

Journal of Fluorine Chemistry 77 (1996) 153-159



Fluorination of tetrafluorobenzenes C₆HF₄R with XeF₂

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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 XeF₂ 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 XeF₂ with benzenes C₆H₅R lead to the formation of fluorobenzenes C₆H₄FR, whereas pentafluorobenzenes C₆F₅R undergo 1,4addition of two fluorine atoms. For instance, the BF₃-catalyzed fluorination of C₆F₅R (R = H, F, Cl, Br, C₆F₅ [2], SiMe₃, SiMe₂F, SiMe₂C₆F₅, GeEt₃ [3]) with XeF₂ in CH₂Cl₂ resulted in 1-R-heptafluoro-1,4-cyclohexadienes. Strong electron-withdrawing groups R = CN, NO₂ [2], SiCl₃, SiF₃, GeCl₃, GeF₃ [3] deactivate the polyfluoroaromatic ring, and the fluorinating system XeF₂-CH₂Cl₂-BF₃ (or BF₃·OEt₂) is ineffective. Ring fluorinations of C₆F₅NO₂, 4-NO₂C₆F₄CF₃ [4], C₆F₅SiF₃, C₆F₅GeF₃ [3], C₆F₅CN [5] and [C₆F₃Xe]⁺ [AsF₆]⁻ [6] have been performed with more powerful fluorooxidants XeF₂-HF or XeF⁺ MF₆⁻ (M = Sb or Nb).

Previous reports indicate that XeF₂ (CH₂Cl₂, BF₃·OR₂) adds fluorine to C₆F₅H [2], but nothing was known about the interaction of XeF₂ with tetrafluorobenzenes. Competitive pathways involving fluorine addition and fluorodeprotonation in the case of the interaction of XeF₂ with highly fluorinated benzenes had not been investigated. Here we report the interaction of some tetrafluorobenzene derivatives C₆HF₄R (R=H, F, Br, CF₃, or NO₂) with XeF₂ in anhydrous HF or CH₂Cl₂-BF₃·OEt₂.

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 1H-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-Hhexafluoro-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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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 XeF₂ 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.



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.



The interaction of xenon difluoride with bromotetrafluorobenzenes proceeded in a more complex way. 1-Bromo-2Hhexafluoro-1,4-cyclohexadiene (27) (major component), 1-bromo-2H-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 $[J_{HF} = 48 \text{ Hz}]$ in the ¹⁹F NMR spectrum seems to indicate the presence of bromooctafluorocyclohexenes with the H-C-F geminal moiety, but their structures were not determined.



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 ¹⁹F NMR spectroscopy.



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 XeF₂ in CH₂Cl₂ in the presence of BF₃ · OEt₂ (catalytic amount) proceeded analogously to that in liquid HF. Additionally, in CH₂Cl₂, partial conversion of the solvent into CH₂FCl and CHF₂Cl was found.

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

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 ₄ F ₄ H ⁺⁺	0.318	0.252	0.117	0.252	0.318	-0.143	0.188	0.210	0.000	0.210	0.188	0.000
$1,2,3,4-C_{6}F_{4}H_{2}^{+}$	0.345	0.148	0.148	0.345	-0.029	-0.029	0.283	0.062	0.062	0.283	0.068	0.068
$1,2,3,5-C_{6}F_{4}H_{2}^{+}$	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 ₆ F ₄ H ₂ ⁺	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 ₆ F ₄ H ^{+**}	-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 ₆ F ₄ H ^{+*} *	-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 ₄ F ₄ H ⁺	-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 ₆ F ₄ H ⁺	- 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-C₆F₄H⁺⁺), 0.216 and 0.051 (1-Br-2,3,4,6-C₆F₄H⁺⁺). For the charge density of the molecules C₆F₅H and C₆F₄H₂ (isomers), see Ref. [22].

