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BF_3-Catalyzed Fluorine Addition to Fluoro-Substituted Benzene Derivatives Using Xenon Difluoride

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BF_3-catalyzed room-temperature reaction of xenon difluoride with pentafluoro-substituted benzene derivatives resulted in 1,4- and 1,2-fluorine addition with regiospecificity depending on the substituent. Reaction with 1-substituted (H, Cl, Br, C_6F_5) pentafluorobenzene resulted in the formation of 1-substituted heptafluorocyclohexa-1,4-dienes, and reactions with *n*-alkoxy-substituted pentafluorobenzenes resulted in two types of 1,4-adducts, while reaction with isopropoxypentafluorobenzene resulted in the formation of hexafluorocyclohexa-2,5-dien-1-one and hexafluorocyclohexa-2,4-dien-1-one.

Results and Discussion

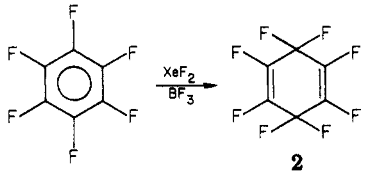
Perfluoroaromatic molecules react with electrophilic reagents under rigorous reaction conditions, while reactions with nucleophiles are typical examples of this class of compound.[1] Hexafluorobenzene reacted with elemental fluorine at 0 °C, giving a complex reaction mixture,[2] while reaction with a mixture of cobalt(III) fluoride and calcium fluoride could be adjusted so that only octafluorocyclohexa-1,4-diene and decafluorocyclohexene were formed.[3]

It has been demonstrated that xenon difluoride is an easy handling, mild reagent for the fluorination of alkenes, acetylenes, aromatic molecules, and some organic molecules containing heteroatoms, and the topic was recently reviewed.[4] Fluorination with xenon difluoride can usually be successful only in the presence of a catalyst, the choice of which depends on the structure of the substrate and its reactivity. The following substrates have been shown to be convenient catalysts: HF, HF/pyridine, CF_3COOH, Br_2, pentafluorothiophenol, BF_3 etherate, BF_3.

We now report that BF_3 is a convenient catalyst for fluorine addition to fluoro-substituted benzene derivatives using xenon difluoride. In a typical experiment, 2 mmol of fluoro-substituted benzene derivatives was dissolved in 4 mL of methylene chloride, 2 mmol of xenon difluoride was added at room temperature, and boron trifluoride was introduced into the reaction mixture. The reaction was complete in 10–30 min. After the usual workup, the crude reaction mixture was analyzed by ^{19}F NMR spectroscopy and the products were isolated by preparative GLC. The crude reaction mixture obtained from hexafluorobenzene (1, Scheme I) shows only two signals in its ^{19}F NMR spectrum at −113 and −156 ppm in the ratio 1:1. After purification by GLC, 74% octafluorocyclohexa-1,4-diene (2) was isolated.

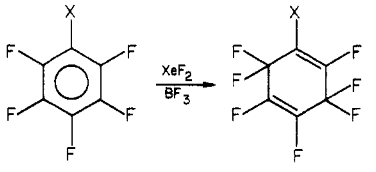
Further, we have studied the regioselectivity of fluorine addition to various pentafluoro-substituted benzene derivatives and found that fluorination of chloropentafluorobenzene (**3a**, Scheme II) resulted in the formation of only one product.

Scheme I



1 2

Scheme II



3a, X = Cl
b, X = Br
c, X = C_6F_5
d, X = H

4

The complete assignment of the NMR spectrum was possible on the basis of a spin–spin decoupling experiment. On the basis of the spectroscopic data we established that 1-chloroheptafluorohexa-1,4-diene (**4a**) was formed. The same regiospecificity of fluorine addition was also observed by bromopentafluorobenzene (**3b**), decafluorobiphenyl (**3c**), and pentafluorobenzene (**3d**). The NMR data of the adducts are presented in Table I. The dependence of the fluorine chemical shifts for F_2 and F_6 in 1-substituted heptafluorocyclohexa-1,4-dienes on the Pauling electronegativity of the halogen atoms is presented in Figure 1. The correlation is good, and it can also be seen that the influence of the halogen atom on δ_{F_2} ($\Delta\delta$ F_2/Δ electronegativity = 28) is greater than on δ_{F_6} ($\Delta\delta$ F_6/Δ electronegativity = 5.5). The conformations of cyclohexa-1,4-dienes have been studied extensively and a planar structure was suggested.[5] The equivalence of the two fluorine atoms on C_3 and C_6 was shown by ^{19}F NMR spectroscopy and this equivalence remained even when 1-chloroheptafluorocyclohexa-1,4-diene was cooled to −135 °C, thus indicating that under these conditions the planar conformation is probably preferred.

