

The Regioselectivity in the Fluorination of Dibenzofuran, Diphenylether and Biphenyl with N-F Type of Reagents

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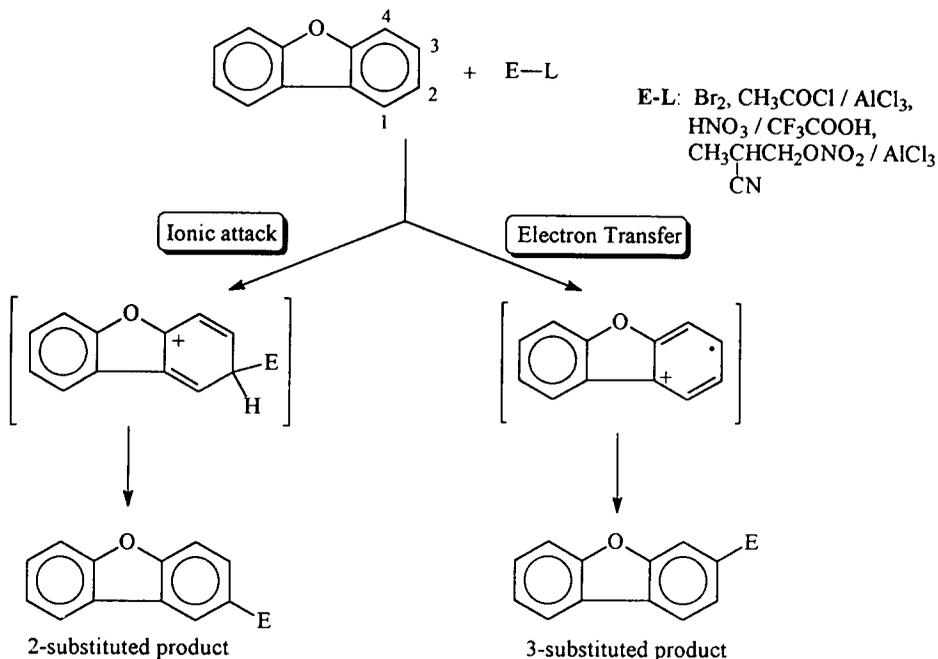
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Abstract: Dibenzofuran, diphenylether and biphenyl were used as a target molecules in an investigation of the effect of N-F type of reagent structure and reaction conditions on the fluorination process. The yields of fluorinated products formed and the regioselectivity depend on the reagent used, and in the reactions with dibenzofuran three products were formed. The ratios of 2-fluorodibenzofuran (4) and 3-fluorodibenzofuran (5) formed were: 1.3 for 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (NFTh, 1b), 1.4 for 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA, 1a), and 1.8 for N-fluoro-2,6-dichloropyridinium tetrafluoroborate (FPD-B, 1c). Ortho regioselectivity predominated for all reagents in the fluorination of biphenyl (ortho : para ratio varied from 4.8 to 1.2), while para attack prevailed for diphenylether (ortho : para = 0.9 - 0.7); however substitution of a phenyl ring by a methyl group enhanced the amount of 2-fluoroanisole. Second order rate constants for the fluorination of aromatic molecules with F-TEDA in acetonitrile at 65°C were established: anisole $4.8 \times 10^{-3} \text{ Lmol}^{-1}\text{s}^{-1}$, diphenylether $6.0 \times 10^{-4} \text{ Lmol}^{-1}\text{s}^{-1}$, dibenzofuran $2.5 \times 10^{-4} \text{ Lmol}^{-1}\text{s}^{-1}$ and biphenyl $1.0 \times 10^{-4} \text{ Lmol}^{-1}\text{s}^{-1}$. Copyright © 1996 Published by Elsevier Science Ltd

Direct introduction of fluorine under mild reaction conditions into aromatic molecules depends on the fluorinating reagent structure (F-L) and the substrate structure (benzene, naphthalene, phenanthrene...), but yields of fluorinated products are usually low, especially in benzene derivatives bearing deactivating groups¹⁻⁹. In the fluorination of benzene derivatives with xenon difluoride¹⁰⁻¹⁴, caesium fluoroxysulphate^{15,16,17}, and some N-F reagents^{18,19,20}, the formation of ion radicals has been suggested.

