C, as compared to higher temperatures, may be due to the physical state of the substrates.

The data in Tables 1 - 14 refer to the percent composition of the liquid products as determined by integrating the area of the gas chromatography peaks. Early in these studies it was determined that the difference in response of the detector for the different compounds was insignificant. Therefore, the data is based on the uncorrected areas.

N. Influence of Pressure on Percent Yield of Difluorides and Tetrafluorides

It was observed that at low temperature (-78°C) an increase or decrease in pressure had little or no effect on either the yield of difluorides or tetrafluorides. As the

TABLE 9
REACTION CONDITIONS AND YIELDS SHOWING RELATIONSHIP BETWEEN PERCENT YIELD AND REACTION PRESSURE

Temperature (°C)	Total Pressure at -196°C (atm)	Mole Ratio F_2/C_6F_5Cl	Time (hour)	%C_6F_5Cl unreacted[a]	%Yield $C_6F_5ClF_2$[a]	%Yield $C_6F_5ClF_4$[a]	%Yield $(C_6F_5ClF)_2$[a]	%Yield Unidentified Products[a]
-78	0	1.0	18	90(87-92)*	7(5-8)*	1(0-1)*		2(1-2)*
-78	2	1.0	18	86(85-86)	8(7-8)	3(2-3)		3(1-4)
-78	4	1.0	18	87(86-87)	8(7-8)	3(3)		2(1-2)
-78	6	1.0	18	89(86-91)	4(3-5)	1(0-1)		6(4-7)
10	0	1.0	18	71(70-71)	3(2-3)	2(1-2)	2(1-2)	22(21-22)
10	2	1.0	18	70(70)	6(6)	4(3-4)	1(1)	19(18-19)
10	4	1.0	18	68(66-69)	16(14-17)	6(5-6)	2(1-3)	8(7-8)
10	6	1.0	18	68(66-69)	12(11-12)	4(2-6)	2(1-2)	14(12-15)
117	0	1.0	18	57(56-58)	29(28-29)		1(1)	13(12-15)
117	2	1.0	18	45(44-45)	44(43-44)		2(1-2)	9(8-9)
117	4	1.0	18	46(45-47)	44(43-44)		3(2-3)	7(6-8)
117	6	1.0	18	47(47)	41(40-41)	1(1)	1(1)	10(9-10)
128	0	1.0	18	47(46-47)	19(18-19)	4(4)	13(12-14)	17(16-17)
128	2	1.0	18	29(29)	31(31)	4(4)	17(17)	19(19)
128	4	1.0	18	30(30)	32(31-32)	5(3-7)	20(18-22)	13(13)
128	6	1.0	18	31(30-31)	32(30-33)	2(1-2)	20(19-20)	15(13-16)
220	0	1.0	18	61(60-62)	8(7-8)	5(4-5)	1(1)	25(25)
220	2	1.0	18	58(57-58)	10(10)	6(5-6)	4(3-5)	22(21-23)
220	4	1.0	18	50(48-51)	20(19-20)	10(9-11)	9(8-9)	11(10-11)
220	6	1.0	18	51(50-51)	15(15)	9(8-10)	8(7-8)	17(16-17)

a average of three results
* range of values

TABLE 10

REACTION CONDITIONS AND YIELDS SHOWING RELATIONSHIP BETWEEN PERCENT YIELD AND REACTION PRESSURE

Temperature ($^\circ$C)	Total Pressure at -196°C (atm.)	Mole Ratio F_2/C_6F_5Cl	Time (hour)	%C_6F_5Cl unreacted[a]	%Yield $C_6F_5ClF_2$[a]	%Yield $C_6F_5ClF_4$[a]	%Yield $(C_6F_5ClF)_2$[a]	%Yield Unidentified Products[a]
-78	0	2.0	18	88(88)*	3(2-3)*	5(5)*	1(1)*	3(2-3)*
-78	2	2.0	18	87(86-87)	3(2-4)	6(5-6)	1(1)	3(2-3)
-78	4	2.0	18	87(86-87)	4(3-4)	6(5-6)	1(0-1)	2(1-2)
-78	6	2.0	18	88(87-88)	4(3-4)	5(5)	1(1)	2(2)
10	0	2.0	18	72(72)	8(7-8)	2(1-2)		18(17-18)
10	2	2.0	18	69(68-69)	12(12)	5(5)	2(2)	12(12)
10	4	2.0	18	63(61-64)	20(19-20)	8(7-8)	4(3-5)	5(4-6)
10	6	2.0	18	65(65)	18(18)	6(5-6)	4(4)	7(6-7)
117	0	2.0	18	46(44-48)	26(23-26)	1(1)		27(26-27)
117	2	2.0	18	33(32-34)	32(32)	8(7-9)	8(8)	19(18-19)
117	4	2.0	18	33(32-33)	34(33-34)	12(12)	10(9-10)	11(10-11)
117	6	2.0	18	36(36)	30(30)	10(9-10)	9(8-9)	15(15)
128	0	2.0	18	30(29-30)	15(14-15)	10(9-10)	13(12-13)	32(31-32)
128	2	2.0	18	13(12-13)	26(25-26)	10(9-11)	17(15-19)	34(32-35)
128	4	2.0	18	10(10)	30(30)	11(11)	18(18)	31(30-31)
128	6	2.0	18	11(11)	29(28-29)	9(8-9)	18(18)	33(33)
220	0	2.0	18	87(87)	4(4)		2(2)	7(7)
220	2	2.0	18	87(85-87)	6(6)		4(2-5)	3(3)
220	4	2.0	18	82(81-82)	9(8-9)	3(2-3)	5(4-6)	1(0-1)
220	6	2.0	18	81(80-82)	7(6-7)	3(2-4)	4(3-4)	5(4-5)

