ISSN 1070-4280, Russian Journal of Organic Chemistry, 2016, Vol. 52, No. 10, pp. 1400–1407. © Pleiades Publishing, Ltd., 2016.
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Reactions of Aromatic Compounds with Xenon Difluoride

V. V. Bardin[a, b] and N. Yu. Adonin[b, c]*

[a] *Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia*

[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*

[c] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, pr. Akad. Lavrent'eva 5, Novosibirsk 630090 Russia*
**e-mail: adonin@catalysis.ru*

Received April 6, 2016

Abstract—Reactions of substituted benzenes C_6H_5R (R = Me, F, Cl, Br, CF_3, NO_2) with xenon difluoride in the presence of boron trifluoride–diethyl ether complex in weakly acidic (1,1,1,3,3-pentafluorobutane) and weakly basic media (acetonitrile) have been studied. These reactions lead to the formation of fluorobenzene derivatives FC_6H_4R (isomer mixture) together with isomeric difluorobenzenes and fluorinated and non-fluorinated biphenyls. The results have been compared with previously reported data obtained in other solvents using other catalysts.

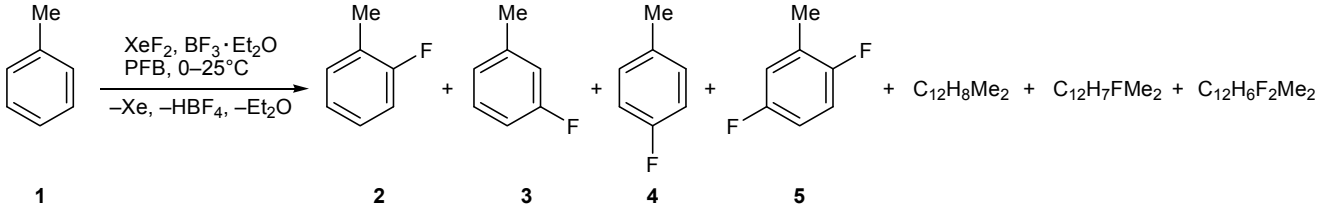
DOI: 10.1134/S1070428016100055

Reactions of xenon difluoride with organic compounds have been extensively studied over several decades since a procedure for its preparation has been developed. Apart from the expected action of XeF_2 as fluorinating agent, some other interesting aspects of its application in organic, organoelement, and inorganic chemistry have been revealed (for reviews, see [1–5]). Of particular interest is the use of xenon difluoride in the synthesis of organic xenon(II) derivatives containing aryl, alkenyl, cycloalkenyl, and alkynyl groups [6–9]. The first data on reactions of XeF_2 with benzene derivatives [10–14], naphthalene [15], and polycyclic arenes [1, 3] were reported in 1969–1975, and some data were later corrected and supplemented [16]. These reactions were commonly carried out in weakly acidic medium (in methylene chloride, chloroform, or carbon tetrachloride in the presence of anhydrous HF or BF_3 or without a catalyst). Fedorov et al. [17] recently reported fluorination of benzene and substituted benzenes C_6H_5R (R = H, Me, Cl, Br, I, NO_2) and nitrobenzenes 4-$RC_6H_4NO_2$ (R = Me, MeO) with xenone difluoride in acetonitrile as weakly basic solvent, which was motivated by possible increase of the fluorination selectivity at reduced temperature with $BF_3 \cdot Et_2O$ as catalyst (Lewis acid). However, the complete substrate conversion required almost 1.5 equiv of $BF_3 \cdot Et_2O$, and the results were partially inconsistent with previously reported data [11, 14].

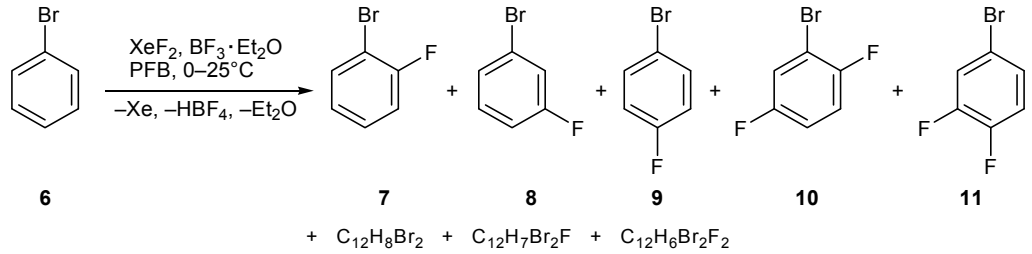
Taking into account that reactions of arenes with xenon difluoride were studied under different experimental conditions (solvent, temperature, catalyst nature and its amount, method of product analysis), we carried out reactions of substituted benzenes C_6H_5R (R = Me, F, Cl, Br, CF_3, NO_2) with XeF_2 under the conditions that minimized side processes, and the products were analyzed by ^{19}F NMR and GC/MS. We did not examine the reaction of XeF_2 with iodobenzene which was thus converted to C_6H_5IO and $[(4\text{-}IC_6H_4)(C_6H_5)I][BF_4]$ assumingly through $C_6H_5IF_2$ [17], since the oxidative fluorination of PhI to $PhIF_2$ and subsequent hydrolytic transformations of the latter into iodosylbenzene and iodonium salts have long been known and are well documented [18–24].

