ELSEVIER

Journal of Fluorine Chemistry 77 (1996) 153–159

JOURNAL OF FLUORINE CHEMISTRY

Fluorination of tetrafluorobenzenes C_6HF_4R with XeF_2

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Abstract

Replacement of hydrogen by fluorine and addition of fluorine atoms to the aromatic ring were found in the reaction of XeF_2 with 1-R-2,3,4,5-tetrafluorobenzene (R = H, F, Br, NO_2) or 1-R-2,3,4,6-tetrafluorobenzene (R = H, CF_3) in HF or CH_2Cl_2–$BF_3 \cdot OEt_2$. Only fluorine addition took place in the case of 1-R-2,3,5,6-tetrafluorobenzenes (R = H, Br, CF_3) or 1-Br-2,3,4,6-tetrafluorobenzene. The role of cation radicals as reactive intermediates is discusseed.

Keywords: Tetrafluorobenzenes; Pentafluorobenzene; Xenon difluoride; Fluorination; Fluorodeprotonation; NMR spectroscopy

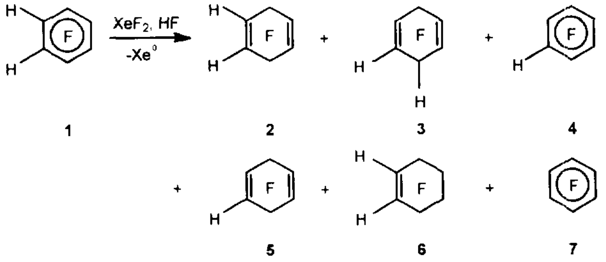
1. Introduction

Xenon difluoride is known as a highly reactive 'electrophilic' fluorinating agent [1]. Reactions of XeF_2 with benzenes C_6H_5R lead to the formation of fluorobenzenes C_6H_4FR, whereas pentafluorobenzenes C_6F_5R undergo 1,4-addition of two fluorine atoms. For instance, the BF_3-catalyzed fluorination of C_6F_5R (R = H, F, Cl, Br, C_6F_5 [2], $SiMe_3$, $SiMe_2F$, $SiMe_2C_6F_5$, $GeEt_3$ [3]) with XeF_2 in CH_2Cl_2 resulted in 1-R-heptafluoro-1,4-cyclohexadienes. Strong electron-withdrawing groups R = CN, NO_2 [2], $SiCl_3$, SiF_3, $GeCl_3$, GeF_3 [3] deactivate the polyfluoroaromatic ring, and the fluorinating system XeF_2-CH_2Cl_2-BF_3 (or $BF_3 \cdot OEt_2$) is ineffective. Ring fluorinations of $C_6F_5NO_2$, 4-$NO_2C_6F_4CF_3$ [4], $C_6F_5SiF_3$, $C_6F_5GeF_3$ [3], C_6F_5CN [5] and $[C_6F_5Xe]^+[AsF_6]^-$ [6] have been performed with more powerful fluorooxidants XeF_2-HF or $XeF^+ MF_6^-$ (M = Sb or Nb).

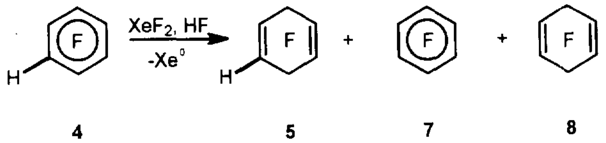
Previous reports indicate that XeF_2 (CH_2Cl_2, $BF_3 \cdot OR_2$) adds fluorine to C_6F_5H [2], but nothing was known about the interaction of XeF_2 with tetrafluorobenzenes. Competitive pathways involving fluorine addition and fluorodeprotonation in the case of the interaction of XeF_2 with highly fluorinated benzenes had not been investigated. Here we report the interaction of some tetrafluorobenzene derivatives C_6HF_4R (R = H, F, Br, CF_3, or NO_2) with XeF_2 in anhydrous HF or CH_2Cl_2-$BF_3 \cdot OEt_2$.