a average of three results

* range of values

TABLE 11
REACTION CONDITIONS AND YIELDS SHOWING RELATIONSHIP BETWEEN PERCENT YIELD AND REACTION PRESSURE

Temperature (°C)	Total Pressure at -196°C (atm.)	Mole Ratio F_2/C_6F_5Br	Time (hour)	%C_6F_5Br unreacted[a]	%Yield $C_6F_5BrF_2$[a]	%Yield $C_6F_5BrF_4$[a]	%Yield $(C_6F_5BrF)_2$[a]	%Yield Unidentified Products[a]
-78	0	1.0	18	52(51-52)*	16(15-16)*	3(2-3)*	2(1-2)*	27(26-27)*
-78	2	1.0	18	50(50)	16(16)	4(4)	2(2)	28(28)
-78	4	1.0	18	51(50-52)	17(16-18)	5(4-6)	4(3-5)	23(22-24)
-78	6	1.0	18	48(47-49)	16(15-17)	5(4-6)	3(2-4)	28(27-29)
10	0	1.0	18	48(48)	18(18)		1(1)	33(33)
10	2	1.0	18	43(42-43)	19(18-19)	5(4-5)	3(2-3)	30(29-30)
10	4	1.0	18	37(37-38)	25(25-26)	7(7-8)	7(7-8)	24(24-25)
10	6	1.0	18	39(37-40)	23(21-24)	6(4-7)	7(7-8)	25(23-26)
117	0	1.0	18	43(43)	24(24)	4(4)		29(29)
117	2	1.0	18	44(43-44)	31(30-31)	6(5-6)		19(18-19)
117	4	1.0	18	38(38)	38(38)	11(11)	1(1)	12(12)
117	6	1.0	18	38(38)	36(36)	10(10)		16(16)
128	0	1.0	18	31(30-31)	35(34-35)		1(0-1)	33(32-33)
128	2	1.0	18	32(32)	37(37)		4(4)	27(27)
128	4	1.0	18	34(33-34)	42(41-42)		9(8-9)	15(14-15)
128	6	1.0	18	29(29)	40(40)		8(8)	23(23)
220	0	1.0	18	49(48-49)	19(18-19)			32(31-32)
220	2	1.0	18	46(45-46)	32(31-32)	2(1-2)		20(19-20)
220	4	1.0	18	50(49-51)	33(32-34)	7(6-8)	3(2-4)	7(6-8)
220	6	1.0	18	51(50-52)	29(28-30)	7(6-8)	2(1-3)	11(10-12)

a average of three results
* range of values

TABLE 12
REACTION CONDITIONS AND YIELDS SHOWING RELATIONSHIP BETWEEN PERCENT YIELD AND REACTION PRESSURE

Temperature (°C)	Total Pressure at -196° C (atm.)	Mole Ratio F_2/C_6F_5Br	Time (hour)	%C_6F_5Br unreacted[a]	%Yield $C_6F_5BrF_2$[a]	%Yield $C_6F_5BrF_4$[a]	%Yield $(C_6F_5BrF)_2$[a]	%Yield Unidentified Products[a]
-78	0	2.0	18	46(46)*	13(13)*	3(3)*		38(38)*
-78	2	2.0	18	46(45-46)	13(12-14)	6(6)	1(1)	34(33-34)
-78	4	2.0	18	46(46)	14(14)	8(8)	1(1)	31(31)
-78	6	2.0	18	49(48-50)	11(9-13)	8(7-8)		32(31-32)
10	0	2.0	18	44(42-44)	15(14-16)	3(2-3)		38(37-38)
10	2	2.0	18	42(42)	19(19)	6(5-7)		33(32-33)
10	4	2.0	18	40(38-41)	22(21-22)	9(9)		29(28-29)
10	6	2.0	18	41(41)	20(20)	8(8)		31(30-31)
117	0	2.0	18	49(48-49)	24(23-24)	5(5)		22(21-23)
117	2	2.0	18	39(38-39)	38(38)	8(7-9)	1(0-1)	14(13-15)
117	4	2.0	18	42(41-42)	40(39-40)	11(10-11)	3(2-3)	4(4)
117	6	2.0	18	43(42-43)	37(36-38)	8(7-8)	3(2-3)	9(8-9)
128	0	2.0	18	35(33-37)	29(29)	12(12)		24(22-26)
128	2	2.0	18	24(22-25)	39(36-41)	20(19-21)		17(17)
128	4	2.0	18	26(25-27)	40(40)	24(24)		10(9-10)
128	6	2.0	18	36(36)	37(37)	16(15-17)		11(10-12)
220	0	2.0	18	42(40-44)	10(8-12)			48(47-48)
220	2	2.0	18	27(26-27)	24(23-25)	10(8-11)		39(39)
220	4	2.0	18	5(5)	39(37-40)	15(14-16)		41(40-41)
220	6	2.0	18	24(23-24)	30(29-30)	9(8-9)		37(37)

[a] average of three results

* range of values

temperature increased above 10°C the pressure became a significant factor in the synthesis of these polyfluorides. As the initial pressure was increased from 0 to 4 atm, the yield of the desired products generally increased (see Tables 9-12).

O. Influence of Mole Ratio on Percent Yield of Difluorides and Tetrafluorides

A mole ratio of 1:1 usually produced difluorides in reasonable yield except in the case of bromine pentafluoride, while a mole ratio of 2:1 favored production of the tetrafluorides. Excess of fluorine or chlorine trifluoride gave 100% yield of solid black compounds and no desired products. The production of the black solid compounds due to the presence of an excess of fluorine or chlorine trifluoride at higher pressure was enhanced when oxygen leaked into the vacuum system. It is suggested that oxygen might interfere with the radical mechanism. A moderate excess of chlorine trifluoride was not harmful, for it was readily removed by pumping at the close of the reaction (see Tables 1, 4).