Table 2 ¹H and ¹⁹F NMR spectra of polyfluorinated cyclohexadienes and cyclohexenes (CH₂Cl₂, RT): chemical shifts

Compound	δ(¹ H)	δ(¹⁹ F) (pp	$\delta(^{19}\text{F}) \text{ (ppm)}$						
	(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	- 133.38 or	-135.16 or			
				- 108.44	-135.16	-133.38			
31	6.19	120.54	-114.70	- 128.25		- 89.75			
34	6.04	- 116.06	- 103.59		- 121.79	-100.62			

 $a - 58.85 \text{ ppm (CF_3)}.$

^b - 58.62 ppm (CF₃).

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 BF₃-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 C₆F₅H and C₆F₅C₆F₅; C₆F₆ 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 XeF₂ in HF or HSO₃F 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 $C_6F_5H^{++}$, isomeric $C_6F_4H_2^{++}$, two $C_6BrF_4H^{++}$ and two $CF_3C_6F_4H^{++}$ 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 C₆H₆ or C₆F₆ 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 occu12 *

15

17 °

18

19

23 ^f

25

27

31

34

11

2

7.2 ^d

9.5

17

5

10

11

5

21

20

16

20

7

19

21

5

20.3

11

6.4

10.6

17

11

11

1.8

¹ H and ¹⁹ F NMR spectra of polyfluorinated cyclohexadienes and cyclohexenes (CH ₂ Cl ₂ , RT): coupling constants													
Compound	Coupling	Coupling constants (Hz)											
	1,2	1,6	2,3	2,4	2,5	2,6	3,4	3,5	3,6	4,5			
2 *		7	7				23	12					
3 ^b	11	6 °	21			7 ^d 4 ^c	19	15	5 ª	6			
10	11	5	20.5			11	20.5		5	11			

5

3

5

6.7

Table 3 ¹H and ¹⁹F NMR spectra of polyfluorinated cyclohexadienes and cyclohexenes (CH₂Cl₂, RT): coupling constants

* 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).

3

7

^b $J(1,3) \approx 7$ Hz, J(F-6,H-6) = 48 Hz.

10

° J(FH).

^d J(FF).

 $^{\circ}$ J(F-6,H-6) = 48.5 Hz.

 $^{f} J(CF_{3},F-2) = 19 \text{ Hz}, J(CF_{3},F-6) = 8 \text{ Hz}.$

Table 4

Fluorination of tetrafluorobenzenes C₆HF₄R with XeF₂ ^a

5

22

5

22.3

7

6

23

22

C ₆ HF₄R (mmol)	XeF ₂ (mmol)	Conversion of substrate (%)	Products (% yield) ^b		
C ₆ F ₅ H (1.97)	2.26	100	5 (84), 7 (7), 8 (trace)		
$1,2,3,4-C_{c}F_{4}H_{2}$ (1.22)	1.41	98	2 (47), 3 (21), 4 (11), 5 (12), 6 (1), 7 (1.5)		
$1,2,3,5-C_{a}F_{a}H_{2}(0.82)$	0.88	96	10 (52), 4 (30), 5 (13), 7(trace)		
$1,2,4,5-C_{a}F_{4}H_{2}(0.56)$	0.60	100	12 (92), 13 (4)		
1-Br-2,3,4,6-C FAH (1.19)	1.52	85	31 (52), 32 (16)		
1-Br-2,3,5,6-C FAH (0.98)	1.08	87	34 (80)		
1-Br-2,3,4,5-C FAH (0.79)	0.92	80	27 (29), 28 (11), 29 (2)		
1-NO2-2,3,4,5-C F4H (0.48)	0.68	96	15 (51), 17 (9), 18 (7), 16 (3.5), 19 (15)		
1-CF ₃ -2.3.5.6-C ₄ F ₄ H (0.85)	0.98	86	24 (70), 25 (16)		
1-CF ₃ -2.3.4.6-C ₄ F ₄ H (0.70)	0.82	100	23 (74), 22 (19)		
C_F_H* (0.54)	0.68	100	5 (91), 7 (3), 8 (3)		
1.2.3.5-C.F.H* (0.91)	0.99	86	10 (50), 4 (25), 5 (7)		
$1.2.4.5-C_{4}F_{4}H^{*}(0.62)$	0.72	93	12 (88), 13 (5)		
1-Br-2.3.5.6-C.F.H* (0.50)	0.59	100	34 (96)		
1-CF ₃ -2,3,4,6-C ₆ F ₄ H* (0.60)	0.69	48	23 (38), 22 (10)		