Most reactions of arenes with XeF_2 were carried out in methylene chloride since both reactants and products are readily soluble in that solvent. However, even traces of Lewis acids promote the fluorination of chloromethanes with XeF_2 to chlorofluoromethanes with liberation of chlorine and/or hydrogen fluoride [25]. Fluorinated compounds such as CCl_3F, $CClF_2CCl_2F$, and CF_3CH_2Cl are stable under these conditions, but they cannot be used as solvent because of very poorly solubility of xenon difluoride therein. The most appropriate solvents turned out to be commercially available fluorinated hydrocarbons, 1,1,1,3,3-pentafluoropropane (PFP, mp –103°C,

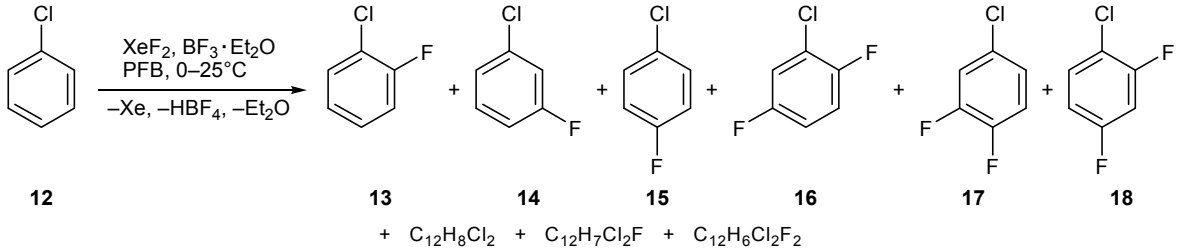
Scheme 1.



Scheme 2.



Scheme 3.



bp 15°C) and 1,1,1,3,3-pentafluorobutane (PFB, mp –35°C, bp 40°C) [26]. The reactor material is also important. The use of glass reactors for reactions in weakly acidic medium is undesirable, as was clearly demonstrated by reactions of XeF_2 with 4-$RC_6H_4SiMe_3$ [27, 28]. Filler et al. [11, 14] used Kel-F (polychlorotrifluoroethylene) tubes, and we carried out the reactions in vessels made of alternative chemically resistant materials such as FEP (a block copolymer of tetrafluoroethylene and hexafluoropropylene) and PFA (a block copolymer of tetrafluoroethylene and perfluoroalkoxytrifluoroethylene) with better mechanical properties.

Treatment of toluene (**1**) with XeF_2 in PFB in the presence of 1.3–1.5 equiv of $BF_3 \cdot Et_2O$ was accompanied by gas evolution, and a dark brown solution was obtained. After washing with a solution of $KHCO_3$, we detected in the reaction mixture initial toluene, isomeric 2-, 3-, and 4-fluorotoluenes **2**–**4**, a small amount of 2,5-difluorotoluene (**5**), and biphenyls $C_{12}H_8Me_2$, $C_{12}H_7FMe_2$, and $C_{12}H_6F_2Me_2$ (according to the ^{19}F NMR and GC/MS data). As reported previously [11], no side chain fluorination was observed (Scheme 1).

Under analogous conditions, the reaction of bromobenzene (**6**) with XeF_2 afforded 2-, 3-, and 4-bromofluorobenzenes **7**–**9**, 2,5- and 3,4-difluorobromobenzenes **10** and **11**, and bromine-containing biphenyls $C_{12}H_8Br_2$, $C_{12}H_7Br_2F$, and $C_{12}H_6Br_2F_2$ (Scheme 2). Chlorobenzene (**12**) reacted with XeF_2 to give 2-, 3-, and 4-chlorofluorobenzenes **13**–**15**, small amounts of 2,4-, 2,5-, and 3,4-difluorochlorobenzenes **16**–**18**, and biphenyls $C_{12}H_8Cl_2$, $C_{12}H_7Cl_2F$, and $C_{12}H_6Cl_2F_2$ (Scheme 3). Reduction of the amount of $BF_3 \cdot Et_2O$ to 0.5 equiv insignificantly changed the substrate conversion. The major products of the reaction of xenon difluoride with fluorobenzene (**19**) were 1,2-, 1,3-, and 1,4-difluorobenzenes **20**–**22**. In addition, 1,2,4-trifluorobenzene (**23**) and (unexpectedly) 3,3,6,6-tetrafluorocyclohexa-1,4-diene (**24**) were formed (Scheme 4). Tetrafluorobiphenyls were also detected among the products, but their amount was considerably smaller than the amount of analogous derivatives obtained from C_6H_5R (R = Me, Cl, Br). We failed to avoid the formation of fluorinated biphenyls by reducing the concentration of initial fluorobenzene (**19**).

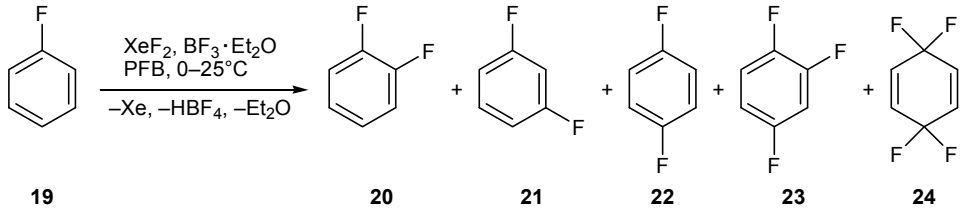
Trifluoromethylbenzene (**25**) and nitrobenzene (**31**) reacted with XeF_2 in PFB in the presence of $BF_3 \cdot Et_2O$

to give products of replacement of one or two hydrogen atoms by fluorine, but no biphenyls were detected. Benzotrifluoroide (**25**) was converted to 2-, 3-, and 4-fluoro(trifluoromethyl)benzenes **26**–**28** and 2,5- and 2,3-difluoro derivatives **29** and **30** (Scheme 5). Likewise, 2-, 3-, and 4-fluoronitrobenzenes **32**–**34** and 2,5- and 2,3-difluoronitrobenzenes **35** and **36** were obtained from nitrobenzene (**31**) (Scheme 6). It should be noted that no 2,3-$F_2C_6H_3R$ isomers were detected in the reactions of xenon difluoride with toluene and halobenzenes **6**, **12**, and **19**.

