Journal of Fluorine Chemistry, *23* (1983) 67–86

Received: November 8, 1982; accepted April 6, 1983

AROMATIC FLUORODERIVATIVES. XCVI. REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS WITH SALTS OF THE FLUOROCHLORONIUM AND FLUOROBROMONIUM CATIONS

V.V.BARDIN, G.G.FURIN and G.G.YAKOBSON *

Institute of Organic Chemistry, Novosibirsk, 630090 (USSR)

SUMMARY

Polyfluorinated derivatives of benzene, naphthalene and pyridine react with salts of the difluorochloronium ClF_2^+, difluorobromonium BrF_2^+ and tetrafluorobromonium BrF_4^+ cations to give fluorinated derivatives of 1,4-cyclohexadiene and 1-aza-1,3-cyclohexadiene respectively.In the absence of fluorine anion acceptors, ClF_3, BrF_3 and BrF_5 are less reactive in these reactions than salts of the $HalF_n^+$ cations.

INTRODUCTION

For the synthesis of polyfluoroaromatic compounds containing various substituents, reactions of the Friedel-Crafts type are widely used.They proceed most readily in the presence of SbF_5 as a catalyst [1].At the same time, reactions of polyfluoroaromatic compounds with electrophilic fluorinating agents with strong oxidative ability have not been systematically studied until recently. There are only a few examples of such reactions.Tatlow and his co-workers have shown that BrF_3 reacts with polyfluorinated derivatives of benzene [2] and naphthalene [3] in the presence of bromine to give the corresponding 1,4-cyclohexadienes and the products of their bromofluorination.We have shown that hexafluorobenzene and pentafluorobenzene do not react with IF_5 at 120°C, but that pentafluorobenzene reacts with IF_4^+ at 20°C to yield the aromatic derivatives of pentavalent iodine [4].

0022-1139/83/$3.00

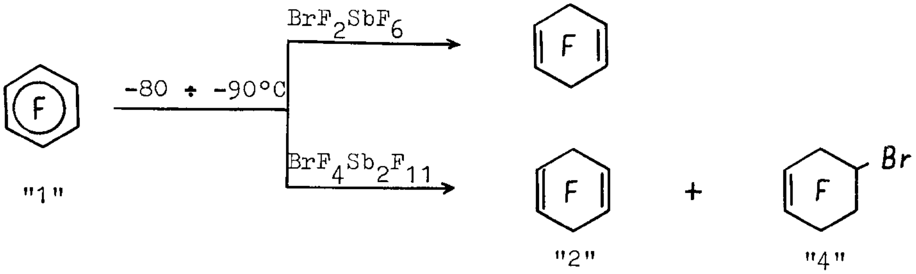
The salts of the fluoroxenonium cation XeF^+ possess strong fluorinating ability. Their reactions with polyfluorinated derivatives of benzene and naphthalene afford 1,4-cyclohexadienes [5]. XeF_2 reacts in a similar way in the presence of HF [5] and BF_3 [6]

This work deals with the reactions of polyfluoroaromatic compounds with electrophilic fluorooxidants of the type $Hal_n^+MF_m^-$ (Hal = Cl, Br; MF_{m-1} = BF_3, SbF_5). The structures of these adducts as solids and non-aqueous solutions have been thoroughly studied [7]. This allows us to judge about the structure of the actual electrophilic reagents, which is not possible for the reactions involving other electrophiles.

REACTIONS WITH SALTS OF THE FLUOROBROMONIUM CATIONS, BrF_2^+ AND BrF_4^+

Hexafluorobenzene "1" reacts with the salts BrF_2BF_4 and BrF_2SbF_6 in SO_2FCl solution at -80 ÷ -90°C to yield perfluoro-1,4-cyclohexadiene "2". Hydrolysis of the products of the reaction of hexafluorobenzene with BrF_2BF_4 gives, along with diene "2", perfluoro-2,5-cyclohexadien-1-one "3" (Table 1).

Interaction of hexafluorobenzene with the salt $BrF_4Sb_2F_{11}$ leads to two main products, one of which is perfluoro-1,4-cyclohexadiene. The second product of this reaction is 4-bromononafluorocyclohexene "4" which is apparently formed as a result of bromofluorination of diene "2" [2].

