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Room-temperature Fluorine Addition to Fluoro-substituted Naphthalene Derivative Using Xenon Difluoride

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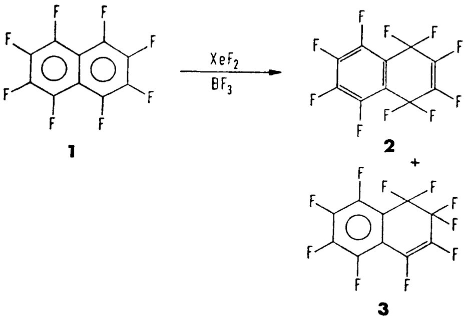
Room-temperature boron trifluoride catalyzed addition of fluorine to octafluoronaphthalene with xenon difluoride proceeds as 1,4- and 1,2-addition, giving decafluoro-1,4-dihydronaphthalene and decafluoro-1,2-dihydronaphthalene. Fluorine addition to 2-methoxy- and 2-ethoxyheptafluoronaphthalene gave only 1,4-adducts, while reaction with 2-isopropoxyheptafluoronaphthalene resulted in octafluoro-1,2-dihydronaphthalene-2-one and 6-isopropoxynonafluoro-1,4-dihydronaphthalene.

Perfluoroaromatic molecules react with electrophilic reagents under rigorous experimental conditions, while reactions with nucleophiles are typical examples of this class of compound.1) Hexafluorobenzene reacted with 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 decafluorocyclohexane were formed.3) Recently we have found that fluorine addition to fluoro substituted benzene derivatives could be carried out at room temperature using xenon difluoride in the presence of boron trifluoride as catalyst.4) Reaction with hexafluorobenzene proceeded regiospecifically as 1,4-addition, thus forming octafluoro-1,4-cyclohexadiene. We now report further studies on the regioselectivity of room-temperature fluorine addition to fluorosubstituted naphthalene derivatives.



Scheme 1.

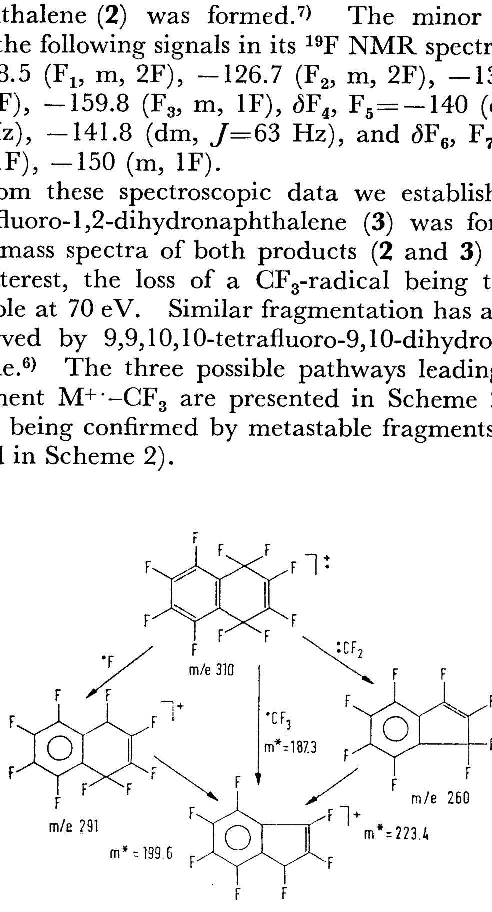
Results and Discussion

Xenon difluoride represents an easy handling, mild reagent for the fluorination of alkenes, acetylenes, aromatic and heteroaromatic molecules and some organic molecules containing hetero atoms, and has recently been reviewed.5) Fluorinations with xenon difluoride are usually successful in the presence of a catalyst and the following substrates proved to be convenient catalyst: HF, HF/pyridine, CF_3COOH, Br_2, pentafluorothiophenol, BF_3/etherate, and BF_3. The choice of catalyst depends on the structure of the organic molecule, its reactivity and its sensitivity to the reaction conditions.

In a typical experiment, 1 mmol of fluoro-substituted naphthalene was dissolved in 2 ml of dichloromethane, 1.1 mmol of xenon difluoride was added at room temperature and BF_3 was introduced into the reaction mixture. The reaction was complete in 30—60 min, the solvent was removed under reduced pressure, the crude reaction mixture was analyzed by ^{19}F NMR spectroscopy and the products were isolated by preparative GLC. After analysis of the crude reaction mixture obtained by fluorination of octafluoronaphthalene (**1**, Scheme 1), we concluded that two products were formed in the ratio 1:6.7.