Being a weakly basic solvent, acetonitrile effectively neutralizes acidic sites on the glass surface [25, 28]. According to our data, the concentration of XeF_2 in CD_3CN (in a standard NMR tube) did not change over 9 months. The reactions of substituted benzenes with XeF_2 were carried out under the conditions analogous to those described in [17], but the product composition was determined twice: (1) by ^{19}F NMR immediately after the reaction completion (see table, procedure **B**) and (2) by ^{19}F NMR and GC/MS after treatment of the reaction mixture with a solution of $NaHCO_3$ and extraction with methylene chloride (see table, procedure **C**). In all cases, consistent results were obtained.

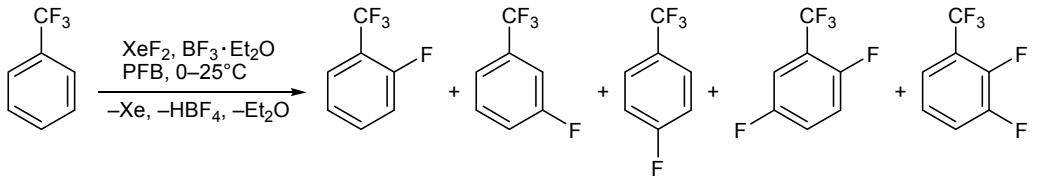
The reaction of toluene (**1**) with XeF_2 (1.2–1.3 equiv) and $BF_3 \cdot Et_2O$ in acetonitrile afforded mainly isomeric fluorotoluenes **2**–**4**, small amounts of 2,5-, 2,4-, and 3,4-difluorotoluenes **5**, **37**, and **38**, and biphenyls $C_{12}H_8(CH_3)_2$, $C_{12}H_7F(CH_3)_2$, and $C_{12}H_6F_2(CH_3)_2$ (Scheme 7). In addition, *N*-tolylacetamides were detected. Likewise, a mixture of isomeric chlorofluorobenzenes **13**–**18** and biphenyls $C_{12}H_7FCl_2$ and $C_{12}H_6F_2Cl_2$ was obtained from chlorobenzene (**12**) (Scheme 8). Under the same conditions fluorobenzene (**19**) was converted into difluorobenzenes **20**–**22**,

Scheme 4.



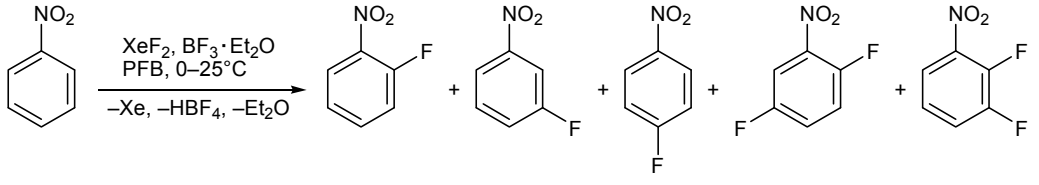
19 **20** **21** **22** **23** **24**

Scheme 5.



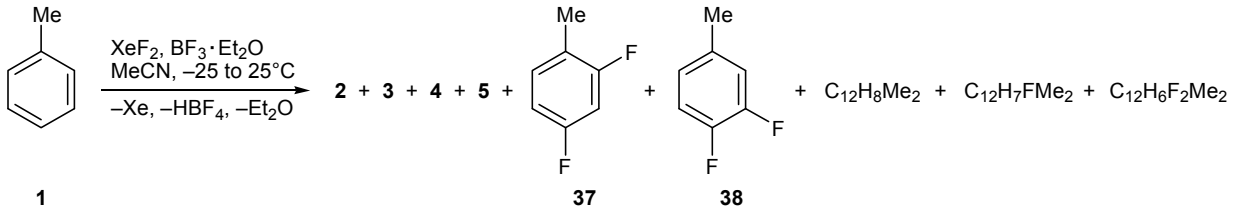
25 **26** **27** **28** **29** **30**

Scheme 6.



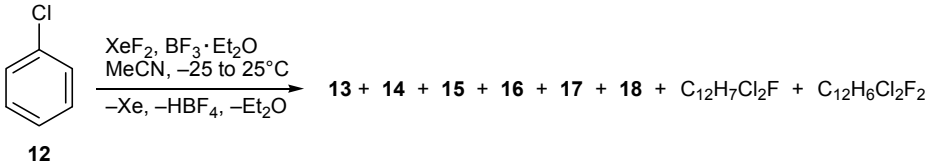
31 **32** **33** **34** **35** **36**

Scheme 7.



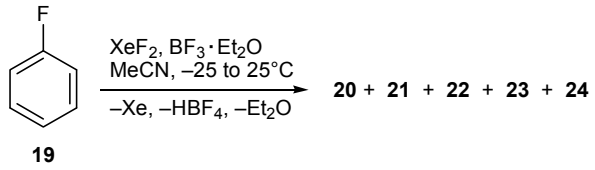
1 **37** **38**

Scheme 8.