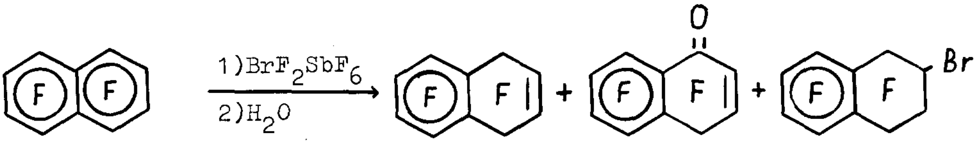


Reactions of salts of the di- and tetrafluorobromonium cations with other polyfluorinated derivatives of benzene also involve regiospecific addition of two fluorine atoms producing polyfluorinated 1,4-cyclohexadienes.It should be noted that the reactivity of polyfluorobenzenes is decreased in these reactions with an increase of their ionization potentials.For example, octafluorotoluene "5" (IP = 10.4 eV [2]) reacts with BrF_2BF_4 already at -80 ÷ -90°C to give perfluoro-1-methyl-1,4-cyclohexa-diene "6" and 4(5)-bromoundecafluoro-1-methylcyclohexene "7". Under these conditions nitropentafluorobenzene "8" (IP = 10.6 eV) is inert towards BrF_2BF_4 and only at 15-20°C it is converted to 1-nitroheptafluoro-1,4-cyclohexadiene "9" and 4(5)-bromo-1-nitro-octafluorocyclohexene "10".

Correlation between IP and the reactivity of polyfluorobenzenes in the reactions with BrF_3 - Br_2 was observed earlier by Tatlow and his co-workers [2,3].

Nitropentafluorobenzene reacts in a similar way with BrF_4BF_4, but this reaction occurs already at -30÷-40°C (Table 1).

At -50÷-60°C the salts of the di- and tetrafluorobromonium cations reacts easily with octafluoronaphthalene "11".Hydrolysis of the reaction mixture leads to perfluoro-1,4-dihydronaphthalene "12", 1-Oxooctafluoro-1,4-dihydronaphthalene "13" and 2-bromoundecafluorotetralin "14".When the relative amount of the BrF_2BF_4 salt is increased from 0.5 to 1 mole per mole of octafluoronaphthalene, the yield of compound "14" is increased from 3 to 46%.



"11" "12" "13" "14"

Pentafluoropyridine "15" and 3-chlorotetrafluoropyridine "16" proved to be more stable in reactions with salts of the difluorobromonium cation BrF_2^+ than polyfluoroderivatives of benzene and naphthalene.They reacted only at temperatures above -10°C.By contrast with benzene and naphthalene derivatives, pyridines "15" and "16" are fluorinated to give conjugated 1-azaheptafluoro-1,3-cyclohexadiene "17" and 1-aza-3-chlorohexafluoro-1,3-cyclohexa-diene "18" respectively (Table 1).

TABLE 1

Reactions of Polyfluoroaromatic Compounds with Salts of the Di- and Tetrafluorobromonium Cations, BrF_2MF_m and BrF_4MF_m

Compound, g	Reagent, g	Solvent, ml	Temperature, °C	Yield, g	Conversion of the starting compound, %	Yields of the reaction products, %[a]
Pentafluorobenzene ("19"), 11.0	BF_3, BrF_3, 4.3	SO_2FCl, 20	-80÷-90	22.2	70	1-H-C_6F_7("20"),10 C_6F_5Br("22"), 47 1-Br-C_6F_7("21"),10
Pentafluorobenzene ("19"), 10.9	28% SbF_5 in BrF_3, 4.5	SO_2FCl, 40	-80÷-90	19.5	52	1-H-C_6F_7("20"),9 3-H-C_6F_5O("23"),13 C_6F_5Br("22"),57
Pentafluorobenzene ("19"), 2.5	BF_3, BrF_5, 1.3	SO_2FCl, 40	-80÷-90	4.6	34	3-H-C_6F_5O("23"),26 C_6F_5Br("22"),46 1-Br-C_6F_7("21"),10

Pentafluorobenzene ("19"), 4.0	SbF_5, 1.1 BrF_5, 2.1	SO_2FCl, 40	-80÷-90	7.3	78	1-H-C_6F_7("20"),26 3-H-C_6F_5O("23"),1 C_6F_5Br("22"),35 1-Br-C_6F_7("21"),17
4-H-Heptafluorotoluene ("24"), 4.0	BF_3, BrF_3, 1.2	SO_2FCl, 40	-80÷-90	5.5	71	1-$CF_3C_6HF_6$("25"),45 1-$CF_3C_6HBrF_7$("27"),4 4-$BrC_6F_4CF_3$("26"), 8
4-H-Heptafluorotoluene ("24"), 6.0	BF_3, BrF_3, 3.5[b]	SO_2FCl, 40	-80÷-90	9.5	89	1-$CF_3C_6HF_6$("25"),11 1-$CF_3C_6HBrF_7$("27"),64 4-$BrC_6F_4CF_3$("26"),1
4-H-Heptafluorotoluene ("24"), 4.2	23% SbF_5 in BrF_5, 2.2	SO_2FCl, 40	-80÷-90	7.1	27	1-$CF_3C_6HF_6$("25"),33 1-$CF_3C_6HBrF_7$("27"),11 4-$BrC_6F_4CF_3$("26"),33
Hexafluorobenzene ("1"), 6.8	BF_3, BrF_3, 2.5	SO_2FCl, 40	-80÷-90	5.0	73	1,4-C_6F_8("2"),34 2,5-C_6F_6O("3"),4

(continued overleaf)

TABLE 1 (cont.)