The mass spectra of 1-substituted heptafluorocyclohexa-1,4-dienes are also of interest, the loss of a CF_3 radical being most notable at 70 eV. Similar fragmentation has also been observed by 9,9,10,10-tetrafluoro-9,10-dihydrophenanthrene.[6] The three possible pathways leading to the fragment $M^+ - CF_3$ are presented in Table II, and in the case of 1-pentafluorophenylheptafluorocyclohexa-1,4-diene, all three pathways were confirmed by metastable fragments (values noted in Table II). The effect of the structure of heptafluorocyclohexa-1,4-dienes is also pres-

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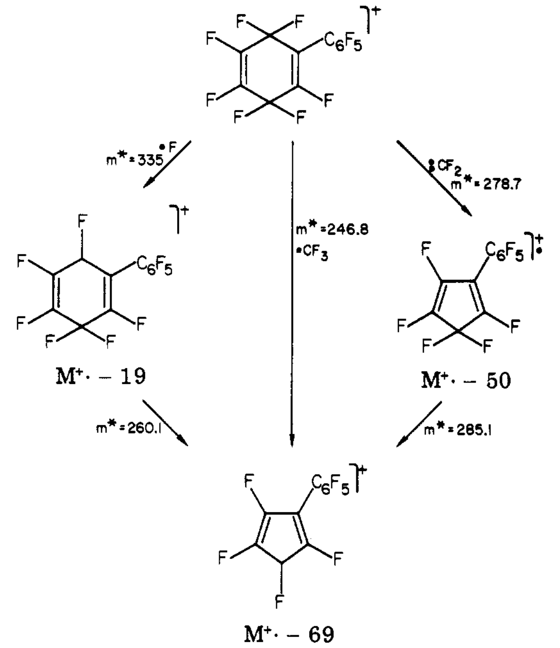
Table I. NMR Data for Heptafluorocyclohexa-1,4-dienes (4)

X	chemical shifts, δ					
	F_2	F_3	F_4	F_5	F_6	H
H	−129 (ttdd)	−116 (dddtd)	−156 (ttdd)	−161 (ttd)	−102 (dddtd)	5.75 (m)
Cl	−131 (ttd)	−115 (dddt)	−156 (ttdd)	−161 (ttd)	−108 (dddt)	
Br	−122 (ttd)	−115 (dddt)	−156 (ttdd)	−162 (ttd)	−105 (dddt)	
C_6F_5	−124 (ttd)	−116 (dddt)	−156 (ttdd)	−161 (ttd)	−107 (dddt)	

X	coupling constants, Hz								
	$^3J_{F_2F_3}$	$^4J_{F_2F_4}$	$^4J_{F_2F_6}$	$^3J_{F_3F_4}$	$^4J_{F_3F_5}$	$^5J_{F_3F_5}$	$^3J_{F_4F_5}$	$^4J_{F_4F_6}$	$^3J_{F_5F_6}$
H[a]	21.0	2.0	10.5	21.10	10.5	5.25	6.0	10.5	21.0
Cl	24.0	3.0	10.5	21.5	10.5	5.25	6.0	10.5	22.5
Br	24.0	3.0	11.5	30.0	12.0	6.0	6.0	11.5	24.0
C_6F_5	22.5	3.0	11.25	22.5	11.25	5.5	5.5	11.25	22.5

[a] $^3J_{F_2H} = 10.5$, $^3J_{F_6H} = 5.25$, $^4J_{F_3H} = 2$ Hz.

Table II. Mass Spectral Data [*m/e* (Relative Intensity, %)]



compd	$M^{+\cdot}$	$M^{+\cdot} - F$	$M^{+\cdot} - CF_2$	$M^{+\cdot} - CF_3$
4c	372 (100)	353 (45)	322 (40)	303 (70)
4d	206 (45)	187 (43)	156 (28)	137 (100)
2	224 (22)	205 (58)	174 (24)	155 (100)

ented, while in the case of chloro, bromo, and alkoxy derivatives, other fragmentations also accompanied the above mentioned pathways.