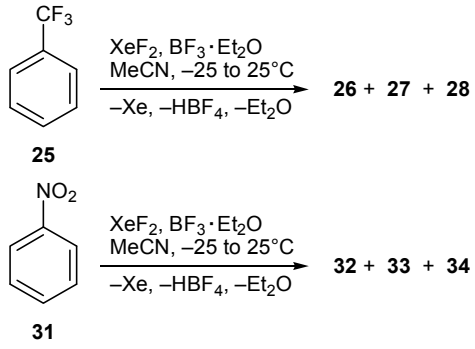
trifluorobenzene **23**, and cyclohexadiene **24**, while no biphenyl derivatives were detected by GC/MS (Scheme 9). The product composition did not change when $BF_3 \cdot Et_2O$ was replaced by $BF_3 \cdot MeCN$, but the yield slightly decreased.

Scheme 9.



Further increase of the electron-withdrawing power of the R substituent in C_6H_5R is accompanied by decrease of the fractions of difluoro derivatives and biphenyls. Thus, the reactions of benzotrifluoride and nitrobenzene with XeF_2 (1.2–1.3 equiv) and $BF_3 \cdot Et_2O$ in MeCN gave only the corresponding isomeric monofluoro derivatives (Scheme 10).

Scheme 10.



Comparison of our results (see table, procedure **A**) with those obtained in the reactions of XeF_2 with C_6H_5R in the presence of anhydrous HF in carbon tetrachloride (procedure **D**) or methylene chloride (procedure **E**) [11] showed a good agreement in isomer distribution for R = Me, Cl, NO_2. However, no *ortho* isomer **26** was detected in the reaction with $C_6H_5CF_3$ in CCl_4, while only traces of *para* isomer **28** were formed [11]. In the reaction carried out in methylene chloride, the fractions of **26** and **28** were larger due to reduced fraction of *meta* isomer **27**. According to our results, the ratio **26**:**27**:**28** is 2:8:1. Analogous disagreement is also observed for the reaction with fluorobenzene: the ratio of isomeric difluorobenzenes determined in [11] considerably differs from that found in the present work. A probable reason is that the products were analyzed in [11] by GLC after treatment of the reaction mixture, whereas we performed the analysis by considerably more reliable ^{19}F NMR and GC/MS methods both before and after treatment of the reaction mixture. Another reason may be HF-initiated side reaction of one FC_6H_4R isomer (R = F, CF_3) with products of decomposition of CCl_4 or CH_2Cl_2 by xenon difluoride [25], which should distort the initial isomer ratio. Furthermore, the authors [11] reported the ratio of FC_6H_4R isomers and their overall yield and noted the formation of a large number of unidentified tarry products, but no substrate conversion was given.

The product compositions in the reactions of C_6H_5R with XeF_2 in the presence of $BF_3 \cdot Et_2O$ in MeCN, determined before and after treatment of the reaction mixtures (see table, procedures **B** and **C**) almost coincided with each other and were consistent with the isomer ratios of FC_6H_4R (R = Me, NO_2) [17] (procedure **F**). However, the isomer ratio **13**:**15** given in [17] contradicts both our data and those reported in [11]. This was due to erroneous assignment of signals in the ^{19}F NMR spectrum of isomer mixture with no account taken of ^{1}H–^{19}F coupling constants. As a result, the authors [17] erroneously concluded that the observed difference in the distributions of FC_6H_4Cl and FC_6H_4Br isomers is related to steric effect of the bromine atom which blocks the *ortho* position. The authors did not specify the action of which reagent could be determined by steric effect of the R substituent.

The reactions of xenon difluoroide with fluorobenzene, benzotrifluoride, and nitrobenzene afforded only products of hydrogen substitution by fluorine atom(s), whereas more electrophilic benzene derivatives C_6H_5R (R = Me, Cl, Br) gave rise to appreciable amounts of biphenyl derivatives $C_{12}H_8R_2$, $C_{12}H_7FR_2$, and $C_{12}H_6F_2R_2$, which were identified by GC/MS and ^{19}F NMR. Determination of their isomeric composition was not the goal of our present study, but each group of congeners included at least three main components.