Compound, g	Reagent, g	Solvent, ml	Temperature, °C	Yield, g	Conversion of the starting compound, %	Yields of the reaction products, %[a]
Hexafluorobenzene ("1"), 16.2	28% SbF_5 in BrF_3, 8.3	SO_2FCl, 40	-80÷-90	19.6	58	1,4-C_6F_8("2"),77
Hexafluorobenzene ("1"), 6.2	23% SbF_5 in BrF_5, 4.2	SO_2FCl, 40	-80÷-90	8.8	100	1,4-C_6F_8("2"),44 4-BrC_6F_9("4"),40
Octafluoronaphthalene ("11"), 5.9	28% SbF_5 in BrF_3, 2.1	SO_2FCl, 40	-50÷-60	5.9	75	1,4-$C_{10}F_{10}$("12"),50 1,4-$C_{10}F_8O$("13"),9 1,2-$C_{10}F_{10}$,4[c] 2-$BrC_{10}F_{11}$("14"),3
Octafluoronaphthalene ("11"), 9.3	28% SbF_5 in BrF_3, 6.5[b]	SO_2FCl, 60	-50÷-60	14.2	96	1,4-$C_{10}F_{10}$("12"),23 1,4-$C_{10}F_8O$("13"),7 2-$BrC_{10}F_{11}$("14"),46
Octafluoronaphthalene ("11"), 4.6	BF_3, BrF_5, 1.5	SO_2FCl, 50	-50÷-60	22.5	37	1,4-$C_{10}F_{10}$("12"),34 1,4-$C_{10}F_8O$("13"),38 1,2-$C_{10}F_{10}$,4[c]

Octafluoro-toluene ("5"), 13.0	BF_3, BrF_3, 3.5	$C_2Cl_2F_4$, 60	-80÷-90	16.5	16	1-$CF_3C_6F_7$("6"),34 1-$CF_3C_6BrF_8$("7"),40
Nitropenta-fluorobenzene ("8"), 13.2	BF_3, BrF_3, 6.5	Perfluoro-heptane, 30	15÷20	61.0	72	1-$NO_2C_6F_7$("9"),44 1-$NO_2C_6BrF_8$("10"),20
Nitropenta-fluorobenzene ("8"), 5.2	BF_3, BrF_5, 2.2	SO_2FCl, 40	-30÷-40	8.4	10	1-$NO_2C_6F_7$("9"),40 1-$NO_2C_6BrF_8$("10"),8
Pentafluoropy-ridine ("15"), 7.3	BF_3, BrF_3, 3.3	45 [d]	15÷25	16.6 [e]	24	1,3-C_5F_7N("17"),61
3-Chlorotetra-fluoropyridine ("16"), 27.0	BF_3, BrF_3, 9.9	$C_2Cl_3F_3$, 25	-3÷5	63.5	27	3-ClC_5F_6N("18"),73

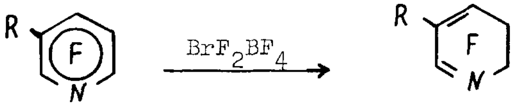
[a] Yield of products to converted substrate.

[b] The ratio of substrate to reagent = 1 : 1.

[c] Perfluoro-1,2-dihydronaphthalene [18].

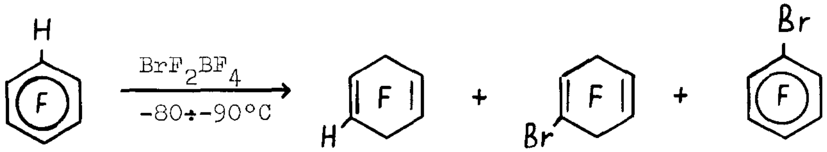
[d] Perfluorodibutyl ether as a solvent.

[e] Fraction with b.p. below 96°C.The still residue (66 g) contained 92% of the solvent and 5% of pentafluoropyridine.



R=F "15" "17"
R=Cl "16" "18"

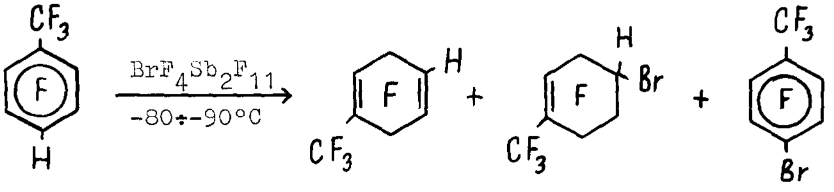
Reactions of the electrophilic fluorooxidants BrF_nMF_m with partly fluorinated aromatic compounds are of particular interest. By analogy with the reaction of C_6F_5H with salts of the fluoroiodonium cation IF_4^+ [4] that gave the aromatic derivatives of pentavalent iodine, this reaction could also be expected to form the corresponding compounds of polyvalent bromine (cf. [8]).But it appeared that pentafluorobenzene "19" reacts with BrF_2BF_4, BrF_2SbF_6, BrF_4BF_4 and $BrF_4Sb_2F_{11}$ to give 1-H-heptafluoro-1,4-cyclohexadiene "20", 1-bromoheptafluoro-1,4-cyclohexadiene "21" and bromopentafluorobenzene "22".In some cases, the reaction products contain also 3-H-pentafluoro-2,5-cyclohexadien-1-one "23", after hydrolysis (Table 1).