P. Influence of Time on Percent Yield of Difluorides and Tetrafluorides

In almost all the reactions in these experiments, the yield of the difluorides and tetrafluorides were

TABLE 13

REACTION CONDITIONS AND YIELDS SHOWING RELATIONSHIP BETWEEN PERCENT YIELD AND REACTION TIME

Temper-ature (°C)	Total Pressure at -196°C (atm)	Mole Ratio F_2/C_6F_5Cl	Time (hour)	%C_6F_5Cl unreacted[a]	%Yield $C_6F_5ClF_2$[a]	%Yield $C_6F_5ClF_4$[a]	%Yield $(C_6F_5ClF)_2$[a]	%Yield Unidentified Products[a]
117	4	1.0	1	65(64-65)*	8(7-8)*			27(26-27)*
117	4	1.0	3	65(64-66)	9(7-11)			26(24-28)
117	4	1.0	7	59(59)	13(13)			28(28)
117	4	1.0	12	54(53-54)	15(14-15)	1(0-1)		30(29-31)
117	4	1.0	18	46(44-48)	44(42-46)		3(2-3)	7(5-8)
117	4	1.0	24	46(46)	43(43)		3(2-3)	8(7-8)
117	4	2.0	1	53(51-54)	7(5-9)			40(39-41)
117	4	2.0	3	50(50)	11(11)	4(3-5)	1(0-1)	34(33-34)
117	4	2.0	7	50(49-51)	24(23-24)	5(5)	5(4-5)	16(16)
117	4	2.0	12	35(34-35)	30(30)	9(8-9)	10(10)	16(15-16)
117	4	2.0	18	33(32-33)	34(33-34)	12(11-12)	10(9-10)	11(10-11)
117	4	2.0	24	33(32-34)	34(33-34)	12(12)	8(8)	13(12-14)

a average of three results

* range of values

TABLE 14
REACTION CONDITIONS AND YIELDS SHOWING RELATIONSHIP
BETWEEN PERCENT YIELD AND REACTION TIME

Temperature (°C)	Total Pressure at -196°C (atm)	Mole Ratio F_2/C_6F_5Br	Time (hour)	% C_6F_5Br unreacted[a]	%Yield $C_6F_5BrF_2$[a]	%Yield $C_6F_5BrF_4$[a]	%Yield $(C_6F_5BrF)_2$[a]	%Yield Unidentified Products[a]
128	4	1.0	1	56(56)*				44(44)*
128	4	1.0	3	49(46-50)	8(6-9)	1(1)	1(0-1)	41(39-42)
128	4	1.0	7	52(50-53)	11(9-13)		3(1-5)	34(32-36)
128	4	1.0	12	41(40-42)	31(31)		2(1-2)	26(25-26)
128	4	1.0	18	34(34)	42(42)		9(8-9)	15(14-15)
128	4	1.0	24	34(33-35)	42(42)		9(8-10)	15(14-15)
128	4	2.0	1	49(46-50)	1(1)			50(47-51)
128	4	2.0	3	43(43)	6(6)	3(3)		48(47-48)
128	4	2.0	7	41(40-42)	17(17)	8(7-9)		34(33-34)
128	4	2.0	12	41(40-41)	32(30-32)	13(12-14)		14(13-14)
128	4	2.0	18	26(25-26)	40(39-40)	24(23-24)		10(9-10)
128	4	2.0	24	25(23-26)	37(36-38)	24(23-24)		14(13-14)

a average of three results
* range of values

found to be small or none at all when the reaction time was less than 18 hours. When the reactions were run for 18 or 24 hours, the yield of products greatly increased. The fact that there was no significant changes in product distribution between the 18 hour reaction and the 24 hour reaction, indicates that after 18 hours, the equilibrium is almost established (see Tables 13 and 14).

Q. Thermal Stability of the Difluorides and Tetrafluorides

All of the difluorides and tetrafluorides were moderately stable at room temperature when out of contact with moisture. Thermal stability of each compound was determined in the absence of moisture by allowing the samples to stand at various temperatures (-78°C, 0°C, 10°C, 25°C, and 117°C) for several days. There was no observable decomposition as shown by the gas chromatograph. The samples of tetrafluoride, especially pentafluorophenylchlorine(V) tetrafluoride at 25°C, showed traces of an oily material after about four months of storage (10°C).

R. Hydrolysis of the Difluorides and Tetrafluorides

Several attempts were made to isolate the oxides produced by hydrolysis of the above compounds. It is known that reactions did occur because hydrogen fluoride was produced. The oxides were apparently not stable under the conditions used in the attempted isolation.

S. Nuclear Magnetic Resonance

^{19}F nuclear magnetic resonance spectroscopy affords insight into the structures of the new difluorides and tetrafluorides. The $-XF_n$ resonances were difficult to locate. All these compounds freeze around -10°C. This prevented low temperature experiments from being conducted on the samples. There are some suggested reasons why the $-XF_n$ groups were difficult to locate (22). Reactivity of these compounds with moisture or an impurity and fluorine exchange which requires a low temperature may be factors.

There are two reports on the nuclear magnetic resonance spectrum of chlorine trifluoride (22, 27) but they do not agree with each other. Attempts were made to obtain the nuclear magnetic resonance spectrum of pure chlorine trifluoride. The result was different from the other two reported data (22, 27). A doublet was found at +12 ppm which was believed to be due to the two axial fluorines. The equatorial fluorine was never observed. Two communications reporting the synthesis of chlorine pentafluoride have appeared (37, 38). Neither of these reported its nuclear magnetic resonance.