* In HF. Fluorinations in CH₂Cl₂ are marked by an asterisk.

^b Determined by quantitative ¹⁹F 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- $C_6F_4H_2^+$: 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-C₆F₄H₂^{+•} [10].

4,6

12

11

5

10.6

9.8 ^d

4.5 °

9.7

10

12

10

5

10

4.4

10.5

7

5

10

8

6

10

10.5

3.8

2 ^d

3.7

5

4

5

7 ^d

5,6

23

28 d

5

22

20.6

31 d

12 °

16

21

22

4

22

5.5

 $1,2,3,4-C_6F_4H_2^+$: 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.

 $1,2,3,5-C_6F_4H_2^+$: 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- $C_6F_5H^+$: 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- $C_6F_4H^{+*}$ and 1-Br-2,3,4,6- $C_6F_4H^{+*}$: The charge and SOMO densities are distributed on carbon atoms similarly to those of the corresponding $C_6F_4H_2^{+*}$ cation radicals. The only difference is the high positive charge on the bromine atom.

 $1-CF_3-2,3,4,6-C_6F_4H^+$: 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.

 $1-CF_3-2,3,5,6-C_6F_4H^{+*}$: The charge and SOMO density distribution on the ring carbon atoms are nearly the same as those of the corresponding $1,2,4,5-C_6F_4H_2^{+*}$ 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[•] to xenon and the fluorine atom was reported recently [11]. The recombination of F 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 penta-fluorobenzene. 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-C₆F₄H₂^{+•} and on C-1 and C-4 in 1-CF₃-2,3,5,6-C₆F₄H^{+•} 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 $C_6F_5H^{+*}$. This contradiction is eliminated if we assume the excitation of $C_6F_5H^{+*}$. It is noteworthy that the lowest excited state of $C_6F_5H^{++}$ 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 $C_6F_5H^{+*}$ and 0.3, 0.4 and 0.7 eV for 1,2,3,4- $C_6F_4H_2^{+*}$, $1,2,3,5-C_6F_4H_2^+$ and $1,2,4,5-C_6F_4H_2^+$, 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 $C_6F_5H^{+}$ in the ground state cannot be excluded either (cf. Ref. [14]).

Fluorination of 1-Br-2,3,4,6-C₆F₄H 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-C₆F₄H^{+•} and 1,2,3,5-C₆F₄H₂^{+•} (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 brominecontaining 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 RC₆H₄Br⁺⁺ [15].



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 NF₄⁺ cation also seems to be a one-electron oxidant.

The composition of reaction mixtures and the structure of products were determined by ¹H and ¹⁹F 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-3H-heptafluorocyclohexene. Indeed, the ¹⁹F NMR spectrum of compound 32 contains resonances at -102.10, -105.00 (J_{AB} = 230 Hz); -123.72, -127.40 ppm $(J_{AB} = 280 \text{ Hz}); -132.51, -137.29 (J_{AB} = 270 \text{ Hz}) \text{ ppm}$ (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-5H-heptafluorocyclohexene seems to be less possible because in this case the resonances of two diffuoromethylene 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 ¹⁹F at 75.40 or 188.28 MHz) using the internal references TMS or C₆F₆. The chemical shifts δ (¹⁹F) are referred to CFCl₃ using δ (C₆F₆) = -162.9 ppm. The ¹H and ¹⁹F 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, ¹⁹F 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 XeF₂ 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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