"19" "20" "21" "22"

The formation of 1-H-heptafluoro-1,4-cyclohexadiene is specific to this reaction, unlike the reaction of pentafluorobenzene with BrF_3 - Br_2 which has not been observed to form hydrogen-containing products [2].This may result from the greater reactivity of the BrF_2^+ cation in SO_2FCl as compared to the reactivity of the fluorooxidant BrF_3 - Br_2 in fluorocarbon solvents.

The major product in the reaction of 4-H-heptafluorotoluene "24" with BrF_2BF_4 at -80÷-90°C is 4-H-decafluoro-1-methyl-1,4-cycle hexadiene "25".In 4-H-heptafluorotoluene, hydrogen is replaced by bromine to a smaller extent than in pentafluorobenzene, so, apart from 4-bromoheptafluorotoluene "26", 4-H-4-bromononafluoro-1-methylcyclohexene "27" is formed.If 4-H-heptafluorotoluene is reacted with an equimolar amount of BrF_2BF_4, cyclohexene "27" becomes the major product, though the yield of bromotoluene "26" remains small (~1%). Interaction of 4-H-heptafluorotoluene with $BrF_4Sb_2F_{11}$ at -80÷-90°C gives the same products as the reaction with BrF_2BF_4, but the yield of bromotoluene is increased up to 33% (compare also the reaction of $BrF_4Sb_2F_{11}$ with benzene "1")(Table 1).



"24" "25" "27" "26"

It should be noted that no aromatic compounds of polyvalent bromine were formed in these reactions.

REACTIONS WITH SALTS OF THE DIFLUOROCHLORONIUM CATION, ClF_2^+

Interaction of polyfluoroaromatic compounds with the tetrafluoroborate or hexafluoroantimonate salts of the difluorochloronium cation, ClF_2^+, generally proceeds in a similar way as the reactions with salts of the fluorobromonium cations. These reactions involve mainly fluorination of polyfluoroaromatic compounds.

Pentafluorobenzene reacts with ClF_2BF_4 or ClF_2SbF_6 at -80÷-90°C to form 1-H-heptafluoro-1,4-cyclohexadiene, 1-chloroheptafluoro-1,4-cyclohexadiene "28" and chloropentafluorobenzene "29". Apart from these, the reaction products may contain 3-H-pentafluoro-2,5-cyclohexadien-1-one (Table 2).

4-H-Heptafluorotoluene reacts at -80÷-90°C with the salts of the difluorochloronium cation to form polyfluorinated 1-methylcyclohexadiene "25", 4-H-4-chlorodecafluoro-1-methylcyclohexene "30" and 4-chloroheptafluorotoluene "31". As in the case of the salts of the fluorobromonium cations, the formation of the aromatic derivatives of polyvalent chlorine was not observed.

TABLE 2

Reactions of Polyfluoroaromatic Compounds with Salts of the Difluorochloronium Cation, ClF_2MF_m

Compound, g	Reagent, g	Solvent, ml	Temperature, °C	Yield, g	Conversion of the starting compound, %	Yields of the reaction products, % [a]
Pentafluorobenzene ("19"), 6.6	BF_3, ClF_3, 1.8	SO_2FCl, 50	-80÷-90	8.6	90	1-H-C_6F_7("20"),19 C_6F_5Cl("29"),41 1-ClC_6F_7("28"),6
Pentafluorobenzene("19"), 6.6	ClF_2SbF_6, 3.9	SO_2FCl, 40	-80÷-90	8.9	88	1-H-C_6F_7("20"),6 C_6F_5Cl("29"),37 1-ClC_6F_7("28"),4 3-H-C_6F_5O("23"),13
4-H-Heptafluorotoluene ("24"), 8.6	BF_3, ClF_3, 1.8	SO_2FCl, 50	-80÷-90	18.2	24	1-$CF_3C_6HF_6$("25"),23 1-$CF_3C_6HClF_7$("30"),39 4-$ClC_6F_4CF_3$("31"),16