The ^{19}F resonance spectrum of bromine trifluoride, consisted of only a single absorption band at room temperature (22). The other fluorines were not found. Muetterties and Phillips (22) reported 43 ppm for axial fluorine in bromine pentafluoride and -142 ppm for the equatorial fluorines; while Gutowsky and Hoffman (27) reported -138 ppm for axial fluorine and -276 ppm as the equatorial fluorine. All of them used fluorotrichloromethane as the internal solvent. Emsley _et_ _al._ (39) tabulated all the ^{19}F nuclear magnetic resonance spectra of interhalogen compounds. Our reported $-XF_n$ groups were found to be shifted upfield in comparison with that of the similar XF_{n+1} compound. This is likely due to the presence of the pentafluorophenyl group. Since the fluorine nuclear magnetic resonance showed only one fluorine environment (other than the aromatic fluorine) for pentafluorophenylchlorine(III) difluoride and pentafluorophenylbromine (III) difluoride, this indicates the pentafluorophenyl ring is located in the equatorial position, predicting sp^2-sp^2 bonding (40). Pentafluorophenylchlorine(III) difluoride and pentafluorophenylbromine(III) difluoride are dsp^3 hybridized. The one equatorial fluorine is thought to be sp^2 while the other two are dp (40). Chlorine pentafluoride and bromine pentafluoride can be either dz^2sp^3 (trigonal bipyramid) or $dx^2-y^2sp^3$ (square pyramid) (41). The fluorine nuclear magnetic resonance data presented earlier showed only one fluorine environment (other than the aromatic fluorine) for pentafluorophenylchlorine(V) tetrafluoride and pentafluorophenylbromine(V) tetrafluoride which indicates the pentafluorophenyl ring is located in the axial position. Consequently, they must be square pyramid with $dx^2-y^2sp^3$ hybridization.

CHAPTER IV

SUMMARY AND CONCLUSION

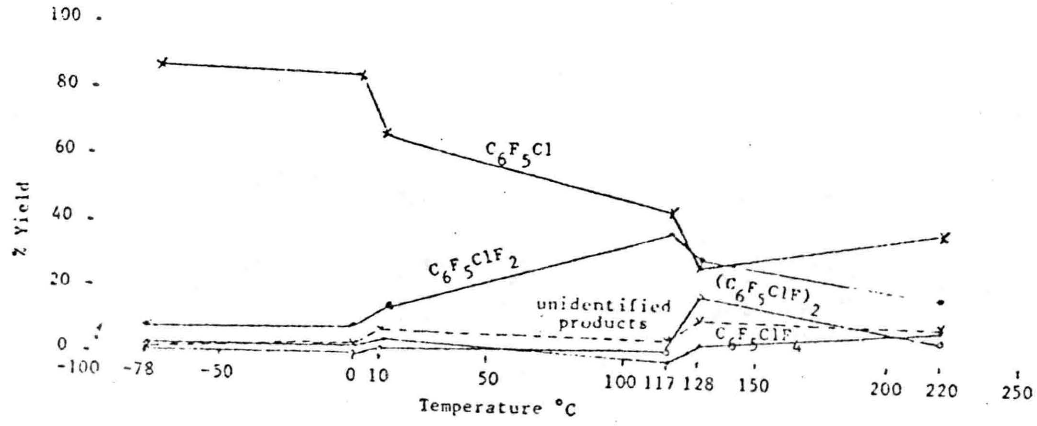
Pentafluorophenylchlorine(III) difluoride, pentafluorophenylchlorine(V) tetrafluoride, pentafluorophenylbromine(III) difluoride and pentafluorophenylbromine(V) tetrafluoride are new classes of derivatives of the interhalogen compounds, chlorine trifluoride, chlorine pentafluoride, bromine trifluoride and bromine pentafluoride, respectively. They were prepared by oxidation of chloropentafluorobenzene and bromopentafluorobenzene with fluorine, chlorine trifluoride, bromine trifluoride or bromine pentafluoride. Pentafluorobenzene was also used as a substrate. 1,2-difluoro-1,2-bis(pentafluorophenyl) dichlorane and 5-chloro-1-(difluorochloro)-2,3,4,5,6,6-hexafluoro-1,3- cyclohexadiene were prepared as by-products in the pentafluorophenylchlorine(III) difluoride synthesis. Evidence for formation of 1,2-difluoro-1,2-bis(pentafluorophenyl) dibromane was also observed. The difluorides were products of reactions between chloropentafluorobenzene, bromopentafluorobenzene or pentafluorobenzene and fluorine, chlorine trifluoride, or bromine trifluoride. The tetrafluorides were products of reactions between chloropentafluorobenzene, bromopentafluorobenzene or pentafluorobenzene and fluorine, chlorine trifluoride, bromine trifluoride or bromine pentafluoride. Safe conditions for synthesis were devised. The new difluorides and tetrafluorides were characterized by their mass spectra, infrared spectra, ^{19}F-nuclear meagnetic resonance spectra and elemental analyses. The new polyfluorides were moderately stable at room temperature and below. It was observed that a slight change in reaction procedure resulted in unexpected changes in product distribution. The first four compounds were well characterized and documented.

CHAPTER V

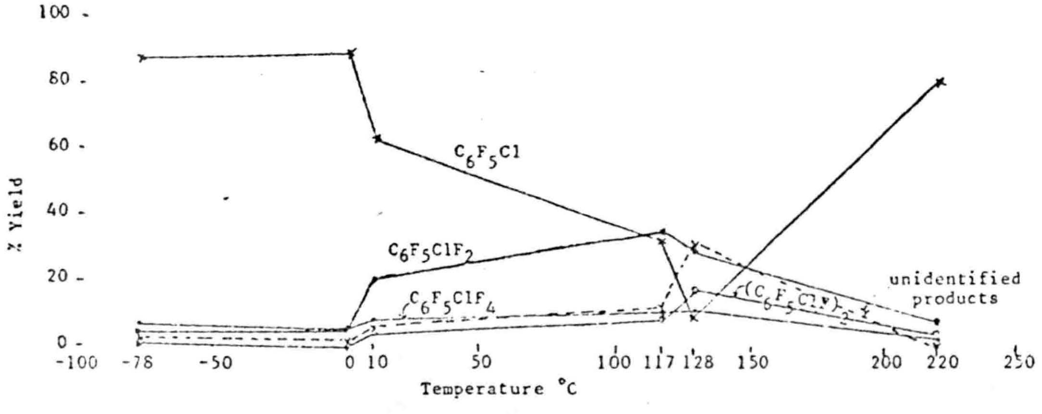
APPENDIX

Graphical Illustration of Table 1 Showing Relationship Between Percent Yield and Reaction Temperature