2. Results

Treatment of 1,2,3,4-tetrafluorobenzene (**1**) with XeF_2 (0.25 equiv.) in HF led to formation of 1,2-di-*H*-hexafluoro-1,4-cyclohexadiene (**2**), 1,6-di-*H*-hexafluoro-1,4-cyclohexadiene (**3**) and pentafluorobenzene (**4**) in the molar ratio of 50:15:35. Further addition of XeF_2 (total amount 1.16 equiv.) gave these compounds together with 1*H*-heptafluoro-1,4-cyclohexadiene (**5**), traces of hexafluorobenzene (**7**) and 1,2-di-*H*-octafluorocyclohexene (**6**)



Hexafluorobenzene and diene **5** were the products of the fluorination of pentafluorobenzene as shown by a control experiment.



Fluorination of 1,2,3,5-tetrafluorobenzene (**9**) gave 1,5-di-*H*-hexafluoro-1,4-cyclohexadiene (**10**), pentafluorobenzene, diene **5** and hexafluorobenzene (traces). However, only 1,4-di-*H*-hexafluoro-1,4-cyclohexadiene (**12**) and 1,4-di-*H*-hexafluoro-1,3-cyclohexadiene (**13**) were obtained from 1,2,4,5-tetrafluorobenzene (**11**), and no replacement of hydrogen by fluorine was detected.

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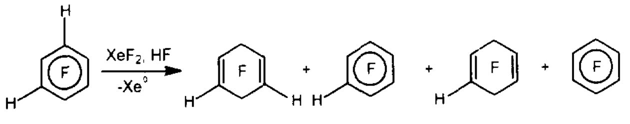
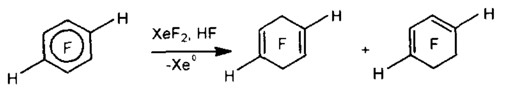
PII S0022-1139(96)03401-X



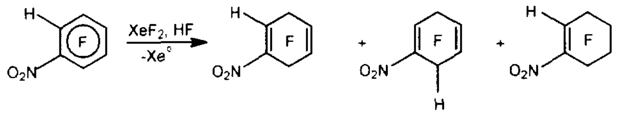
9 10 4 5 7



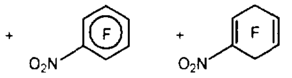
11 12 13

The observed difference in the course of the reaction of tetrafluorobenzenes **1**, **9** or pentafluorobenzene compared to tetrafluorobenzene **11** prompted us to investigate the fluorination of some other hydrogen-containing tetrafluorobenzene derivatives.

The reaction of 1-nitro-2,3,4,5-tetrafluorobenzene (**14**) with xenon difluoride (0.6 equiv.) resulted in the formation of 1-nitro-2*H*-hexafluoro-1,4-cyclohexadiene (**15**) and nitropentafluorobenzene (**16**) in ca. 2:1 molar ratio. When 1.4 equiv. of XeF_2 was added and the reaction mixture kept at 35 °C for 4 h, 1-nitro-6*H*-hexafluoro-1,4-cyclohexadiene (**17**), 1-nitro-2*H*-octafluorocyclohexene (**18**) and 1-nitroheptafluoro-1,4-cyclohexadiene (**19**) were detected together with compounds **15** and **16**.

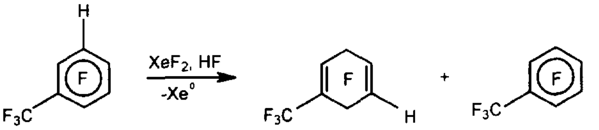


14 15 17 18

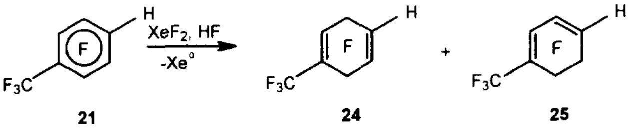


16 19

Fluorination of 1-trifluoromethyl-2,3,4,6-tetrafluorobenzene (**20**) and 1-trifluoromethyl-2,3,5,6-tetrafluorobenzene (**21**) proceeded similarly to that of tetrafluorobenzenes **9** and **11**. Octafluorotoluene (**22**) and 1-trifluoromethyl-5*H*-hexafluoro-1,4-cyclohexadiene (**23**) were formed from toluene **20**, while no fluorodeprotonation occurred in the reaction of toluene **21**.