Valuable information about the role of the F-L reagent in the fluorination of organic molecules could be obtained if the reactions were studied on several target molecules under comparable reaction conditions. It is known that the functionalization of dibenzofuran (DBF) strongly depends on the reagent used and the reaction conditions^{21,22}. Bromination²³ and acylation²⁴ occurred mainly at position 2, while nitration with nitric acid in trifluoroacetic acid gave predominantly the 3-nitro derivative²⁵. It was suggested that functionalization on position 2 occurred via an ionic intermediate, while ion radicals are involved in the formation of the 3-substituted product^{24,25} (Scheme 1). However nitration with alkylnitrates in nitromethane in the presence of aluminium chloride²⁵ was forced at position 2 and reaction with 1-cyano-1-methylethyl nitrate gave products with changed regioselectivity²⁵, namely 1-nitro (11%), 2-nitro (51%), 3-nitro (36%), 4-nitro (2%).

SCHEME 1



The important role of ion radical formation in the functionalization of aromatic molecules has been pointed out several times^{26,27,28}; however Kochi and coworkers made an important contribution to the understanding of inner-sphere electron transfer in the transformation of aromatic molecules, with special attention to reagents with high oxidizing properties (nitration, nitrosation...)²⁹⁻³².

The above mentioned sensitivity of dibenzofuran functionalization stimulated us to study the effect of N-F type of fluorinating reagent structure and reaction conditions on the fluorination of DBF and structurally related diphenylether and biphenyl.

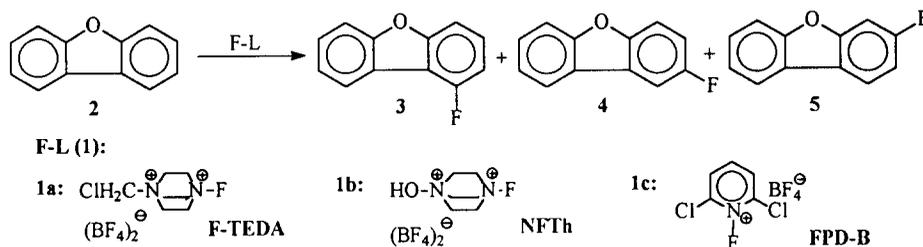
RESULTS AND DISCUSSION

First we investigated the effect of reagent structure on fluorination within a new class of N-F reagents. The three families of reagents, R₁R₂NF type³³, N-fluoropyridinium and related salts³⁴ and F-N⁺R₁R₂R₃A⁻ type³⁵ differ very much in their behaviour. Four commercially available reagents were used in this study³⁶: 1-chloromethyl-4-fluoro-1,4-diazonia bicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA, **1a**), 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (NFTh, **1b**), N-fluoro-2,6-dichloropyridinium tetrafluoroborate (FPD-B, **1c**) and N-fluorobis(phenylsulfonyl)amine (NFS).

In a typical experiment 1 mmol of dibenzofuran (**2**) was dissolved in 10 mL of acetonitrile, 1 mmol of F-TEDA (**1a**) was added and the reaction mixture heated at 70°C for 27 hours. The crude reaction mixture showed three major signals: -113.7 ppm (ddd), -118.8 ppm (ddd) and -121.0 ppm (ddd); and one minor signal

at -137.0 ppm (ddd). Three main products were isolated by preparative TLC and GLC, and the following structures determined on the basis of spectroscopic data and comparison with literature data or independently prepared samples³⁷: 1-fluorodibenzofuran (**3**), 2-fluorodibenzofuran (**4**) and 3-fluorodibenzofuran (**5**).