Graph I

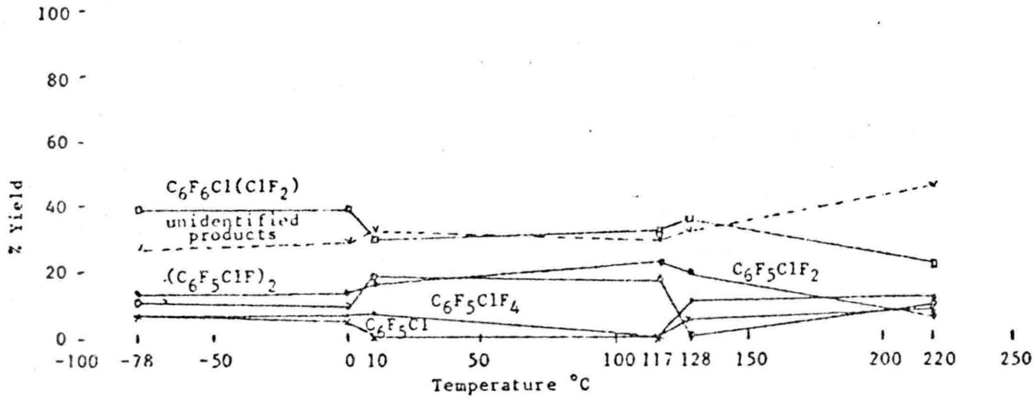


Graph II

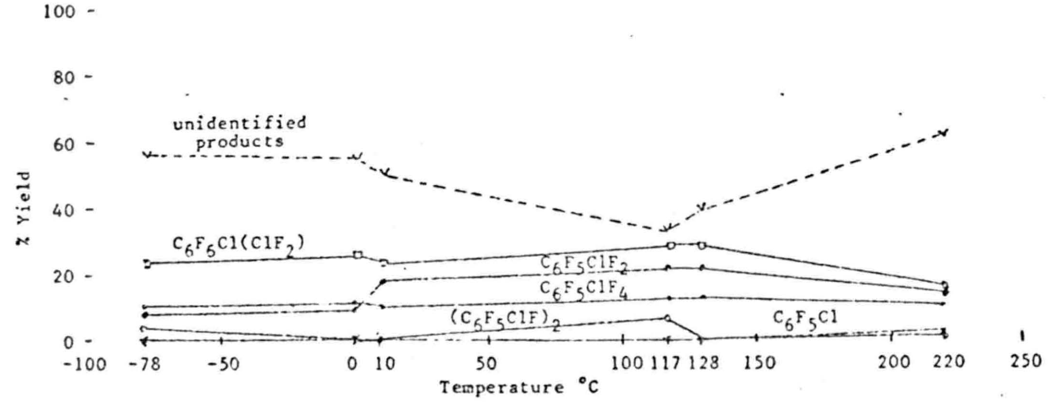


Graphical Illustration of Table 2 Showing Relationship Between Percent Yield and Reaction Temperature

Graph III

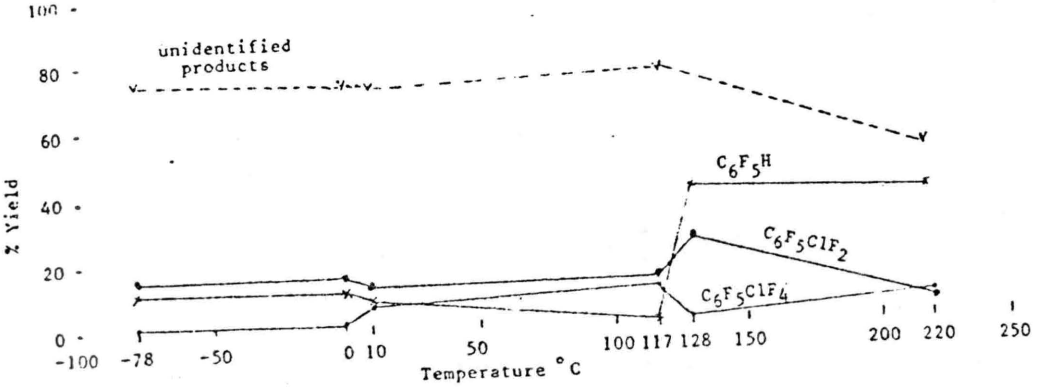


Graph IV

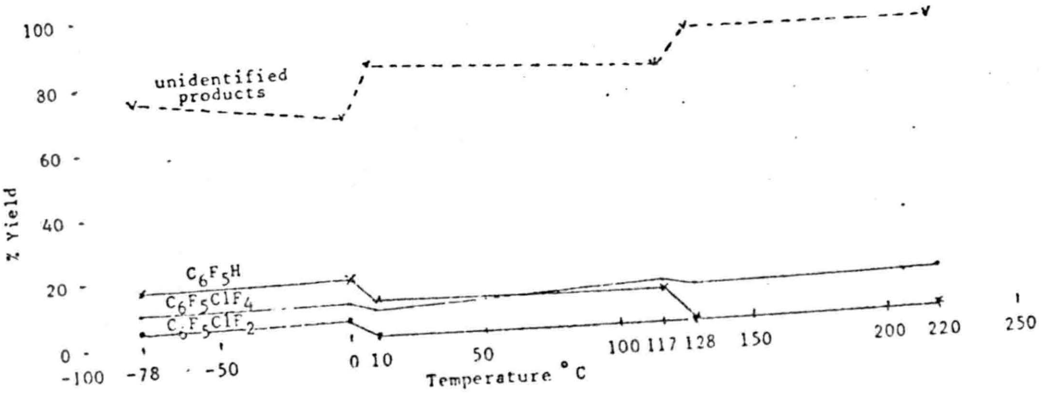


Graphical Illustration of Table 3 Showing Relationship Between Percent Yield and Reaction Temperature