4-H-Hepta-fluorotoluene ("24"), 6.0	ClF_2SbF_6, 8.8 [b]	SO_2FCl, 20 HF, 30	$-70 \div -80$	8.2	96	$1-CF_3C_6HF_6$("25"),28 $1-CF_3C_6HClF_7$("30"),27 $4-ClC_6F_4CF_3$("31"),12
Hexafluoro-benzene ("1"), 7.3	BF_3, ClF_3, 1.8	SO_2FCl, 40 [c]	$-70 \div -80$	8.2	75	$1,4-C_6F_8$("2"),12 $2,5-C_6F_6O$("3"),25 $3-ClC_6F_7$("32"),13
Hexafluoro-benzene ("1"), 6.3	ClF_2SbF_6, 5.2	SO_2FCl, 30 HF, 30	$-70 \div -80$	10.1	55	$1,4-C_6F_8$("2"),26 $2,5-C_6F_6O$("3"),5 $3-ClC_6F_7$("32"),49
Octafluoro-naphthalene ("11"), 10.6	ClF_2SbF_6, 6.5 [b]	SO_2FCl, 50	$-50 \div -60$	18.4 [d]	95	$1,4-C_{10}F_{10}$("12"),49 $1-ClC_{10}F_9$ ("33"),17 $1,2-C_{10}F_{10}$ [e] , 2

[a] Yield of products to converted substrate.

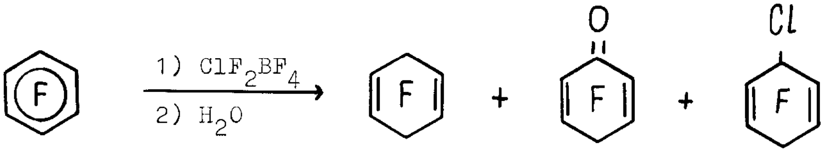
[b] The ratio of substrate to reagent is equal 1 : 1 (mole).

[c] After keeping, the reaction mixture was diluted with 40 ml of HF and treated as usual.

[d] Extracted with dichloromethane.

[e] Perfluoro-1,2-dihydronaphthalene [18].

Hydrolysis of the reaction mixture of hexafluorobenzene or octafluoronaphthalene and ClF_2BF_4 or ClF_2SbF_6 quite unexpectedly gave, apart from the derivatives of cyclohexadiene "2", "3" and dihydronaphthalene "12", "13", the products of chlorofluorination of the starting compounds: 3-chloroheptafluoro-1,4-cyclohexadiene "32" and 1-chlorononafluoro-1,4-dihydronaphthalene "33", respectively (Table 2).



"1" "2" "3" "32"

Neither 4-chlorononafluorocyclohexene nor 2-chloroundecafluorotetralin were observed to be formed in these reactions. Suggested pathways of these reactions giving chlorine-containing dihydroaromatic compounds "32" and "33" and the reasons of difference between chloro- and bromofluorination mechanisms will be discussed in a later paper.

The reactivities of chlorine and bromine trifluorides and bromine pentafluoride turned to be essentially lower in the absence of Lewis acids than those of the corresponding fluorohalogenonium cations. Thus, octafluorotoluene and 4-H-heptafluorotoluene do not react with BrF_3 and BrF_5 at -80÷-90°C, while pentafluoropyridine and 3-chlorotetrafluoropyridine do not react with these compounds at 0÷20°C, though in these conditions they react readily with BrF_nMF_m salts.

The case is similar for the reactions of hexafluorobenzene, pentafluorobenzene and 4-H-heptafluorotoluene with chlorine trifluoride. Octafluoronaphthalene is less stable in the reactions with these halogen fluorides and reacts with BrF_3, BrF_5 and ClF_3 at -50÷-60°C to form perfluoro-1,4-dihydronaphthalene.

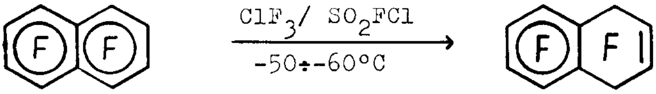


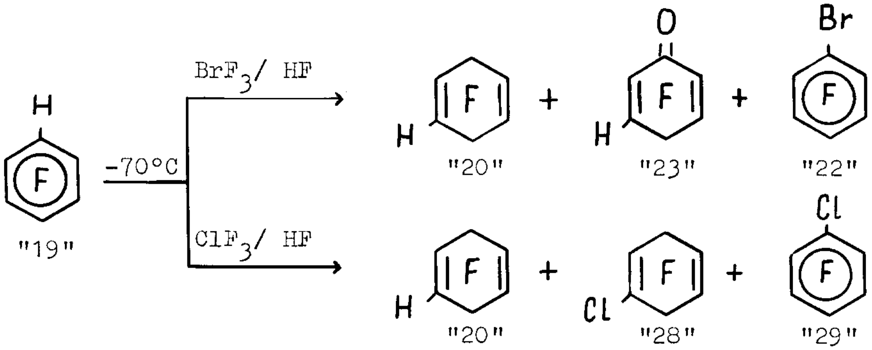
TABLE 3

Reactions of Polyfluoroaromatic Compounds with Chlorine and Bromine Trifluorides in the Presence of Hydrogen Fluoride