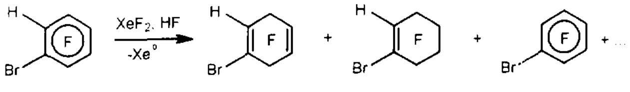


20 23 22



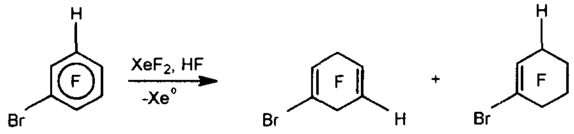
21 24 25

The interaction of xenon difluoride with bromotetrafluorobenzenes proceeded in a more complex way. 1-Bromo-2*H*-hexafluoro-1,4-cyclohexadiene (**27**) (major component), 1-bromo-2*H*-octafluorocyclohexene (**28**) and bromopentafluorobenzene were identified among the products of the fluorination of 1-bromo-2,3,4,5-tetrafluorobenzene (**26**), but the reaction mixture contained other unrecognized polyfluorinated unsaturated compounds The doublet at − 192.08 ppm [J_{HF} = 48 Hz] in the ^{19}F NMR spectrum seems to indicate the presence of bromooctafluorocyclohexenes with the H-C-F geminal moiety, but their structures were not determined.

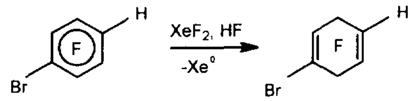


26 27 28 29

Neither bromopentafluorobenzene nor the products of its further fluorination were obtained by the reaction of 1-bromo-2,3,4,6-tetrafluorobenzene (**30**) or 1-bromo-2,3,5,6-tetrafluorobenzene (**33**). The latter compound was converted to 1-bromo-4*H*-hexafluoro-1,4-cyclohexadiene (**34**), whereas 1-bromo-5*H*-hexafluoro-1,4-cyclohexadiene (**31**) and another compound assigned as 1-bromo-3*H*-octafluorocyclohexene (**32**) were detected by ^1H and ^{19}F NMR spectroscopy.



30 31 32



33 34

3. Discussion

Reactions of tetrafluorobenzenes C_6HF_4R with xenon difluoride proceed by two major routes: (a) addition of fluorine atoms to the polyfluoroaromatic ring and (b) substitution of hydrogen by fluorine in some cases. The latter pathway is not a result of the specific influence of anhydrous HF. Indeed, the fluorination of tetrafluorobenzene derivatives **9**, **20**, **33** and pentafluorobenzene with XeF_2 in CH_2Cl_2 in the presence of $BF_3 \cdot OEt_2$ (catalytic amount) proceeded analogously to that in liquid HF. Additionally, in CH_2Cl_2, partial conversion of the solvent into CH_2FCl and CHF_2Cl was found.

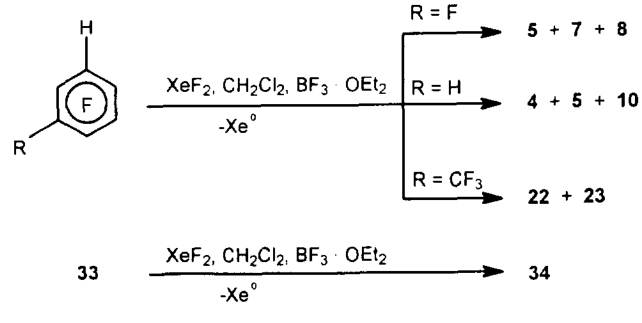


Table 1
The charge and SOMO density distribution in some tetrafluorobenzene cation radicals $RC_6F_4H^{+\bullet}$

Radical cation	Charge density						SOMO density					
	C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6
1,2,3,4,5-$C_6F_5H^{+\bullet}$	0.318	0.252	0.117	0.252	0.318	−0.143	0.188	0.210	0.000	0.210	0.188	0.000
1,2,3,4-$C_6F_4H_2^{+\bullet}$	0.345	0.148	0.148	0.345	−0.029	−0.029	0.283	0.062	0.062	0.283	0.068	0.068
1,2,3,5-$C_6F_4H_2^{+\bullet}$	0.221	0.296	0.221	−0.104	0.387	−0.104	0.066	0.353	0.066	0.060	0.217	0.060
1,2,4,5-$C_6F_4H_2^{+\bullet}$	0.292	0.292	−0.127	0.292	0.292	−0.127	0.201	0.201	0.000	0.201	0.201	0.000
1-Br-2,3,4,5-$C_6F_4H^{+\bullet}$ [a]	−0.069	0.356	0.116	0.195	0.332	−0.050	0.113	0.263	0.026	0.101	0.257	0.029
1-Br-2,3,4,6-$C_6F_4H^{+\bullet}$ [a]	−0.138	0.200	0.275	0.268	−0.141	0.402	0.115	0.024	0.306	0.103	0.024	0.213
1-CF_3-2,3,4,6-$C_6F_4H^{+\bullet}$	−0.250	0.302	0.288	0.277	−0.089	0.431	0.105	0.355	0.038	0.089	0.192	0.037
1-CF_3-2,3,5,6-$C_6F_4H^{+\bullet}$	−0.251	0.343	0.288	−0.110	0.288	0.343	0.000	0.196	0.201	0.000	0.196	0.201