Graph V

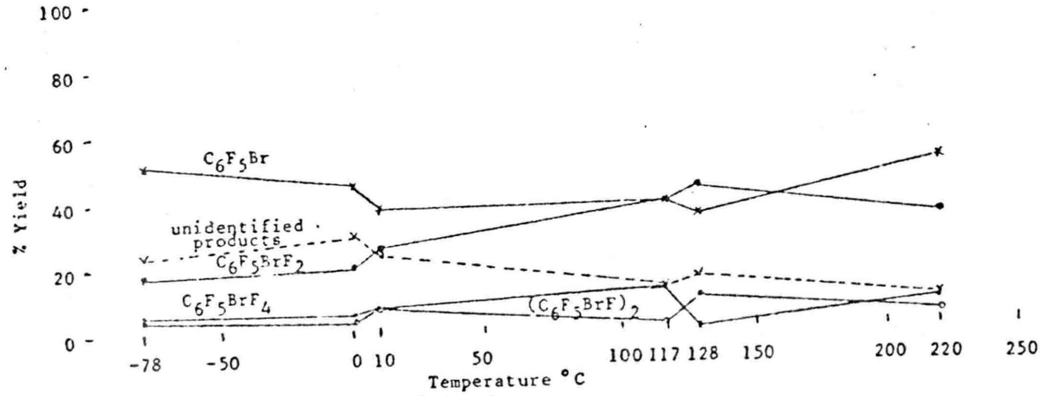


Graph VI

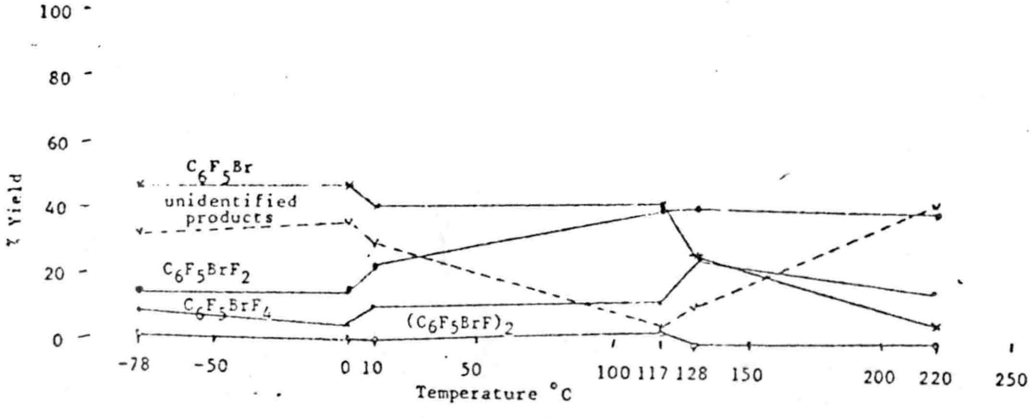


Graphical Illustration of Table 4 Showing Relationship Between Percent Yield and Reaction Temperature

Graph VII

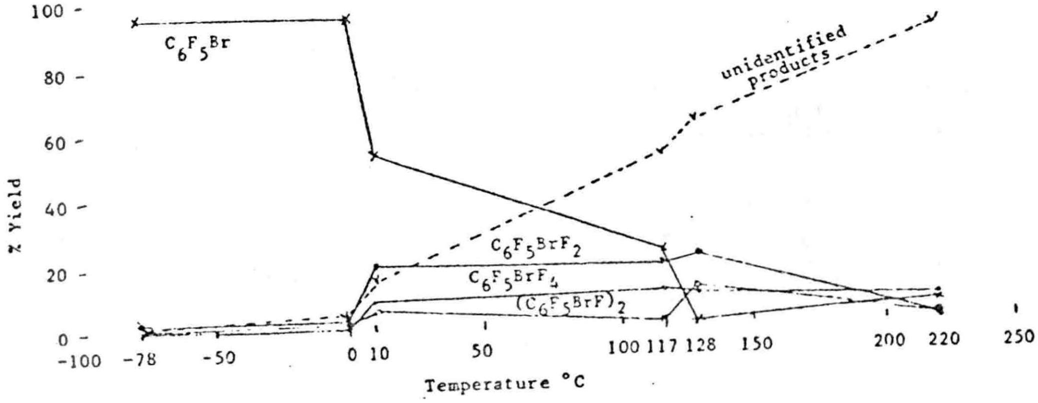


Graph VIII

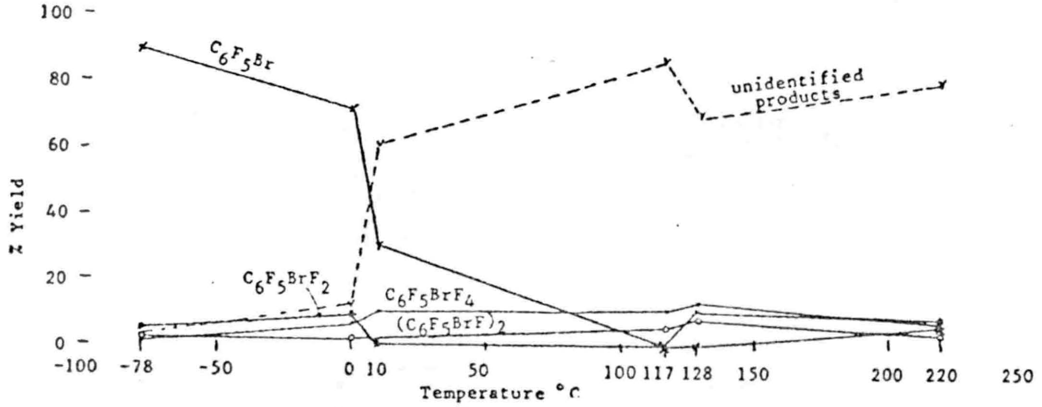


Graphical Illustration of Table 5 Showing Relationship Between Percent Yield and Reaction Temperature