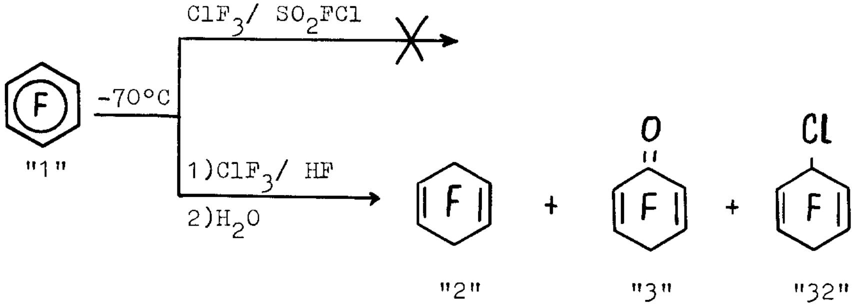
Compound, g	Reagent, g	Solvent, ml	Temperature, °C	Yield, g	Conversion of the substrate, %	Yields of the reaction products, % *
Pentafluorobenzene ("19"), 7.6	BrF_3, 3.1	SO_2FCl ,10 HF ,60	-80÷-90	13.6	59	1-H-C_6F_7("20"),5 3-H-C_6F_5O("23"),14 C_6F_5Br("22"),56
Pentafluorobenzene ("19"), 6.6	ClF_3, 1.8	HF, 40	-70÷-80	6.9	77	1-H-C_6F_7("20"),14 C_6F_5Cl("29"),39 1-Cl-C_6F_7("28"),17
Hexafluorobenzene ("1"), 7.3	ClF_3, 1.8	HF, 40	-70÷-80	8.0	18	1,4-C_6F_8("2"),5 2,5-C_6F_6O("3"),23 3-Cl-C_6F_7("32"),48

* Yield of products to converted substrate.

At the same time, in the presence of even as weak an acceptor of fluorine anions as HF, the reactivity of these fluorides is considerably increased. Thus, in the presence of HF, pentafluorobenzene reacts at -70÷-80°C with bromine and chlorine trifluorides to yield compounds "20", "22", "23" and "20", "28", "29", respectively (Table 3).



In these conditions, hexafluorobenzene is converted to polyfluorinated derivatives of cyclohexadiene "2", "3" and "32", though in the absence of HF the reaction does not take place.



Possibly, the increased reactivity of these halogen fluorides in the presence of HF as compared to that in the absence of HF is caused by the increased concentration of $HalF_n^+$ cations, resulting from the interaction of these fluorides with hydrogen fluoride, which was reported in [9] to proceed in the following way:

$$BrF_3 + HF \rightleftharpoons BrF_2^+ + HF_2^-$$

The mechanism of transformation of polyfluoroaromatic compounds to cyclohexadiene derivatives by regiospecific addition of two fluorine atoms requires special investigation.Nevertheless, our ESR studies showed the formation of a radical cation of octafluoronaphthalene with chlorine and bromine trifluorides, and bromine pentafluoride in SO_2FCl at -50÷-70°C.It is possible that these species are key intermediates in the reactions of polyfluoroaromatic compounds with adducts Hal_nMF_m (cf.[2,3]).

The structures of new compounds "9", "10", "18", "27" and "30" were revealed from the data of elemental analysis, IR, ^1H and ^{19}F NMR spectra.

EXPERIMENTAL

^1H and ^{19}F NMR spectra were measured on a Varian A 56/60 A instrument at 60 and 56.4 MHz, respectively (HMS and C_6F_6 as internal standards).ESR spectra were measured on an EPR-3 instrument.GLC analysis was carried out on an LHM-7A instrument (15% SE-30, SKTFT-50 or SKTFV-803 on chromosorb W, He flow rate 3.6 l h^{-1}).New compounds were isolated by preparative GLC in conditions of analytical determination.Infrared spectra were measured on an UR-20 and a Specord 75 IR instruments (5% solutions in CCl_4).The elemental analysis of new compounds was conducted according to high-resolution mass-spectra, measured on an MS-902 instrument.

Reactions of polyfluoroaromatic compounds with halogen fluorides and their adducts with SbF_5 or BF_3 were conducted in a 100 ml Kel-F reactor, kept cooled, equipped with a copper or Teflon stirrer and a Teflon coated thermocouple.Charges and yields of the reaction products are given in Tables 1,2 and 3.

Compounds "3","20","21","23" [11] , "12","13" [12], "28" [13] were found to be identical with the samples obtained earlier at our laboratory.Compounds "4","6","7" [2], "14" [3], "17" [14] , "25" [15], "32" [16] , "33" [17] were identified by GLC and NMR with the authentic samples.

Reactions of polyfluoroaromatic compounds with:

A. BrF_2BF_4 and BrF_4BF_4

Boron trifluoride was passed through a stirred solution of the polyfluoroaromatic compound at the appropriate temperature and then bromine trifluoride (pentafluoride) was added dropwise at a rate that caused no temperature increase.After all the fluoride had been added, the reaction mixture was stirred for additional 15-20 min, the BF_3 flow was cut off and the products were poured on to ice cooled with liquid nitrogen.The organic layer was separated, washed with water and dried over $MgSO_4$.The content of each reaction product was determined by GLC.