[a] The charge and SOMO density on the bromine atom are 0.201 and 0.047 (1-Br-2,3,4,5-$C_6F_4H^{+\bullet}$), 0.216 and 0.051 (1-Br-2,3,4,6-$C_6F_4H^{+\bullet}$). For the charge density of the molecules C_6F_5H and $C_6F_4H_2$ (isomers), see Ref. [22].

Table 2
^1H and ^{19}F NMR spectra of polyfluorinated cyclohexadienes and cyclohexenes (CH_2Cl_2, RT): chemical shifts

Compound	$\delta(^1H)$ (ppm)	$\delta(^{19}F)$ (ppm)				
		F-2	F-3	F-4	F-5	F-6
2	6.28		−104.42	−156.01	−156.01	−104.42
3	5.95(H-1) 7.00(H-6)	−129. 36	−109.66(A) −110.98(B)	−161.25	−140.10	−186.72
10	6.07	−129.31	−118.00	−129.31		−89.11
12	5.90	−124.47	−102.67		−124.47	−102.67
15	6.55		−104.12	−155.37	−154.76	−109.03
17	6.90	−119.96	−108.40	−158.69	−139.18	−187.94
18	6.42		−110.71	−135.53	−134.65	−115.32
19		−119.03	−112.48	−157.00	−152.80	−106.31
23 [a]	6.12	−117.00	−116.75	−128.46		−91.62
25 [b]	6.00	−110.08	−120.30		−119.10	−115.57
27	6.58		−102.81	−154.80	−153.20	−102.49
28	6.70		−108.44 or −109.37	−109.37 or −108.44	−133.38 or −135.16	−135.16 or −133.38
31	6.19	−120.54	−114.70	−128.25		−89.75
34	6.04	−116.06	−103.59		−121.79	−100.62

[a] −58.85 ppm (CF_3).

[b] −58.62 ppm (CF_3).

The most exciting aspect of these results is the fluorodeprotonation of polyfluorinated benzenes which was not reported until recently. For instance, Stavber and Zupan reported on the BF_3-catalyzed regiospecific addition of two fluorines to pentafluorobenzene to yield diene **5** but did not mention the formation of C_6F_6 [2]. In our opinion, the replacement of hydrogen by fluorine via an intermediate arylxenon(II) species is unlikely. Indeed, the cation $[C_6F_5Xe]^+$ is stable in anhydrous HF and no C_6F_6 is formed when fluoride ions (KF) are added. Furthermore, its decomposition by the fluoride anion (CsF) in acetonitrile leads to the formation of C_6F_5H and $C_6F_5C_6F_5$; C_6F_6 was not observed [7]. We assume that the reaction pathway involves the generation of polyfluorobenzene cation radicals as reactive key intermediates. It should be noted that the oxidation of polyfluoroaromatic compounds by XeF_2 in HF or HSO_3F to cation radicals was shown by electron spin resonance spectrometry [8].

In this case, further conversion of the initially generated cation radical intermediates should be determined by the distribution of the unpaired electron. Therefore we performed semiempirical MNDO calculation on $C_6F_5H^{+\bullet}$, isomeric $C_6F_4H_2^{+\bullet}$, two $C_6BrF_4H^{+\bullet}$ and two $CF_3C_6F_4H^{+\bullet}$ cation radicals in the half-electron approximation using the MNDO-90 program [9].