Reaction of xenon difluoride with substituted benzenes

Comp. no.	Procedure[a]	Conversion of C_6H_5R, % (GC/MS)	Overall yield of C_6H_4FR, [b, c] %	Yield of C_6H_4FR,[c] mmol			Isomer fractions of C_6H_4FR, %			Yield of $C_6H_3F_2R$,[c] mmol		
				2-F	3-F	4-F	2-F	3-F	4-F	2,4-F_2	2,5-F_2	3,4-F_2
1	**A**	87 (0.87)	25	0.14	0.01	0.10	55	4	41		0.001	
	B			0.28	0.05	0.14	60	10	30	0.03	0.04	0.01
	C	96 (0.94)	59	0.30	0.02	0.14	66	4	30	0.03	0.04	0.01
	D		32				50	8	42			
	F	94	21				62	9	29			
6	**A**[d]	78 (0.31)	74	0.06	0.03	0.16	24	12	64		0.01	0.004
	F	99	56				29	9	62			
12	**A**	86 (0.86)	47	0.08	0.02	0.31	19	5	76	0.01	0.01	0.01
	A[e]	83 (0.83)	35	0.06	0.02	0.23	20	6	74	0.007	0.007	0.007
	B			0.10	0.02	0.21	30	6	64	0.005	0.007	0.006
	C	65 (0.62)	62	0.12[f]	0.03[f]	0.24[f]	31[f]	8[f]	61[f]	0.005	0.005	0.005
	D		66				24	5	71			
	F	99	42				63	8	29			
19	**A**	93 (0.93); 88 (0.88)[c]	45	0.03	0.01	0.35	8	3	89	0.01		
	A[g]	99 (1.19) 93 (1.12)[c]	42	0.04	0.01	0.28	12	3	85	0.01		
	A	94 (1.00)[c]	32	0.03	0.01	0.28	9	3	88	0.01		
	B	68 (0.77)[c]	41	0.08	0.01	0.21	27	3	70	0.01		
	C[h]	92 (1.09)[c]	21	0.05	0.01	0.17	22	4	74	0.01		
	D		47				25	6	69	0.01		
	E		52				27	6	67			
25	**A**	82 (0.90) 88 (0.88)[c]	50	0.11	0.41	0.05	19	72	9		0.06	Traces
	B			0.01	0.03	0.002	24	71	5			
	C	58 (0.62)	5	0.01	0.03	0.002	24	71	5			
	D		76				0	95	5			
	E		80				31	55	14			
31	**A**	83 (0.79)	27	0.05	0.16	0.01	23	72	5		0.016	0.001
	B	30 (0.32)	9	0.003	0.025	0.001	10	86	4			
	D		68				21	62	1			
	E		81				23	63	14			
	F	10	6				9	89	2			

[a] Procedure **A**: FEP or PFA reactor, 1.2–1.3 equiv of XeF_2, 1.3–1.5 equiv of $BF_3 \cdot Et_2O$, PFB, 0–25°C, 1 h, washing with aqueous $KHCO_3$, drying over $MgSO_4$, analysis by GC/MS and ^{19}F NMR; procedure **B**: glass reactor, 1.2–1.3 equiv of XeF_2, 1.3–1.5 equiv of $BF_3 \cdot Et_2O$, MeCN, –25 to 25°C, analysis by ^{19}F NMR; procedure **C**: glass reactor, 1.2–1.3 equiv of XeF_2, 1.3–1.5 equiv of $BF_3 \cdot Et_2O$, MeCN, –25 to 25°C, washing with aqueous $NaHCO_3$, extraction with CH_2Cl_2, analysis by GC/MS and ^{19}F NMR; procedure **D**: Kel-F reactor, 1.2 equiv of XeF_2, anhydrous HF, CCl_4, –75 to 20°C, washing with aqueous NaOH, drying over Na_2SO_4, analysis by GLC [11]; procedure **E**: the same as **D**, but CH_2Cl_2 instead of CCl_4; procedure **F**: glass reactor, 1.25 equiv of XeF_2, 1.4 equiv of $BF_3 \cdot Et_2O$, MeCN, –25 to 25°C, washing with aqueous $NaHCO_3$, extraction with diethyl ether, drying over Na_2SO_4, analysis by GLC and ^1H and ^{19}F NMR [17].

[b] Calculated on the reacted C_6H_5R.

[c] ^{19}F NMR data.

[d] 0.4 mmol of C_6H_5Br.

[e] 0.5 equiv of $BF_3 \cdot Et_2O$.

[f] GC/MS data; signals of 2-FC_6H_4Cl and 4-FC_6H_4Cl overlapped each other in the ^{19}F NMR spectrum.

[g] 4 mL of PFB per mmol of C_6H_5F.

[h] 1.8 equiv of $MeCN \cdot BF_3$ instead of $BF_3 \cdot Et_2O$.

It should be noted that, in contrast to the data of [11] according to which the reactions were accompanied by considerable tarring, the formation of polyphenylenes was observed in [17] only in the reaction with benzene.

The formation of fluorinated arenes, as well as of biphenyls, from substituted benzenes in reactions with xenon difluoride may be rationalized in terms of single-electron oxidation of the aromatic substrate to the corresponding radical cation by the action of XeF_2 molecule polarized by Lewis acid (the role of $BF_3 \cdot Et_2O$ consists of just polarization of XeF_2 molecule rather than of binding liberated HF as presumed in [17]). Intermediate radical cations react with fluoride ion to give fluoroarenes such as FC_6H_4R. Concurrently, radical cations derived from substituted benzenes can react with parent neutral molecules C_6H_5R via electrophilic substitution of hydrogen to produce biphenyls $C_{12}H_8R_2$. Fluorination of the latter with XeF_2 leads to $C_{12}H_7FR_2$ and $C_{12}H_6F_2R_2$. Fluorinated biphenyls can also be formed as a result of combination of $[C_6H_5R]^+$ with FC_6H_4R. This scheme was proposed in [13, 14] and confirmed experimentally by studying the reaction of C_6D_6 with XeF_2 [29]. Moreover, reactions of trimethylsilyl-substituted arenes $4\text{-}RC_6H_4SiMe_3$ [27, 28] and $C_6H_{5-n}F_nSiMe_3$ (n = 1–4) [30] and polyfluorobenzenes C_6HF_4R with XeF_2, catalyzed by anhydrous HF or $BF_3 \cdot Et_2O$ [31], are also well described by analogous schemes involving the corresponding radical cations $[C_6HF_4R]^+$ as key intermediates [31]. The above scheme also explains the absence of biphenyl derivatives in the reactions of XeF_2 with arenes containing electron-withdrawing substituents. The combination of radical cations derived from such arenes with negatively charged highly nucleophilic fluoride ions is much faster than with initial arenes. Unlike electronic factors, steric effect of substituents in the aromatic ring is insignificant, as demonstrated by the formation of 2-fluoro-1,3,5-trineopentylbenzene from 1,3,5-trineopentylbenzene and XeF_2 in CCl_4 in the presence of HF [11].