After keeping them for a while, the products of the reactions of nitropentafluorobenzene, pentafluoropyridine and 3-chlorotetrafluoropyridine were diluted with water, washed with 10% aq. $K_2S_2O_5$, 10% aq. K_2CO_3 and with water, and dried over $MgSO_4$.

B. BrF_2SbF_6 and $BrF_4Sb_2F_{11}$

A solution of SbF_5 in bromine trifluoride (pentafluoride) was added slowly to a stirred solution of the polyfluoroaromatic compound at the appropriate temperature.The mixture was stirred for 20-30 min and then treated as above.

C. ClF_2BF_4

Chlorine trifluoride (1 ml) was condensed in a Kel-F graduated test tube.Boron trifluoride was passed through a cooled solution of polyfluoroaromatic compound while it was being stirred, then ClF_3 vapour was passed in a stream of dry argon at a rate which caused no temperature increase.The solution was stirred for additional 15-25 min, then the BF_3 flow was cut off and the solution treated as above.

D. ClF_2SbF_6

ClF_2SbF_6 was added slowly to a cooled solution of the polyfluoroaromatic compound while it was being stirred and kept at the appropriate temperature.The solution was stirred for an additional 20-30 min and treated as above.

4-Bromo-4-H-decafluoro-1-methylcyclohexene "27", (n.c.)

Infrared spectrum: 2890 (C - H), 1720 ($FC = CCF_3$) cm^{-1}. ^1H NMR spectrum, δ : 4.43 (m). ^{19}F NMR spectrum, δ : 104.3 (3F - α), 63.7(1F - 6A), 59.2,58.5(1F - 3, 1F - 3'), 54.9(1F - 2), 41.5 (2F - 5), 40.9 (1F - 6B); J_{FF}^{AB} = 287 Hz, J (F_6^A - CF_3)= 22 Hz, J (F_2 - CF_3)= 12 Hz. M 353.9122 (^{79}Br). C_7HBrF_{10}. B.p. 129-130°C.

1-Nitroheptafluoro-1,4-cyclohexadiene "9", (n.c.)

Infrared spectrum: 1778 (FC = CF), 1722 ($FC = CNO_2$), 1568 (NO_2) cm^{-1}. ^{19}F NMR spectrum, δ : 57.1 (2F - 6), 50.9(2F - 3), 42.2(1F - 2), 10.5(1F - 4), 6.3(1F - 5); J (F_2 - F_4)= 3 Hz, J (F_3 - F_2)=J (F_3 - F_4)= 21 Hz, J (F_4 - F_5)= 5 Hz, J (F_2 - F_6)=J (F_3 - F_5)=J (F_4 - F_6)= 10 Hz, J (F_5 - F_6)= 20 Hz. M 250.9842. $C_6F_7NO_2$.

4(5)-Bromo-1-nitrooctafluorocyclohexene "10", (n.c.)

Infrared spectrum: 1717 ($FC = CNO_2$), 1572 (NO_2) cm^{-1}. M 348.8970 (^{79}Br). $C_6BrF_8NO_2$. ^{19}F NMR spectrum is complex, it indicates the presence of two components with nearly equal content of each.

1-Aza-3-chlorohexafluoro-1,3-cyclohexadiene "18", (n.c.)

Infrared spectrum: 1751, 1715, 1671 cm^{-1}. ^{19}F NMR spectrum, δ : 124.6(1F - 2), 61.3(2F - 6), 50.0 (1F - 4), 37.6 (2F - 5); J (F_2 - F_4)= 28 Hz, J (F_4 - F_5)= 19 Hz, J (F_5 - F_6)= 6 Hz, J (F_4 - F_6)= 4 Hz. M 222.9617. C_5ClF_6N.

4-Chloro-4-H-decafluoro-1-methylcyclohexene "30", (n.c.)

Infrared spectrum: 2972 (C - H), 1723 (FC = CCF_3) cm^{-1}. ^1H NMR spectrum, δ : 4.50 (m). ^{19}F NMR spectrum, δ : 103.5 (3F - α), 62.0(1F - 6A), 54.6(2F - 3), 54.1(1F - 2), 41.0(1F - 6B), 37.2(2F - 5); J_{FF}^{AB} = 287 Hz.

M 310 (^{35}Cl) (mass-spectrum). Found, %: C 27.1, H 0.6, Cl 12.0, F 60.5. C_7HClF_{10}. Requires, %: C 27.1, H 0.3, Cl 11.4, F 61.2.

E. BrF_3 and BrF_5

Bromine trifluoride (2.4 g) was added dropwise to a stirred solution of 9.5 g of octafluoronaphthalene in 40 ml of SO_2FCl at -50÷-60°C.The solution was stirred for 20 min, hydrolysed, extracted with dichloromethane, washed with water and dried over $MgSO_4$.The solvent was distilled off to give 11.0 g of product containing 45% of octafluoronaphthalene, 23% of perfluoro-1,4-dihydronaphthalene, 14% of 1-oxooctafluoro-1,4-dihydronaphthalene and 3% hexafluoronaphthoquinone-1,4 (GLC data).