Table 1 displays the charge and unpaired electron density distributions obtained with fully optimized geometries. The results suggest a simple quantitative interpretation. The remarkable positive resonance effect of fluorine atoms on the highest π-MO of benzene is the main factor which determinates the single occupied molecular orbital (SOMO) structure of the cation radicals. The highly symmetric C_6H_6 or C_6F_6 molecules have doubly degenerate HOMOs (Fig. 1).

In going to fluorobenzene molecules of lower symmetry, the structure of these π-MOs varies slightly, but their energy levels are split. One of these MOs becomes the single occu-

Table 3
^1H and ^{19}F NMR spectra of polyfluorinated cyclohexadienes and cyclohexenes (CH_2Cl_2, RT): coupling constants

Compound	Coupling constants (Hz)											
	1,2	1,6	2,3	2,4	2,5	2,6	3,4	3,5	3,6	4,5	4,6	5,6
2 [a]		7	7				23	12			12	23
3 [b]	11	6 [c]	21			7 [d] 4 [c]	19	15	5 [d]	6	7 [d]	28 [d]
10	11	5	20.5			11	20.5		5	11	11	5
12 [a]	10	5	22	5		11	5	11		10	5	22
15			5			2	21		3.8	4.4	10.6	20.6
17 [e]						7.2 [d]	20	6.4	2 [d]	10.5	9.8 [d] 4.5 [c]	31 [d] 12 [c]
18				3			16			7		16
19			22.3		3	9.5	20.3	10.6	3.7	5	9.7	21
23 [f]							20			10	10	5.5
25			7		7	17	7	17		8		
27			6	5		5	19	11	5	6	12	22
31			23			10	21	1.8	4	10	10	4
34			22	6.7		11	5	11	5	10.5	5	22

[a] The signals involve the apparent coupling constants 5 Hz (diene **13**, F-3,3 and F-6,6), 2.5 Hz (diene **2**, F-3,3 and F-6,6), 6 Hz (diene **2**, F-4 and F-5).
[b] $J(1,3) \approx 7$ Hz, J(F-6,H-6) = 48 Hz.
[c] J(FH).
[d] J(FF).
[e] J(F-6,H-6) = 48.5 Hz.
[f] $J(CF_3$,F-2) = 19 Hz, $J(CF_3$,F-6) = 8 Hz.

Table 4
Fluorination of tetrafluorobenzenes C_6HF_4R with XeF_2 [a]

C_6HF_4R (mmol)	XeF_2 (mmol)	Conversion of substrate (%)	Products (% yield) [b]
C_6F_5H (1.97)	2.26	100	**5** (84), **7** (7), **8** (trace)
1,2,3,4-$C_6F_4H_2$ (1.22)	1.41	98	**2** (47), **3** (21), **4** (11), **5** (12), **6** (1), **7** (1.5)
1,2,3,5-$C_6F_4H_2$ (0.82)	0.88	96	**10** (52), **4** (30), **5** (13), **7**(trace)
1,2,4,5-$C_6F_4H_2$ (0.56)	0.60	100	**12** (92), **13** (4)
1-Br-2,3,4,6-C_6F_4H (1.19)	1.52	85	**31** (52), **32** (16)
1-Br-2,3,5,6-C_6F_4H (0.98)	1.08	87	**34** (80)
1-Br-2,3,4,5-C_6F_4H (0.79)	0.92	80	**27** (29), **28** (11), **29** (2)
1-NO_2-2,3,4,5-C_6F_4H (0.48)	0.68	96	**15** (51), **17** (9), **18** (7), **16** (3.5), **19** (15)
1-CF_3-2,3,5,6-C_6F_4H (0.85)	0.98	86	**24** (70), **25** (16)
1-CF_3-2,3,4,6-C_6F_4H (0.70)	0.82	100	**23** (74), **22** (19)
C_6F_5H* (0.54)	0.68	100	**5** (91), **7** (3), **8** (3)
1,2,3,5-$C_6F_4H_2^*$ (0.91)	0.99	86	**10** (50), **4** (25), **5** (7)
1,2,4,5-$C_6F_4H_2^*$ (0.62)	0.72	93	**12** (88), **13** (5)
1-Br-2,3,5,6-C_6F_4H* (0.50)	0.59	100	**34** (96)
1-CF_3-2,3,4,6-C_6F_4H* (0.60)	0.69	48	**23** (38), **22** (10)

[a] In HF. Fluorinations in CH_2Cl_2 are marked by an asterisk.
[b] Determined by quantitative ^{19}F NMR reference ($C_6H_5CF_3$).

pied one in the corresponding cation radical. The charge densities depend on the SOMO structure and on the charge distribution in the parent molecule. The latter is mainly determined by the strong σ-accepting ability of fluorine atoms (Fig. 2).