SCHEME 2

*Regioselectivity of Dibenzofuran (2) Fluorinations*

REAGENT	REACTION CONDITIONS	Yield (%) ^a	Product distribution(%) ^b			4 / 5
			3	4	5	
F-TEDA (1a)	CH ₃ CN, 70°C, 27h	35	27	42	31	1.4
	CH ₃ CN, PhNO ₂ ^c , 70°C, 27h	34	28	41	31	1.3
	CH ₃ CN+CH ₂ Cl ₂ (9+1), 70°C, 27h	30	26	42	32	1.3
	CH ₃ CN+CH ₃ OH(5+5), 70°C, 27h	17	24	47	29	1.6
	CH ₃ CN+CF ₃ COOH(9+1), 70°C, 16h	38	26	42	32	1.3
	CH ₃ CN+CF ₃ COOH(5+5), 70°C, 12h	39	23	44	33	1.3
	CF ₃ COOH, 50°C, 6h	30	22	39	39	1.0
NFTh (1b)	CH ₃ CN, 70°C, 24h	35	26	42	32	1.3
FPD-B (1c)	CH ₃ CN, 70°C, 24h	38	18	53	29	1.8

a) Yields of fluorinated products were calculated from ¹⁹F NMR with octafluoronaphthalene as internal reference;

b) Product distributions were determined by ¹⁹F NMR.

c) An equimolar amount of nitrobenzene was added.

The amount of fluorinated products formed was only 35%, and it is evident that the formation of 1- and 2-substituted products (**3** and **4**) is predominant over 3-substituted (**5**), while the minor product not isolated formed in 2% yield could be ascribed to 4-fluorodibenzofuran. Further, we investigated the role of the solvent on the fluorination and found that no reaction occurred in methanol or methylene chloride; however, rate enhancement was observed in trifluoroacetic acid, but the overall yield was not improved. Nitrobenzene was usually used as a free radical scavenger, but the course of fluorination with F-TEDA was not affected. The effect of solvent polarity variation is evident from Scheme 2 and only a slow enhancement of the formation of fluorinated products was observed in a mixture of CH₃CN and CF₃COOH (39% of fluorinated products). 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (NFTh, **1b**) under

similar reaction conditions as for F-TEDA gave a very similar product distribution. N-fluoro-2,6-dichloropyridinium tetrafluoroborate (FPD-B, **1c**) was also able to fluorinate dibenzofuran, but no reaction was observed with N-fluorobis(phenylsulphonyl)amine. As is evident from Scheme 2, the regioselectivity of dibenzofuran fluorination strongly depends on the reagent used, but nevertheless reactions differ very much from earlier functionalization (bromination at position 2, nitration at 3). It is apparent that the regioselectivity of fluorination is very similar to that observed for nitration with 1-cyano-1-methylethyl nitrate²⁵, but the 1-fluoro derivative was obtained in a higher amount.

In order to obtain some further information about the effect of the geometry of the molecule on the regioselectivity of fluorination, we studied the reactions with biphenyl (**6a**) and diphenylether (**6b**). F-TEDA (**1a**) with biphenyl in acetonitrile gave much higher amounts of fluorinated products than with DBF, though very high ortho regioselectivity was established. Nitrobenzene had no effect on the yield or regioselectivity, while reactivity was enhanced when trifluoroacetic acid was used as solvent. Fluorinations with NFTh (**1b**) resulted in lower yields of fluorinated products, while regioselectivity remained the same, but it changed with FPD-B (**1c**). Bromination of biphenyl occurred predominantly at the para position^{22,38}, a higher degree of

Table: *Regioselectivity in Fluorinations of Monosubstituted Benzene Derivatives(6)*