Likewise, 5.0 g of octafluoronaphthalene and 1.5 g of bromine pentafluoride afforded 8.6 g of the product containing 39% of SO_2FCl, 46% of octafluoronaphthalene, 1% of perfluoro-1,4-dihydronaphthalene and 9% of 1-oxooctafluoro-1,4-dihydronaphthalene.

F. ClF_3

Chlorine trifluoride (1.8 g) was passed through a stirred solution of 10.6 g of octafluoronaphthalene in 60 ml of 1,2-dichlorotetrafluoroethane at -50÷-60°C.The solution was stirred for 25 min and was then poured onto ice.It was extracted with dichloromethane, washed with water, dried over $MgSO_4$, and the solvent distilled off to yield 29.9 g of product containing 62% of the solvent, 30% of octafluoronaphthalene and 3% of perfluoro-1,4-dihydronaphthalene.

REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS WITH CHLORINE AND BROMINE TRIFLUORIDE IN THE PRESENCE OF HF

The solution of polyfluoroaromatic compound was stirred at an appropriate temperature and BrF_3 was added slowly (or ClF_3 vapour was passed in a stream of dry argon).After 20-25 min the mixture was poured onto ice.The organic layer was separated and dried.

Charges and yields of the reaction products are given in Table 3.

OXIDATION OF OCTAFLUORONAPHTHALENE WITH CHLORINE AND BROMINE TRIFLUORIDES AND BROMINE PENTAFLUORIDE

Octafluoronaphthalene (0.005-0.010 g) was placed in an ESR tube and then SO_2FCl (0.03 ml) was condensed in.The tube was cooled down to -50÷-70°C and BrF_3 (or BrF_5) added using a quartz pipette.Chlorine trifluoride was condensed in the tube at -80°C. After stirring the tube was placed in a thermostated detector of the instrument.ESR spectra were recorded at -50÷-70°C.The resulting ESR spectra were identical to an ESR spectrum of the octafluoronaphthalene radical cation [10].

REFERENCES

1 G.G.Yakobson, G.G.Furin, Synthesis, (1980), 345.

2 T.W.Bastock, M.E.Harley, A.E.Pedler, J.C.Tatlow, J.Fluor. Chem.,6 (1975), 331.

3 T.W.Bastock, A.E.Pedler, J.C.Tatlow, J.Fluor.Chem.,8 (1976), 11.

4 V.V.Bardin, G.G.Furin, G.G.Yakobson, Zh. Org.Khim.,16 (1980), 1256.

5 V.V.Bardin, G.G.Furin, G.G.Yakobson, Zh.Org.Khim.,18 (1982), 604.

6 S.Stavber, M.Zupan, J.Org.Chem.,46 (1981), 300.

7 R.Gillespie, M.Morton, Halogen Cation, In: Main Group Elements Group VII and Noble Gases, Ed.V.Gutman, London; Butterworth, 1973, p.199.

8 A.N.Nesmejanov, A.N.Vanchikov, I.N.Lisichkina, N.S.Khrushcheva, T.P.Tolstaja, Dokl.Akad.Nauk SSSR, 254 (1980), 652; C.A., 94 (1981), 174489.

9 T.Surles, L.A.Quaterman, H.H.Hyman, J.Fluor.Chem.,3 (1973/74), 293.

10 N.E.Akhmetova, N.M.Bazhin, Yu.V.Pozdnjakovich, V.D.Shteingarts L.N.Shchegoleva, Teor. i eksperim.Khim.,10 (1974), 613; C.A.,82 (1975), 42643.

11 A.A.Shtark, V.D.Shteingarts, Zh.Org.Khim.,12 (1976), 1499; C.A.,85 (1976),176505.

12 V.D.Shteingarts, G.G.Yakobson, N.N.Vorozhtsov,Yr, Dokl.Akad. Nauk SSSR, 170 (1966), 1348; C.A.,66 (1967), 55263.

13 V.D.Shteingarts, Yu.V.Pozdnjakovich, Zh.Org.Khim.,7 (1971),734

14 J.Hotchkiss, R.Stephens, J.C.Tatlow, J.Fluor.Chem.,10 (1977), 541.

15 S.Campbell, A.Hudson, E.Mooney, A.E.Pedler, R.Stephens, K.Wood, Spectrochim.Acta, 23A (1967), 2119.

16 V.D.Shteingarts, P.N.Dobronravov, Zh.Org.Khim.,12 (1976), 2005; C.A.,86 (1977), 72059.

17 P.N.Dobronravov, T.V.Chuikova, Yu.V.Pozdnjakovich, V.D.Shteingarts, Zh.Org.Khim.,16 (1980), 796.

18 T.V.Chuikova, V.D.Shteingarts, Zh.Org.Khim.,9 (1973), 1733; C.A.,79 (1973), 115340.