Further, we have studied the effect of electron-withdrawing groups (X = CN, NO_2) bonded to the pentafluorobenzene ring on fluorine addition with xenon difluoride and found that both molecules remained unchanged, while reaction with alkoxy pentafluoro derivatives occurred more quickly than with hexafluorobenzene. A 20-min reaction of xenon difluoride with pentafluoroanisole (**5a**, Scheme III) resulted in the formation of two products in the ratio 1:1, which could be separated by preparative GLC.

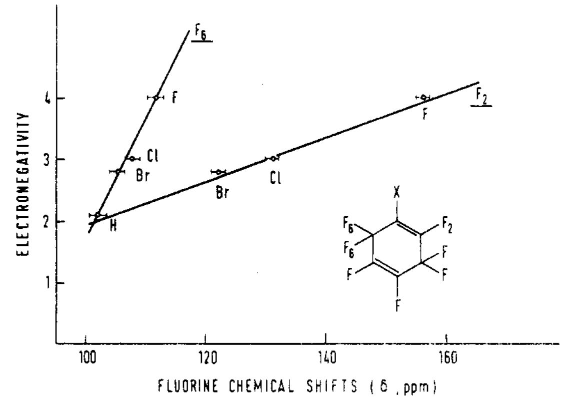
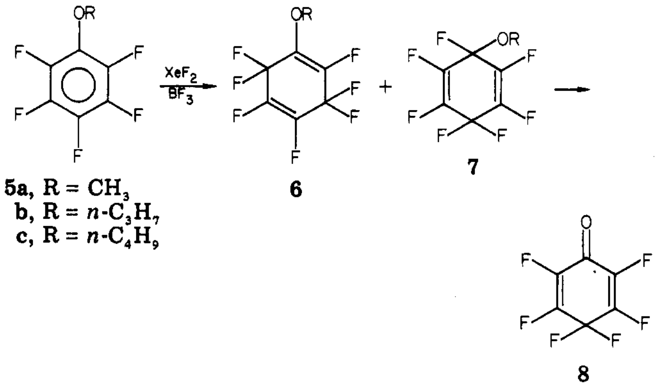


Figure 1.

Scheme III

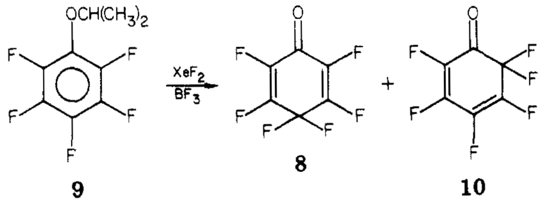


On the basis of the spectroscopic data we established that 1-methoxyheptafluorocyclohexa-1,4-diene (**6a**) was formed. The second product was assigned as 3-methoxyheptafluorocyclohexa-1,4-diene (**7a**). Product **7a** is unstable under the reaction conditions and in the case of longer reactions times (*t* = 60 min), it transformed into hexafluorocyclohexa-2,5-dien-1-one (**8**). Reactions with *n*-propoxy- (**5b**) and *n*-butoxy- (**5c**) pentafluorobenzenes also resulted in 1-alkoxyheptafluorocyclohexa-1,4-dienes (**6b**, **6c**), their NMR data being presented in Table III, while no evidence for 3-alkoxyheptafluorocyclohexa-1,4-diene

Table III. NMR Data (Chemical Shifts, δ) for 1-Alkoxyheptafluorocyclohexa-1,4-dienes (6)

R	F_2	F_3	F_4	F_5	F_6	OCH_2R
CH_3	−167.5 (m)	−112.5 (dddt)	−159 (m)	−160.5 (ttd)	−111.5 (dddt)	4.15 (d)
CH_2CH_3	−166.5 (m)	−113.5 (dddt)	−159.5 (m)	−161 (ttd)	−112.5 (dddt)	4.3 (gd)
$(CH_2)_2CH_3$	165.5 (m)	−112 (dddt)	−159 (m)	−160.5 (ttd)	−111 (dddt)	4.15 (td)
$(CH_2)_3CH_3$	−165 (m)	−112 (dddt)	−159.5 (m)	−161 (ttd)	−111 (dddt)	4.25 (td)