1,2,4,5-$C_6F_4H_2^{+\bullet}$: The charge distribution in this species favours nucleophilic attack at C-1, C-2, C-4 or C-5 atoms bearing equal positive charges (C-3 and C-6 are negatively charged). However, the calculated SOMO density on C-3 and C-6 is equal to zero (the SOMO has a nodal plane passing though these atoms). This is in agreement with the ESR data for 1,2,4,5-$C_6F_4H_2^{+\bullet}$ [10].

1,2,3,4-$C_6F_4H_2^{+\bullet}$: All carbon atoms bonded to fluorine possess positive charges, whereas C-5 and C-6 are negatively charged. The unpaired electron is predominantly located at positions 1 and 4, although a considerable amount of SOMO density is also cumulated in other positions. Hence, the attachment of 'hard' nucleophiles (charge-controlled reaction) should be expected at positions 1 and 4 rather than at 2

Fig. 1. The degenerate HOMO of benzene or hexafluorobenzene.

or 3. However, a radical partner can also attack the carbon atoms bonded to hydrogen.

1,2,3,5-$C_6F_4H_2^{+\bullet}$: According to the charge and SOMO density distribution, positions 2 and 5 are the most favoured sites of attachment for both nucleophiles and radicals. However, positions 1 and 3 are still accessible to nucleophiles, while radicals can also attack positions 1, 3, 4 and 6 as well.

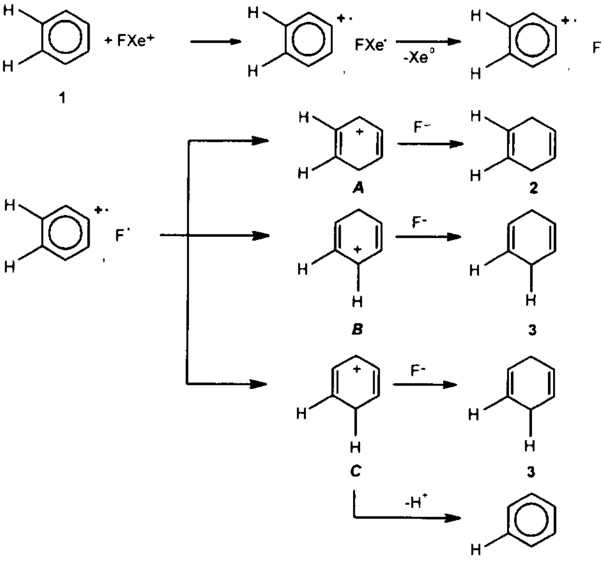
1,2,3,4,5-$C_6F_5H^{+\bullet}$: All carbon atoms bonded to fluorine are approachable by nucleophiles, but the attachment of radicals must be expected at positions 1, 2, 4 and 5 (see also the ESR spectral data [10]).

1-Br-2,3,4,5-$C_6F_4H^{+\bullet}$ and 1-Br-2,3,4,6-$C_6F_4H^{+\bullet}$: The charge and SOMO densities are distributed on carbon atoms similarly to those of the corresponding $C_6F_4H_2^{+\bullet}$ cation radicals. The only difference is the high positive charge on the bromine atom.

1-CF_3-2,3,4,6-$C_6F_4H^{+\bullet}$: The C-2, C-3, C-4 and C-6 atoms of the aromatic ring are positively charged, while the SOMO density is mainly located on C-2 and C-5.

1-CF_3-2,3,5,6-$C_6F_4H^{+\bullet}$: The charge and SOMO density distribution on the ring carbon atoms are nearly the same as those of the corresponding 1,2,4,5-$C_6F_4H_2^{+\bullet}$ cation radical.

Both reaction conditions (anhydrous HF and CH_2Cl_2, $BF_3 \cdot OR_2$) are acidic and thus do not favour the attack of strong nucleophiles like the fluoride ion. We assume the following scheme of fluorination which is characterized by radical attacks on the fluoroaromatic cation radical.