Thus, analysis of published data and results of our study shows that the ratio of fluorination products in the reactions of substituted benzenes C_6H_5R with XeF_2 in the presence of fluoride ion acceptor does not depend on the temperature and solvent nature (provided that the latter is inert toward xenon fluoride). Therefore, these factors do not control the fluorination selectivity. The effect of catalyst is determined only by its Lewis acidity in the given solvent. The presence of an electron-donating group or chlorine or bromine atom in the aromatic substrate favors formation of biphenyl derivatives and (probably) polyphenylenes. No biphenyl derivatives are formed from substrates containing electron-withdrawing substituents.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 282.40 MHz, respectively. The chemical shifts were measured relative to tetramethylsilane (^1H) or hexafluorobenzene (^{19}F, δ_F –162.9 ppm relative to CCl_3F). GC/MS analyses were obtained on a Hewlett Packard 1800A instrument using an HP-5MS column.

1,1,1,3,3-Pentafluorobutane (PFB, Solkane® 365mfc; Solvay Fluor) was stored over 4-Å molecular sieves. Acetonitrile was distilled first over P_4O_{10} and then over CaH_2 and was stored over 4-Å molecular sieves. Boron trifluoride–diethyl ether complex was distilled under dry argon and was stored in sealed ampules. Boron fluoride–acetonitrile complex was prepared from BF_3 and MeCN according to [32]. Substituted benzenes C_6H_5R (R = F, Cl, Br, CF_3, NO_2) were passed through a short column charged with Al_2O_3 which was preliminarily calcined at 500°C for 4 h. 2-, 3-, and 4-Fluorotoluenes [33–35], 2,4- [36], 2,5- [35, 37], and 3,4-difluorotoluenes [38], 2-, 3-, and 4-fluoro-1-bromobenzenes [33, 39], 2,5- [37] and 3,4-difluoro-1-bromobenzenes [40], 2-, 3-, and 4-fluoro-1-chlorobenzenes [33, 39], 2,5- [33, 37] and 3,4-difluoro-1-chlorobenzenes [33, 41], 2- [33, 42], 3- [33, 41, 42], and 4-fluorobenzotrifluorides [33, 43], 2,5- [43] and 3,4-difluorobenzotrifluorides [43], 2-, 3-, and 4-fluoro-1-nitrobenzenes [33, 39], 2,5- [33, 37] and 3,4-difluoro-1-nitrobenzenes [33, 41], and 3,3,6,6-tetrafluorocyclohexa-1,4-diene [44, 45] were identified by comparing their ^{19}F NMR spectra (chemical shifts and ^{19}F–^1H and ^{19}F–^{19}F coupling constants) with those of authentic samples and by GC/MS data. The yields were determined from the ^{19}F NMR and GC/MS data using hexafluorobenzene as internal standard. The reactions in PFB were carried out in reactors made of FEP (tetrafluoroethylene–hexafluoropropylene block copolymer; i.d. 8.0 mm, e.d. 9.0 mm) or PFA (tetrafluoroethylene–perfluoroalkoxytrifluoroethylene block copolymer; i.d. 11.7 mm, e.d. 14.0 mm).

Reaction of substituted benzenes with xenon difluoride in the presence of boron trifluoride–diethyl ether complex in PFB (procedure A). A FEP or PFA reactor equipped with a Teflon-lined magnetic stir bar and connected to a gas-washing bottle was charged with substituted benzene (0.95–1.10 mmol),

1,1,1,3,3-pentafluorobutane (1–2 mL per mmol of C_6H_5R), and $BF_3 \cdot Et_2O$ (1.3–1.5 mmol per mmol of C_6H_5R). The mixture was stirred for 10–15 min at 0–5°C (ice bath), and XeF_2 (1.2–1.3 mmol per mmol of C_6H_5R) was added in portions. After addition of each portion, the mixture was stirred for 3–5 min at 22–25°C and cooled again. When the addition was complete, the dark solution was stirred for 15–30 min at 22–25°C, 10% aqueous $KHCO_3$ was added, and the upper organic layer was separated, passed through a short column charged with silica gel (40–60 μm), and dried over $MgSO_4$. The solution was analyzed by ^{19}F NMR and GC/MS. The main products are given in table, and the others are listed below (GC/MS data).

From toluene: $C_{12}H_8Me_2$ (M^+ 182), $C_{12}H_7FMe_2$ (M^+ 200), $C_{12}H_6F_2Me_2$ (M^+ 218) (total 0.26 mmol).

From bromobenzene: $C_{12}H_8Br_2$ (M^+ 310), $C_{12}H_7Br_2F$ (M^+ 328), $C_{12}H_6Br_2F_2$ (M^+ 346) (total 0.08 mmol).

From chlorobenzene: $C_{12}H_8Cl_2$ (M^+ 223), $C_{12}H_7Cl_2F$ (M^+ 240), $C_{12}H_6Cl_2F_2$ (M^+ 256) (total 0.22 mmol).

From fluorobenzene: $C_{12}H_8F_2$ (M^+ 190) (<0.01 mmol), 3,3,6,6-tetrafluorocyclohexa-1,4-diene (**24**, 0.02 mmol) (^{19}F NMR).