Scheme IV



was found, and only hexafluorocyclohexa-2,5-dien-1-one (8) was isolated. Reactions of xenon difluoride with *n*-alkoxypentafluorobenzene derivatives (5) resulted in two types of 1,4-fluorine addition, while reaction with isopropoxypentafluorobenzene (9, Scheme IV) resulted in the formation of hexafluorocyclohexa-2,5-dien-1-one (8) and hexafluorocyclohexa-2,4-dien-1-one (10) in the ratio 1:1, which could be explained by 1,4- and 1,2-fluorine addition.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 727B spectrometer and ^1H and ^{19}F NMR spectra by a JEOL-C60 HL from CCl_4 solutions with $SiMe_4$ or CCl_3F as internal reference. Mass spectra and high-resolution measurements were taken on a CEC-21-110 spectrometer. Gas-liquid partition chromatography was carried out on a Varian Aerograph Model 1800. Boron trifluoride of Fluka Purum quality was used without further purification, while methylene chloride was purified and stored over molecular sieves. Xenon difluoride was prepared by a photosynthetic method[7] and its purity was better than 99.5%.

Addition and Isolation Procedures. To a solution of 2 mmol of 1-substituted pentafluorobenzene derivative in methylene chloride (4 mL) in a Kel-F vessel was added 2 mmol of xenon difluoride at 25 °C, and under stirring, anhydrous boron trifluoride (trace amounts) was introduced into the reaction mixture. After 10–30 min xenon gas evolution ceased and the reaction appeared to be complete. The solvent was partially removed by distillation under reduced pressure, the crude reaction mixture was analyzed by ^{19}F NMR and the products were isolated by preparative GLC.

Fluorination of Hexafluorobenzene (1). The product was isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 35 °C).

Octafluorocyclohexa-1,4-diene (2): yield 330 mg (74%); bp 58–59 °C (lit.[8] bp 57–58 °C); NMR data are in agreement with the literature ones;[9] mass spectrum, *m/e* 224 (M^+, 22), 205 (58), 174 (24), 155 (100), 124 (50), 117 (38), 93 (40), 69 (32).

Fluorination of Chloropentafluorobenzene (3a). The product was isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 35 °C).

1-Chloroheptafluorocyclohexa-1,4-diene (4a): yield 395 mg (83%); bp 84–85 °C (lit.[10] bp 83–84 °C); NMR data are stated in Table I; mass spectrum, *m/e* 242 ($M^+ + 2$, 5), 240 (M^+, 15), 223 (16), 221 (48), 205 (74), 190 (18), 186 (60), 173 (20), 171 (60), 155 (100), 117 (95), 98 (50), 93 (70), 86 (50), 79 (50), 74 (50), 69 (50).

Fluorination of Bromopentafluorobenzene (3b). The product was isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 75 °C).

1-Bromoheptafluorocyclohexa-1,4-diene (4b): yield 460 mg (81%); bp 94–96 °C (lit.[11] bp 96–98 °C); NMR data are stated in Table I; mass spectrum, *m/e* 286 ($M^+ + 2$, 28), 284 (M^+, 28), 205 (100), 186 (60), 144 (78), 107 (55), 83 (37), 69 (25).

Fluorination of Decafluorobiphenyl (3c). The product was isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 125 °C).

1-(Pentafluorophenyl)heptafluorocyclohexa-1,4-diene (4c): yield 540 mg (73%); mp 46–46.5 °C; NMR data are stated in Table I; mass spectrum, mol wt calcd for $C_{12}F_{12}$ 371.9809, found 371.9810, *m/e* 372 (M^+, 100), 353 (45), 322 (40), 303 (70), 272 (25), 265 (10), 241 (10), 233 (10), 141 (10), 118 (15), 94 (18), 69 (18).

Fluorination of Pentafluorobenzene (3d). The product was isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 35 °C).

2,3,3,4,5,6,6-Heptafluorocyclohexa-1,4-diene (4d): yield 310 mg (75%); bp 66–68 °C (lit.[11] bp 67–68 °C); NMR data are stated in Table I; mass spectrum, *m/e* 206 (M^+, 45), 187 (43), 156 (28), 137 (100), 106 (23), 69 (20).

Fluorination of Pentafluoroanisole (5a). The products were isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 80 °C).