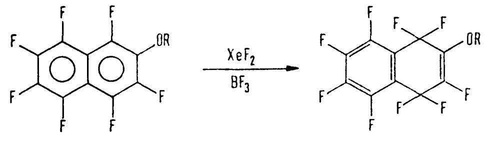
The products were separated by preparative GLC and the major product showed the following singals in its ^{19}F NMR spectrum: $\delta=-99.6$ (F_1, F_4, m, 4F), -137.6 (F_5, F_8, m, 2F), -147.2 (F_6, F_7, m, 2F), and -155.8 (F_2, F_3, m, 2F). On the basis of the spectroscopic data we established that decafluoro-1,4-dihydronaphthalene (**2**) was formed.7) The minor product had the following signals in its ^{19}F NMR spectrum: $\delta=-118.5$ (F_1, m, 2F), -126.7 (F_2, m, 2F), -136.7 (F_8, m, 1F), -159.8 (F_3, m, 1F), δF_4, $F_5=-140$ (dm, $J=63$ Hz), -141.8 (dm, $J=63$ Hz), and δF_6, $F_7=-147$ (m, 1F), -150 (m, 1F).

From these spectroscopic data we established that decafluoro-1,2-dihydronaphthalene (**3**) was formed.7,8) The mass spectra of both products (**2** and **3**) are also of interest, the loss of a CF_3-radical being the 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 $M^{+\cdot}-CF_3$ are presented in Scheme 2, all of them being confirmed by metastable fragments (values noted in Scheme 2).



Scheme 2.

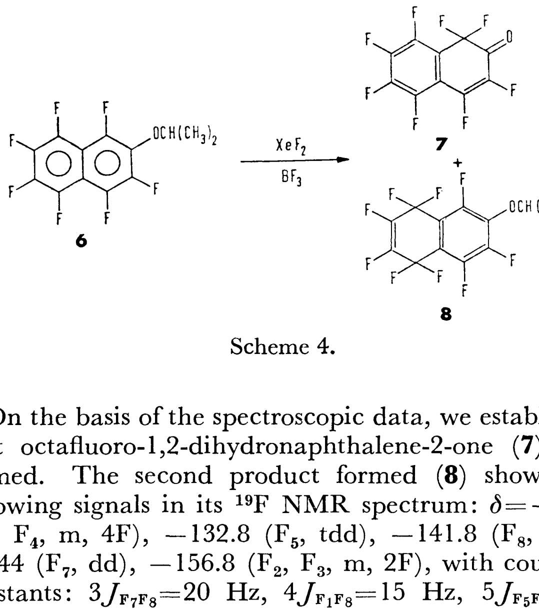
Further, we have studied the regioselectivity of fluorine addition to various alkoxy-substituted heptafluoronathalenes and found that fluorination of 2-methoxy (**4a**, Scheme 3) and 2-ethoxy (**4b**) derivatives resulted in the formation of only one product to each. In the case of **4a** the ^{19}F NMR signals are the following: $\delta=-97.2$ (F_1, m, 2F), -98.6 (F_4, m, 2F), -140 (F_5, F_8, m, 2F), -150.4 (F_6, F_7, m, 2F), and -163.1 (F_3, m, 1F), with the following coupling constants: $^4J_{F_4F_5}=$ $^4J_{F_1F_8}=17$ Hz, $^4J_{F_1F_3}=12$ Hz, $^3J_{F_3F_4}=24$ Hz, and $^5J_{F_3CH_3}=4$ Hz. On the basis of the spectroscopic data, we established that 2-methoxynonafluoro-1,4-dihydronaphthalene (**5a**) was formed.



4a: R=CH$_3$
4b: R=CH$_2$CH$_2$

Scheme 3.

1,4-Addition of fluorine with xenon difluoride had also been observed in the case of the 2-ethoxy derivative (**4b**), while reaction with 2-isopropoxyheptafluoronaphthalene (**6**) gave two products in the ratio 1 : 6.7, which could be separated by preparative GLC. The major product formed (**7**) shows a peak in its IR spectrum at 1715 cm^{-1}, characteristic of the CO group, and the following signals in its ^{19}F NMR spectrum: $\delta=-100.5$ (F_1, m, 2F), -123 (F_4, dm), -135.8 (F_8, tddd), -139 (F_5, dddd), -148.5 (F_6, F_7, m, 2F), and -157.8 (F_3, dt), with the following coupling constants: $^4J_{F_1F_8}=18$ Hz, $^4J_{F_1F_3}=7.5$ Hz, $^3J_{F_3F_4}=15$ Hz, $^4J_{F_4F_5}=81$ Hz, $^3J_{F_5F_6}=18$ Hz, $^4J_{F_5F_7}=7.5$ Hz $^5J_{F_5F_8}=18$ Hz, $^3J_{F_7F_8}=18$ Hz, and $^4J_{F_6F_8}=8$ Hz.



Scheme 4.

On the basis of the spectroscopic data, we established that octafluoro-1,2-dihydronaphthalene-2-one (**7**) was formed. The second product formed (**8**) shows the following signals in its ^{19}F NMR spectrum: $\delta=-99.8$ (F_1, F_4, m, 4F), -132.8 (F_5, tdd), -141.8 (F_8, dtd), -144 (F_7, dd), -156.8 (F_2, F_3, m, 2F), with coupling constants: $^3J_{F_7F_8}=20$ Hz, $^4J_{F_1F_8}=15$ Hz, $^5J_{F_5F_8}=15$ Hz, $^4J_{F_5F_7}=12$ Hz, and $^4J_{F_4F_5}=15$ Hz. On the basis of spectroscopic data we established that 6-iso-propoxynonafluoro-1,4-dihydronaphthalene was formed.