From (trifluoromethyl)benzene: 1,2-difluoro-3-(trifluoromethyl)benzene (**30**, 0.006 mmol). ^{19}F NMR spectrum (PFB), δ_F, ppm: –136.2 d.d.d (1F, 1-F, $^3J_{FF}$ = 19, $^3J_{FH}$ = 10, $^4J_{FH}$ = 4 Hz), –139.4 t.d.d (1F, 2-F, $^4J_{FH}$ = 6 Hz, $^4J_{FF}$ = 13, $^3J_{FF}$ = 19 Hz); the CF_3 signal was overlapped by the signal of $C_6H_5CF_3$. GC/MS: *m*/*z* 182 $[M]^+$.

From nitrobenzene: 1,2-difluoro-3-nitrobenzene (**36**, 0.002 mmol). ^{19}F NMR spectrum (PFB), δ_F, ppm: –133.8 d.d.d (1F, 1-F, $^3J_{FF}$ = 19, $^3J_{FH}$ = 10, $^4J_{FH}$ = 4 Hz), –143.2 t.d (1F, 2-F, $^4J_{FH}$ = 6, $^3J_{FF}$ = 19 Hz); published data [46]: ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: –134.1 m (1F, 1-F), –143.5 d.t (1F, 2-F); erroneous data were given in [47]: ^{19}F NMR spectrum (THF) δ_F, ppm: –127.00 to –128.30 m (1F), –134.40 to –135.05 m (1F). GC/MS: *m*/*z* 159 $[M]^+$.

Reaction of C_6H_5R with XeF_2 and $BF_3 \cdot Et_2O$ in acetonitrile (procedures B and C). A glass reactor equipped with a Teflon-lined magnetic stir bar and connected to a gas-washing bottle was charged with C_6H_5R (0.95–1.14 mmol), MeCN (1–2.5 mL per mmol of C_6H_5R), and $BF_3 \cdot Et_2O$ (1.3–1.6 mmol per mmol of C_6H_5R). The solution was stirred for 10–15 min at –25°C, and XeF_2 (1.2–1.3 mmol per mmol of C_6H_5R) was added in portions. The mixture was allowed to warm up to 22°C over a period of 1 h and stirred for 40–60 min more, hexafluorobenzene (internal standard) was added, and a sample was withdrawn for ^{19}F NMR analysis (procedure **B**). The mixture was treated with a saturated aqueous solution of $NaHCO_3$ and extracted with methylene chloride (1–2 mL). The extract was dried over $MgSO_4$ and analyzed by ^{19}F and GC/MS (procedure **C**). The main products are given in table, and the others are listed below (GC/MS data).

From toluene: *N*-tolylacetamides (M^+ 221, (0.10 mmol); $C_{12}H_8Me_2$ (M^+ 182), $C_{12}H_7FMe_2$ (M^+ 200), $C_{12}H_6F_2Me_2$ (M^+ 218) (total 0.31 mmol).

From fluorobenzene: 3,3,6,6-tetrafluorocyclohexa-1,4-diene (**24**, 0.01 mmol; ^{19}F NMR).

From chlorobenzene: $C_{12}H_8Cl_2$ (M^+ 223, 0.10 mmol).

The reaction of fluorobenzene with XeF_2 and $MeCN \cdot BF_3$ in acetonitrile was carried out with 115 mg (1.19 mmol) of C_6H_5F, 241 mg (2.21 mmol) of $MeCN \cdot BF_3$, and 252 mg (1.49 mmol) of XeF_2 in 3 mL of acetonitrile according to procedure **C** (see table).

The ^1H and ^{19}F NMR and GC/MS data were obtained at the Joint Center, Siberian Branch, Russian Academy of Sciences.

REFERENCES

1. Filler, R., *Isr. J. Chem*., 1978, vol. 17, p. 71.
2. Tius, M.A., *Tetrahedron*, 1995, vol. 51, p. 6605.
3. Bardin, V.V. and Yagupol'skii, Yu.L., *New Fluorinating Agents in Organic Synthesis*, German, L.S. and Zemskov, S.V., Eds., Berlin: Springer, 1989, p. 1.
4. Yagupolskii, Y.L., *Houben-Weyl Methods of Organic Chemistry*, Stuttgart: Thieme, 2000, vol. E10 b/2, p. 219.
5. Zajc, B., *Advances in Organic Synthesis: Modern Organofluorine Chemistry. Synthetic Aspects*, Atta-ur-Rahman and Laali, K.K., Eds., Bentham Science, 2006, p. 61.
6. Frohn, H.J. and Bardin, V.V., *Recent Developments in Carbocation and Onium Ion Chemistry*, Laali, K.K., Ed., Washington: Am. Chem. Soc., 2007, p. 428.
7. Frohn, H.J. and Bardin, V.V., *Organometallics*, 2001, vol. 20, p. 4750.
8. Brel, V.K., Pirguliyev, N.S., and Zefirov, N.S., *Rus. Chem. Rev*., 2001, vol. 70, p. 231.
9. Tyrra, W. and Naumann, D., *Organoxenon Compounds. Inorganic Chemistry Highlights*, Meyer, G., Naumann, D., and Wesemann, L., Weinheim: Wiley-VCH, 2002, p. 297.