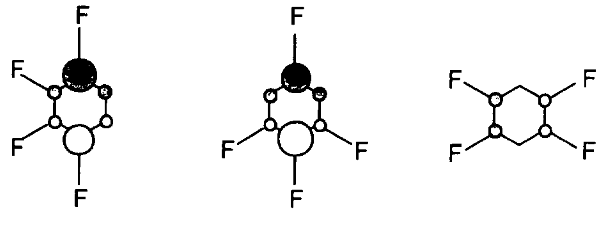


(All unmarked bonds are to fluorine)

The dissociation of the short-lived radical $FXe^\bullet$ to xenon and the fluorine atom was reported recently [11]. The recombination of $F^\bullet$ with the carbon radical partner in the solvent cage gives the polyfluorinated benzenonium cations A, B and C. Their further interaction with the fluoride anion leads to the formation of cyclohexadiene derivatives **2** and **3**. Alternatively, the loss of a proton from cation C results in pentafluorobenzene. Of course, the isomerization of polyfluorinated benzenonium cations cannot be excluded (cf. Ref. [12]). However, the presence of the thermodynamically unfavoured compound **3** with the H-C-F geminal moiety seems to indicate kinetic control in these processes.

This scheme accounts for the direction of fluorine addition to the aromatic ring of tetrafluorobenzenes C_6HF_4R, the fluorodeprotonation of compounds **1**, **9**, **14**, **20** and **26**, as well as the absence of the latter process in the case of compounds **11**, **21** and **33**. Indeed, the SOMO nodal plane, i.e. zero magnitude of the SOMO density on C-3 and C-6 in 1,2,4,5-$C_6F_4H_2^{+\bullet}$ and on C-1 and C-4 in 1-CF_3-2,3,5,6-$C_6F_4H^{+\bullet}$ prevents recombination of the cation radical with the fluorine atom at these sites. The fluorodeprotonation of pentafluorobenzene formally conflicts with the absence of the SOMO density at C-3 and C-6 in $C_6F_5H^{+\bullet}$. This contradiction is eliminated if we assume the excitation of $C_6F_5H^{+\bullet}$. It is noteworthy that the lowest excited state of $C_6F_5H^{+\bullet}$ is characterized by the maximum SOMO density on C-3 and C-6. The energy gap between the ground and first excited state is 0.2 eV for $C_6F_5H^{+\bullet}$ and 0.3, 0.4 and 0.7 eV for 1,2,3,4-$C_6F_4H_2^{+\bullet}$, 1,2,3,5-$C_6F_4H_2^{+\bullet}$ and 1,2,4,5-$C_6F_4H_2^{+\bullet}$, respectively [13]. The probable source of excitation may be the 'hot' fluorine atom derived from the FXe^- radical. However, addition of the fluoride anion to $C_6F_5H^{+\bullet}$ in the ground state cannot be excluded either (cf. Ref. [14]).

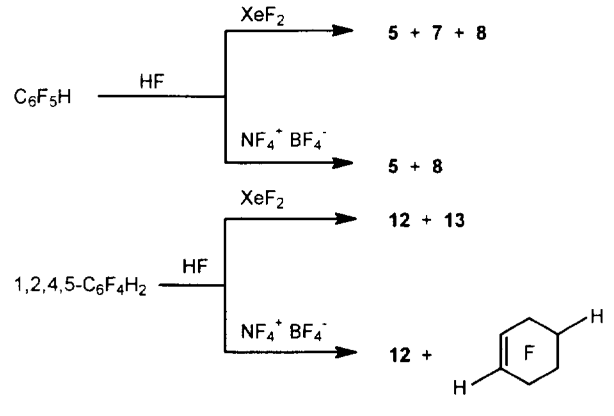
Fluorination of 1-Br-2,3,4,6-C_6F_4H proceeded without fluorodeprotonation, although there is negligible difference in the charge and SOMO density distributions on the corresponding carbon atoms in 1-Br-2,3,4,6-$C_6F_4H^{+\bullet}$ and 1,2,3,5-$C_6F_4H_2^{+\bullet}$ (Table 1). A peculiarity of this bromotetrafluorobenzene and its isomer **26** is the formation of polyfluorinated bromocyclohexenes. We do not exclude an attack on the positivity charged bromine atom by the fluoride anion and intermediate formation of a two-coordinated bromine-containing species (the SOMO density on bromine is negligible). This assumption agrees with the interpretation of the reactivity of the chemically or electrochemically generated bromobenzene cation radicals $RC_6H_4Br^{+\bullet}$ [15].