Experimental

IR spectra were recorded using a Perkin-Elmer 727 B spectrometer and ^{1}H and ^{19}F NMR spectra with a JEOL-JNM-PS 100 from CCl$_4$ or CDCl$_3$ solutions with Me$_4$Si or CCl$_3$F 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.

Fluorination of Octafluoronaphthalene (1). Yield: 279 mg of oily products, separated by GLC (10% SE-30 Chromosorb A 45/60, $T=80$ °C).

Decafluoro-1,4-dihydronaphthalene (2). Yield: 113.8 mg (36.5%), mp 31.5—32 °C (mp[7] 33—34 °C). Found: *m/e* 309.9840. Calcd for C$_{10}$F$_{10}$: 309.9840. MS, *m/e* (rel intensity): 310 (M$^+$, 34), 291(26), 272(9), 260(20), 242(10), 241 (100), 222(6), 210(12), and 141(9).

Decafluoro-1,2-dihydronaphthalene (3) Yield: 10.1 mg (3.3%) of oily product. Found: *m/e* 309.9841. Calcd for C$_{10}$F$_{10}$: 309.9840. MS, *m/e* (rel intensity): 310 (M$^+$, 34), 291(28), 272(8), 260(21), 242(12), 241(100), 210(15), and 141(13).

Fluorination of 2-Methoxyheptafluoronaphthalene (4a). Yield: 264 mg of crude reaction mixture; separation by preparative GLC (12% DDP Chromosorb Regular 100, $T=135$ °C).

2-Methoxynonafluoro-1,4-dihydronaphthalene (5a). Yield: 112 mg (35%), bp 212—213 °C. Found: *m/e* 322.0030. Calcd for C$_{11}$H$_3$F$_9$O: 322.0024. MS, *m/e* (rel intensity): 323 (M$^+$+1, 13), 322(M$^+$, 100), 307(13), 303(40), 292(10), 291(72), 279(70), 272(32), 260(25), 257(14), 253(14), 241(74), 229(66), 223(25), 222(10), 210(37), 203(10), 179(25), 160(10), 141(27), 117(17), 93(18), 81(75), and 69(13). Found: C, 41.0; H, 0.8%. Calcd for C$_{11}$H$_3$F$_9$O: C, 41.0; H, 0.9%.

Fluorination of 2-Ethoxyheptafluoronaphthalene (4b). Yield: 296 mg of crude reaction mixture, separated by preparative GLC (12% DDP Chromosorb Regular 100, $T=135$ °C).

2-Ethoxynonafluolo-1,4-dihydronaphthalene (5b). Yield: 133.8 mg (39.8%), bp 220—221 °C. ^{19}F NMR: -96.9 (F_1, m, 2F), -98.6 (F_4, m, 2F), -140.3 (F_5, F_8, m, 2F), -150.4 (F_6, F_7, m, 2F), and -162.4 (F_3, m, 1F) with the following coupling constants: $^4J_{F_1F_8}=17$ Hz, $^4J_{F_1F_3}=12$ Hz, $^3J_{F_3F_4}=24$ Hz, $^4J_{F_4F_5}=17$ Hz, and $^5J_{F_3CH_2}=3$ Hz. Found: *m/e* 336.0200. Calcd for C$_{12}$H$_5$F$_9$O: 336.0197. MS, *m/e* (rel intensity): 336 (M$^+$, 30), 309 (11), 308 (100), 289 (25), 288 (28), 272 (24), 269 (12), 260 (82), 258 (18), 242 (11), 241 (91), 239 (37), 229 (15), 222 (14), 210 (29), 179 (16), 141 (22), 117 (12), 93 (12), 86 (23), and 84 (38). Found: C, 42.2, H, 1.7%. Calcd for C$_{12}$H$_5$F$_9$O: C, 42.7, H, 1.5%.

Fluorination of 2-Isopropoxyheptafluoronaphthalene (6). Yield: 244 mg of the crude reaction mixture. The products were separated by preparative GLC (10% SE-30 Chromosorb A 45/60, $T=130$ °C).

Octafluoro-1,2-dihydronaphthalene-2-one (7). Yield: 145 mg (50.3%), mp 33—34.5 °C. Found: *m/e* 287.9800. Calcd for C$_{10}$F$_8$O: 287.9805. MS, *m/e* (rel intensity): 288 (M$^+$, 39), 260 (48), 242 (10), 241 (100), 210 (50), 160 (11), 141 (33), 122 (12), 117 (17), 93 (14), and 79 (12). IR; 1715 cm^{-1} (C=O).

6-Isopropoxynonafluoro-1,4-dihydronaphthalene (8). Yield: 22 mg (6.3%), mp 35—38.5 °C. Found: *m/e* 350.0350. Calcd for C$_{13}$H$_7$F$_9$O: 350.0353. MS, *m/e* (rel intensity): 350 (M$^+$, 8), 335 (20), 309 (12), 308 (100), 289 (30), 288 (12), 260 (13), 258 (12), 241 (33), 239 (30), 210 (25), 179 (10), 141 (17), 119 (15), and 117 (18).

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