10. Yang, N.-C., Shieh, T.-C., Feit, E.D., and Chernick, C.L., *J. Org. Chem*., 1970, vol. 35, p. 4020.
11. Hyman, H.H., Shaw, M.J., and Filler, R., *J. Am. Chem. Soc*., 1970, vol. 92, p. 6498.
12. MacKenzie, D.R. and Fajer, J., *J. Am. Chem. Soc*., 1970, vol. 92, p. 4994.
13. Shaw, M.J., Weil, J.A., Hyman, H.H., and Filler, R., *J. Am. Chem. Soc*., 1970, vol. 92, p. 5096.
14. Shaw, M.J., Hyman, H.H., and Filler, R., *J. Am. Chem. Soc*., 1969, vol. 91, p. 1563.
15. Anand, S.P., Quarterman, L.A., Christian, P.A., Hyman, H.H., and Filler, R., *J. Org. Chem*., 1975, vol. 40, p. 3796.
16. Rabinovitz, M., Agranat, I., Selig, H., and Lin, C.-H., *J. Fluorine Chem*., 1977, vol. 10, p. 159.
17. Fedorov, A.E., Zubarev, A.A., Mortikov, V.Yu., Rodinovskaya, L.A., and Shestopalov, A.M., *Russ. Chem. Bull., Int. Ed*., 2015, vol. 64, p. 1049.
18. Maletina, I.I., Orda, V.V., Aleinikov, N.N., Korsunskii, B.L., and Yagupol'skii, L.M., *Zh. Org. Khim*., 1976, vol. 12, p. 1371.
19. Zhdankin, V.V., *Sci. Synth*., 2007, vol. 31, p. 164.
20. Zhdankin, V.V. and Stang, P.J., *Chem. Rev*., 2008, vol. 108, p. 5299.
21. Zhdankin, V.V. and Stang, P.J., *Chem. Rev*., 2002, vol. 102, p. 2523.
22. Gibson, J.A., Marat, R.K., and Janzen, A.F., *Can. J. Chem*., 1975, vol. 53, p. 3044.
23. Zupan, M. and Pollak, A., *J. Fluorine Chem*., 1976, vol. 7, p. 445.
24. Gregorcic, A. and Zupan, M., *Bull. Chem. Soc. Jpn*., 1977, vol. 50, p. 517.
25. Dukat, W.W., Holloway, J.H., Hope, E.G., Townson, P.J., and Powell, R.L., *J. Fluorine Chem*., 1993, vol. 62, p. 293.
26. Frohn, H.-J., Adonin, N.Y., and Bardin, V.V., *Z. Anorg. Allg. Chem*., 2003, vol. 629, p. 2499.
27. Lothian, A.P. and Ramsden, C.A., *Synlett*, 1993, p. 753.
28. Ramsden, C.A. and Smith, R.G., *J. Am. Chem. Soc*., 1998, vol. 120, p. 6842.
29. Turkina, M.Ya. and Gragerov, I.P., *Zh. Org. Khim*., 1975, vol. 11, p. 340.
30. Bardin, V.V. and Frohn, H.J., *J. Fluorine Chem*., 1998, vol. 90, p. 93.
31. Bardin, V.V., Shchegoleva, L.N., and Frohn, H.J., *J. Fluorine Chem*., 1996, vol. 77, p. 153.
32. Laubengayer, A.W. and Sears, D.S., *J. Am. Chem. Soc*., 1945, vol. 67, p. 164.
33. Berger, S., Braun, S., and Kalinowski, H.-O., *NMR-Spekroskopie von Nichtmetallen*, Stuttgart: Thieme, 1994, vol. 4, p. 39.
34. Dubbaka, S.R., Narreddula, V.R., Gadde, S., and Mathew, T., *Tetrahedron*, 2014, vol. 70, p. 9676.
35. Momota, K., Yonezawa, T., Mukai, K., and Morita, M., *J. Fluorine Chem*., 1998, vol. 87, p. 173.
36. Olah, G.A. and Kiovsky, T.E., *J. Am. Chem. Soc*., 1968, vol. 90, p. 2583.
37. Kerr, C.A., Quinn, K.J., and Rae, I.D., *Aust. J. Chem*., 1980, vol. 33, p. 2627.
38. Weigert, F.J. and Davis, R.F., *J. Fluorine Chem*., 1993, vol. 63, p. 69.
39. Dolbier, W.R., Jr., *Guide to Fluorine NMR for Organic Chemists*, Hoboken NJ: Wiley, 2009, p. 75.
40. Bolton, R. and Owen, E.S.E., *J. Fluorine Chem*., 1990, vol. 46, p. 393.
41. Chambers, R.D., Hutchinson, J., Sparrowhawk, M.E., Sandford, G., Moilliet, J.S., and Thomson, J., *J. Fluorine Chem*., 2000, vol. 102, p. 169.
42. Olah, G.A. and Mo, Y.K., *J. Org. Chem*., 1973, vol. 38, p. 2686.
43. Schaefer, T., Niemczura, W., Wong, C.-M., and Marat, K., *Can. J. Chem*., 1979, vol. 57, p. 807.
44. Momota, K., Yonezawa, T., Hayakawa, Y., Kato, K., Morita, M., and Matsuda, Y., *J. Appl. Electrochem*., 1995, vol. 25, p. 651.
45. Zweig, A., Fischer, R.G., and Lancaster, J.E., *J. Org. Chem*., 1980, vol. 45, p. 3597.
46. Selivanova, G.A., Starichenko, V.F., and Shteingarts, V.D., *Russ. J. Org. Chem*., 1995, vol. 31, p. 200.
47. Lv, H.B., Cai, Y.B., and Zhang, J.L., *Angew. Chem., Int. Ed*., 2013, vol. 52, p. 3203.