1,2,3,4-$C_6F_4H_2^{+\bullet}$ 1,2,3,5-$C_6F_4H_2^{+\bullet}$ 1,2,4,5-$C_6F_4H_2^{+\bullet}$

Fig. 2. The SOMOs of tetrafluorobenzene cation radicals.

The results obtained may be compared with fluorination of pentafluorobenzene or 1,2,4,5-tetrafluorobenzene with $NF_4^+ BF_4^-$ in HF [16].



There is an obvious similarity between both electrophilic fluorooxidants, which display partial fluorodeprotonation of pentafluorobenzene, the absence of this process for 1,2,4,5-tetrafluorobenzene and fluorine addition to the aromatic ring. It should be noted that the NF_4^+ cation also seems to be a one-electron oxidant.

The composition of reaction mixtures and the structure of products were determined by ^1H and ^{19}F NMR spectrometry. The resonances of polyfluorinated 1,3- and 1,4-cyclohexadienes and cyclohexenes were assigned using the known spectral-structure correlations. Compound **32** derived from 1-bromo-2,3,4,6-tetrafluorobenzene was identified as 1-bromo-3*H*-heptafluorocyclohexene. Indeed, the ^{19}F NMR spectrum of compound **32** contains resonances at − 102.10, − 105.00 (J_{AB} = 230 Hz); − 123.72, − 127.40 ppm (J_{AB} = 280 Hz); − 132.51, − 137.29 (J_{AB} = 270 Hz) ppm (three AB systems, F-6,6 or 4,4 or 5,5 respectively), a multiplet at − 108.33 (F-2) ppm and a resonance at − 198.66 [dd, J = 32 Hz, J_{HF} = 45 Hz] (F-3) ppm. An alternative structure for 1-bromo-5*H*-heptafluorocyclohexene seems to be less possible because in this case the resonances of two difluoromethylene groups should be located at − 100 ppm to − 120 ppm, as for those of bromononafluorocyclohexene and 1,2-dibromooctafluorocyclohexene [17].

4. Experimental details

The NMR spectra were measured on Bruker WP 80 SY, 200 SY or AC 200 spectrometers (^1H at 80 or 200 MHz and ^{19}F at 75.40 or 188.28 MHz) using the internal references TMS or C_6F_6. The chemical shifts $\delta(^{19}F)$ are referred to $CFCl_3$ using $\delta(C_6F_6) = -162.9$ ppm. The ^1H and ^{19}F NMR spectra of compounds **5** and **8** [2] and of **6**, **13**, **24** [17] have been described previously. Compounds **2**, **10** [18], **12** [18,19], **34** [20] and **19** [21] were partially characterized by NMR spectroscopy and their ^1H, ^{19}F NMR data are given in Table 2 and Table 3 together with those of the new compounds **3**, **15**, **17**, **18**, **25**, **27**, **28**, and **31**.

4.1. *Fluorination of tetrafluorobenzenes C_6HF_4R with XeF_2 (general procedure)*

Method A Tetrafluorobenzene C_6HF_4R and anhydrous HF (0.2–0.4 ml) were loaded in an FEP reactor, cooled to − 10 to − 5 °C, and XeF_2 added in portions. After each addition, the reaction mixture was warmed up to room temperature with shaking until the evolution of the xenon gas ceased. The total reaction time was 15–25 min. The fluorination of nitrotetrafluorobenzene **14** was carried out at 35 °C for 4 h. Finally, dichloromethane (0.3–0.5 ml) was added and HF distilled off. The internal quantitative reference (benzotrifluoride) was then added and NMR spectra measured.

Method B Xenon difluoride was added in portions to a solution of tetrafluorobenzene C_6HF_4R and $BF_3 \cdot OEt_2$ (ca. 10 mol%) in dichloromethane (0.2–0.4 ml) at − 10 to − 5 °C. After each addition, the reaction mixture was warmed up to room temperature with shaking until the liberation of the xenon gas ceased. After ca. 20 min the reaction was completed, and NMR analysis was performed as described above.

The results are presented in Table 4.

Acknowledgements

We gratefully thank Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

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