 6	REAGENT	REACTION CONDITIONS	Yield (%) ^{a)}	 7	 8
C ₆ H ₅ (6a)	F-TEDA	CH ₃ CN, 70°C, 97h	77	22	78
		CH ₃ CN, PhNO ₂ ^{b)} , 70°C, 97h	73	22	78
		CF ₃ COOH, 60°C, 4h	69	17	83
	NFTh	CH ₃ CN, 70°C, 96h	50	23	77
	FPD-B	CH ₃ CN, 70°C, 24h	53	40	60
OC ₆ H ₅ (6b)	F-TEDA	CH ₃ CN, 70°C, 24h	65	56	44
		CH ₃ CN, PhNO ₂ ^{b)} , 70°C, 24h	73	56	44
		CF ₃ COOH, 50°C, 4h	68	59	41
	NFTh	CH ₃ CN, 70°C, 24h	62	53	47
	FPD-B	CH ₃ CN, 70°C, 24h	72	59	41
OCH ₃ (6c)	F-TEDA	CH ₃ CN, 70°C, 3h	47	40	60
		CH ₃ CN, PhNO ₂ ^{b)} , 70°C, 3h	55	42	58
		CF ₃ COOH, 50°C, 2.5h	42	42	58
	NFTh	CH ₃ CN, 70°C, 3h	58	40	60
	FPD-B	CH ₃ CN, 70°C, 3h	56	36	64

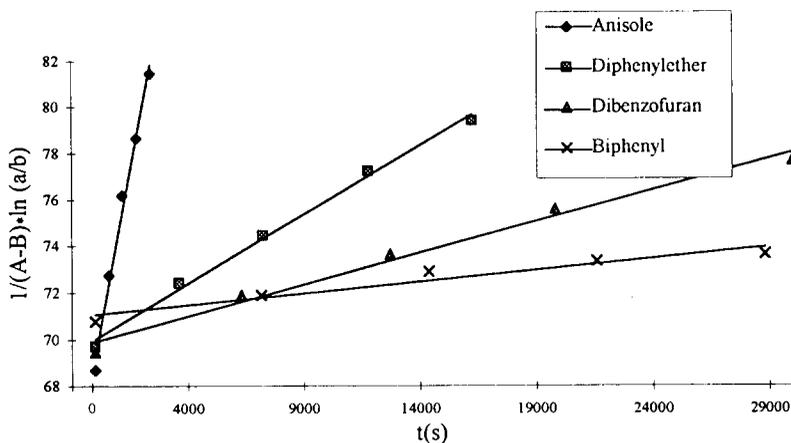
a) Yields of fluorinated products were calculated from ¹⁹F NMR with octafluoronaphthalene as internal reference; product distributions were determined by ¹⁹F NMR.

b) An equimolar amount of nitrobenzene was added.

ortho substitution was observed in nitration³⁹ (ortho : para = 2.2:1), while the introduction of oxygen enhanced para substitution and a 1:1 mixture of nitro derivatives was observed with diphenylether^{40,41}. In the fluorination of diphenylether (**6b**) with F-TEDA in CH₃CN the para isomer slightly prevailed, the use of CF₃COOH enhanced the rate of fluorination, but regioselectivity remained the same, while a similar course of fluorination also took place with NFTh and FPD-B (Table). Substitution of a phenyl ring by a methyl group enhanced the ortho regioselectivity in fluorination of anisole (**6c**) with N-F reagents.

Finally, we investigated the effect of substrate structure on the rate of fluorination in acetonitrile at 65°C with F-TEDA. The course of fluorination was followed by titration of iodine liberated after addition of potassium iodide solution at various times, and very good second order relations were observed (Figure). For fluorination of dibenzofuran a k_2 of 2.5×10^{-4} Lmol⁻¹s⁻¹ was established at 65°C, fluorination of diphenylether was 2.4 times faster (6.0×10^{-4} Lmol⁻¹s⁻¹), while substitution of the phenyl ring in diphenylether by a methyl group enhanced the reactivity and anisole was twenty times more reactive (4.8×10^{-3} Lmol⁻¹s⁻¹) than DBF. However, fluorination of biphenyl was 2.5 as slow (1.0×10^{-4} Lmol⁻¹s⁻¹) as DBF.