Graph IX

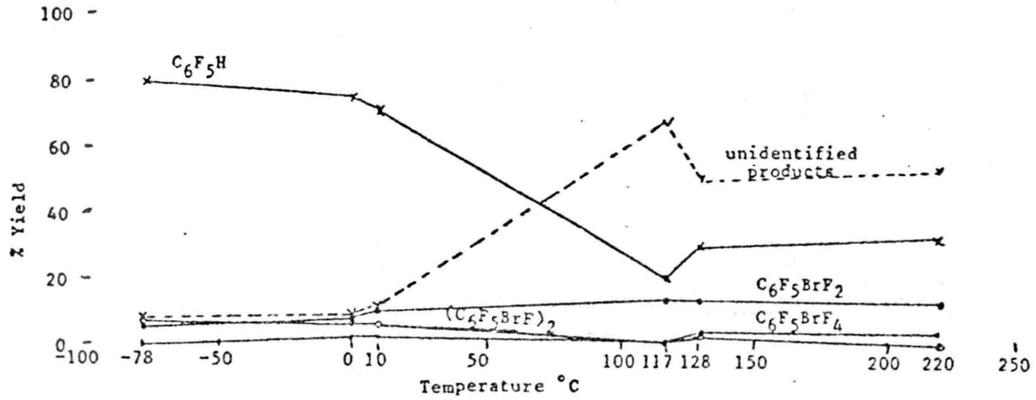


Graph X

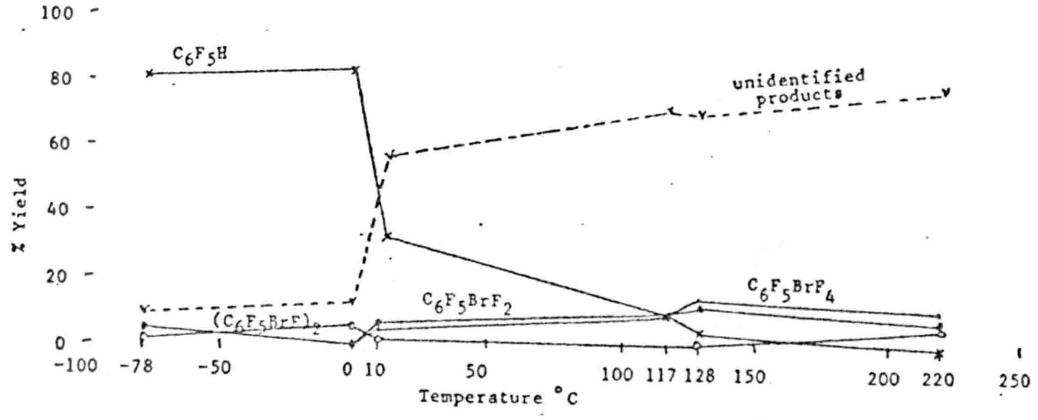


Graphical Illustration of Table 6 Showing Relationship Between Percent Yield and Reaction Temperature

Graph XI

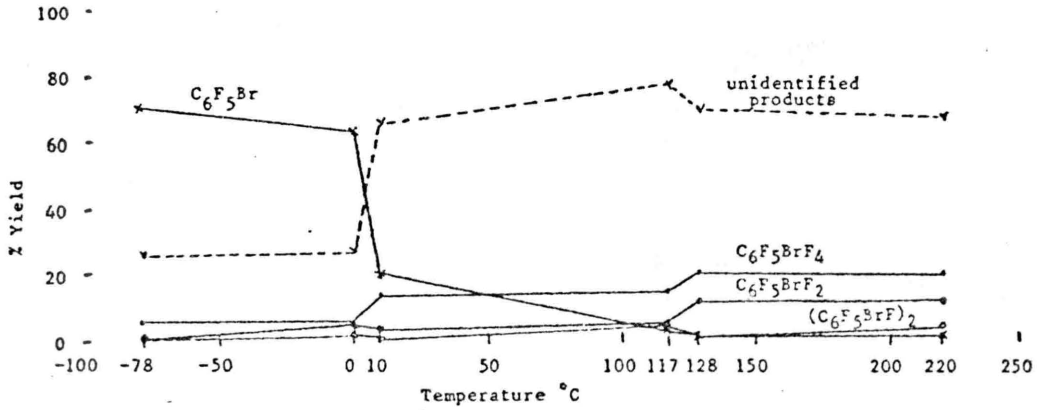


Graph XII

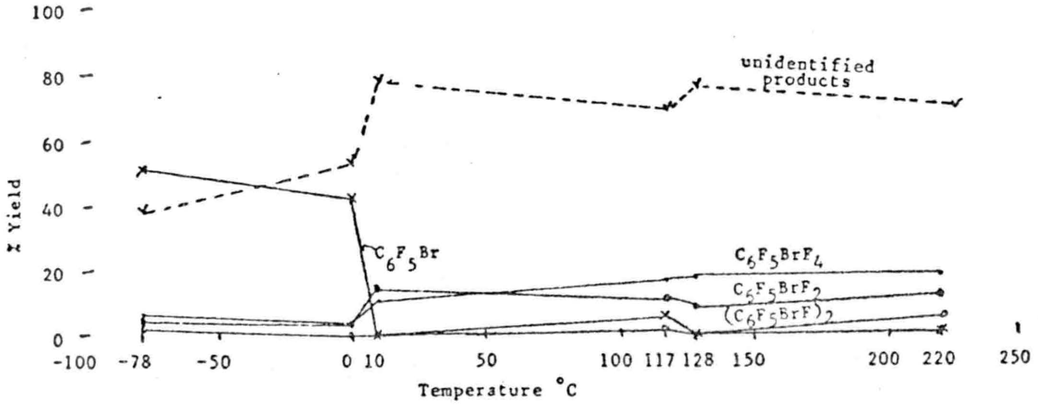


Graphical Illustration of Table 7 Showing Relationship Between Percent Yield and Reaction Temperature