1-Methoxyheptafluorocyclohexa-1,4-diene (6a): yield 135 mg (29%); bp 116–117 °C (lit.[12] bp 114 °C); NMR data are presented in Table III; mass spectrum, *m/e* 236 (M^+, 100), 217 (50), 193 (80), 186 (25), 183 (25), 174 (27), 155 (33), 143 (88), 124 (60), 117 (28), 93 (58), 81 (43), 74 (17), 69 (30).

3-Methoxyheptafluorocyclohexa-1,4-diene (7a): yield 120 mg (25%); bp 109–110 °C (lit.[12] bp 108 °C); NMR data are in agreement with the literature ones;[12] mass spectrum, *m/e* 236 (M^+, 30), 217 (35), 205 (90), 194 (40), 186 (35), 183 (20), 174 (18), 155 (100), 143 (45), 124 (40), 117 (60), 98 (18), 93 (60), 86 (20), 81 (40), 74 (20), 69 (38).

Fluorination of 1-*n*-Propoxypentafluorobenzene (5b). The products were isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 100 °C.

1-*n*-Propoxyheptafluorocyclohexa-1,4-diene (6b): yield 150 mg (28%); bp 132–133 °C; NMR data are stated in Table III; mass spectrum, mol wt calcd for $C_9H_7OF_7$ 264.0497, found 264.0386, *m/e* 264 (M^+, 5), 245 (6), 203 (10), 183 (15), 43 (100).

Hexafluorocyclohexa-2,5-dien-1-one (8): yield 65 mg (16%); bp 114–115 °C (lit.[12] bp 113–115 °C); NMR δ −152 (m, 2 F, F_2, F_6), −146 (tm, 2 F, F_3, F_5), −116 (tt, 2 F, F_4) ($^3J_{F_3F_4} = 20$, $^4J_{F_2F_4} = 10$ Hz); mass spectrum, *m/e* 202 (M^+, 73), 183 (15), 174 (20), 155 (30), 124 (100), 117 (10), 112 (10), 105 (15), 93 (33), 74 (15), 69 (20); IR $\nu_{C=O}$ 1650 cm^{-1}.

Fluorination of 1-*n*-Butoxypentafluorobenzene (5c). The products were isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 110 °C).

1-*n*-Butoxyheptafluorocyclohexa-1,4-diene (6c): yield 130 mg (23%); bp 141–143 °C; NMR data are stated in Table III; mass spectrum, mol wt calcd for $C_{10}H_9OF_7$ 278.0541, found 278.0550, *m/e* 278 (M^+, 3), 222 (5), 203 (10), 182 (15), 57 (100), 41 (60).

Hexafluorocyclohexa-2,5-dien-1-one (8): yield 70 mg (17%).

Fluorination of 1-Isopropoxypentafluorobenzene (9). The products were isolated by preparative GLC (12% DDP-Chromosorb Regular 100 at 90 °C).

Hexafluorocyclohexa-2,4-dien-1-one (10): yield 80 mg (20%); bp 118–119 °C; NMR δ −114 (m, 2 F, F_6), −134.5 (m, 1 F), −155 (m, 1 F), −157 (m, 1 F), −162 (m, 1 F); mass spectrum, mol wt calcd for C_6OF_6 201.9853, found 201.9860, *m/e* 202 (M^+, 70), 183 (18) 174 (30), 155 (30), 124 (100), 117 (8), 105 (12), 93 (30), 74 (20), 69 (24); IR $\nu_{C=O}$ 1650 cm^{-1}.

Hexafluorocyclohexa-2,5-dien-1-one (8): yield 90 mg (22%).

Acknowledgment. We thank Professor J. Slivnik for xenon difluoride.

Registry No. 1, 392-56-3; 2, 775-51-9; 3a, 344-07-0; 3b, 344-04-7; 3c, 434-90-2; 3d, 363-72-4; 4a, 830-23-9; 4b, 57113-81-2; 4c, 57020-22-1; 4d, 773-53-5; 5a, 389-40-2; 5b, 54099-27-3; 5c, 54099-28-4; 6a, 31665-14-2; 6b, 75767-97-4; 6c, 75780-69-7; 7a, 31673-24-2; 8, 41481-25-5; 9, 61874-51-9; 10, 41481-22-5; XeF_2, 13709-36-9; BF_3, 7637-07-2.

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