Graph XIII

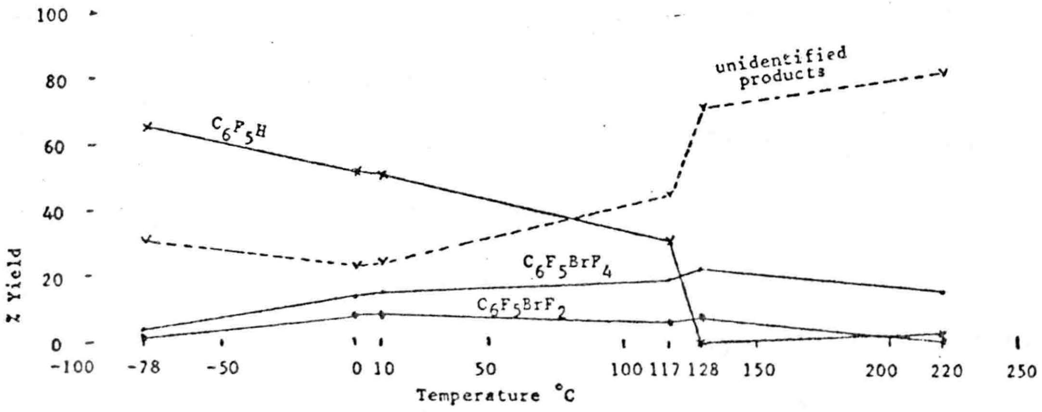


Graph XIV

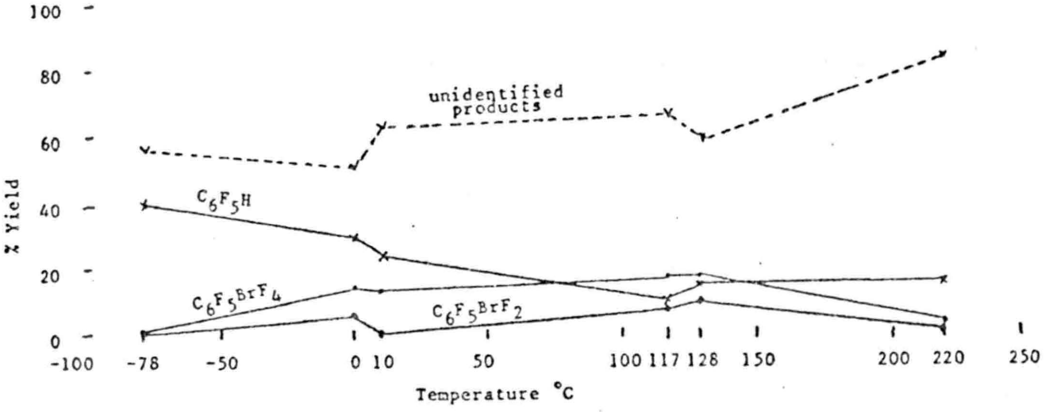


Graphical Illustration of Table 8 Showing Relationship Between Percent Yield and Reaction Temperature

Graph XV



Graph XVI



Safe Handling Procedures

Fluorine and the halogen fluorides are extremely dangerous materials and should be handled only in proper equipment. Fluorine is extremely hazardous primarily because the weak F-F bond in molecular fluorine (37 kcal/mol) (19) leads to extraordinary reactivity. Based on experience with elemental fluorine, the following major safety precautions are recommended.

Fluorine cylinders should be kept behind steel barricades and the valve operated remotely. Monel valves with Teflon packing are highly recommended. Stainless steel or Monel tubing (properly passified) is recommended for transfer of the gas. The reactor should be shielded and all lines containing fluorine under pressure should be located behind a heavy barricade. The latter precaution eliminates a potential danger in the event of rupture of pressure lines. The amount of fluorine delivered to the reaction was measured by pressure drop in a metering tank (accuracy 1-2%).

There were two potential hazards associated with the use of chlorine trifluoride. 1) It is a vigorous fluorinating agent. 2) It reacts with limited amounts of water and with many chemical trapping agents to produce chlorine oxides which are themselves very unstable materials. When uncontrolled amounts of chlorine trifluoride are inadvertently mixed with compounds containing carbon and hydrogen, an explosion almost always results, initiated by the very large heat of reaction. Safe handling procedures are largely designed for use of chlorine trifluoride in the vapor phase.

Reactions involving chlorine trifluoride were carried out in gas phase by passing it through an 1/8 inch OD Teflon tube attached to the manifold. All metal lines were passivated with chlorine trifluoride before use. The amount of chlorine trifluoride delivered to the reaction was also measured by pressure drop.

Bromine trifluoride is essentially as reactive, from the safety standpoint, as chlorine trifluoride. It does not, however, produce a series of explosive oxides comparable to the chlorine oxides. From this viewpoint, it is less hazardous than chlorine trifluoride. On the other hand, it also is a powerful fluorinating agent with a much lower volatility than chlorine trifluoride. Its greatest hazard arises, therefore, from its being inadvertently condensed, thus being retained where some later operation may introduce an easily oxidized material. Liquid bromine trifluoride will explode if accidentally dropped into carbon dioxide-acetone mixtures. Unsuccessful attempts had been made to handle this compound as a gas.

Bromine trifluoride was handled as a liquid; dispensed under high pressure (20 lb.) from its storage cylinder which was clamped in an upside down position and then passed through a Monel valve and an 1/8 inch OD Teflon tube into previously weighed Teflon bottle through a dry funnel. All reactions were performed under a hood. At all times moisture was rigorously excluded.

Mass spectroscopy, infrared spectroscopy and nuclear magnetic spectroscopy are considered radiation chemistry as defined for the doctoral program at Texas Woman's University.

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