Figure. The Effect of Substrate Structure on the Reaction with F-TEDA in CH₃CN at 65°C



The important role of ion radical formation in the functionalization of aromatic molecules with reagents of high oxidation ability has been pointed out several times^{19,20,29-32}. Regiospecific nitration of dibenzofuran at position 3 was explained by ion radical formation, which is also in accordance with the higher electron density calculated by the MNDO method (HOMO electron densities: 1- 0.125, 2- 0.061, 3- 0.301 and 4- 0.041)²⁴. It is evident that the regioselectivity of fluorination of dibenzofuran is influenced by the structure of the fluorinating reagent, but the product distribution is more similar to the regioselectivity observed in nitration with 1-cyano-1-methylethyl nitrate²⁵. The formation of radical intermediates during fluorination is less likely because of the absence of the nitrobenzene inhibition effect. The fluorination of dibenzofuran with F-L reagents could be

explained as a competitive process between ionic attack giving a 2-fluorocarbonium ion, and the formation of an ion radical intermediate which can be further transformed, mainly to 3-fluoroderivative (Scheme 1, E= F). Competition between this two processes depends mainly on the structure of the reagent.

EXPERIMENTAL SECTION

Materials:

1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA, **1a**), 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (NFTh, **1b**), N-fluoro-2,6-dichloropyridinium tetrafluoroborate (FPD-B, **1c**), N-fluorobis(phenylsulfonyl)amine (NFS), dibenzofuran (Matheson Coleman), diphenylether (Fluka), anisole (Fluka), biphenyl (Fluka), nitrobenzene, trifluoroacetic acid (Fluorochem), and octafluoronaphthalene (Fluorochem) were obtained from commercial sources and used without further purification, except for kinetic measurements where substrates were distilled (**6b**, **6c**) or crystallized (**2**, **6a**). Acetonitrile (Merck), methylene chloride (Merck) and methanol (Merck) were purified by distillation and stored over molecular sieves. ^1H and ^{19}F NMR spectra were recorded at 60 or 56.45 MHz with Me_4Si or CCl_3F as internal standards.

Fluorination with N-F Reagents (**1a**, **1b**, **1c**):

A solution of 1.0 mmol of substrate (**2**, **6**) and 1.0 mmol of reagent (**1a**, **1b**, **1c**) in 10 mL of CH_3CN (or in solvent mixtures with CH_2Cl_2 , CH_3OH or TFA, or 1 mmol of PhNO_2 was added in fluorination with F-TEDA) was heated at 70°C (or at 50°C in the case of TFA) for 3 to 96 hours (consumption of reagent was followed by KI starch paper). The solvent was partially removed under reduced pressure, the residue diluted with 30 mL of CH_2Cl_2 , washed with water (10 mL), a saturated solution of NaHCO_3 (10 mL) (in reactions with FPD-B organic phases were washed with 15 mL 0.5M HCl) and dried over Na_2SO_4 . After evaporating the solvent the crude reaction mixture was analyzed by ^1H and ^{19}F NMR spectroscopy; yields of fluorinated products were determined with octafluoronaphthalene as internal reference. Results are presented in Scheme 2 and Table.

Pure products were isolated by preparative TLC or GLC and the structures determined on the basis of their spectroscopic data and by comparison with known data: 4-fluorobiphenyl⁴² (**7a**): $\delta_{\text{F}} = -118.2$ ppm (m), 2-fluorobiphenyl⁴² (**8a**): $\delta_{\text{F}} = -116.0$ ppm (m), 4-fluorodiphenylether⁴³ (**7b**): $\delta_{\text{F}} = -120.0$ ppm (dd), 2-fluorodiphenylether⁴³ (**8b**): $\delta_{\text{F}} = -130.5$ ppm (m), 4-fluoroanisole⁴³ (**7c**): $\delta_{\text{F}} = -122.4$ ppm (dd), 2-fluoroanisole⁴³ (**8c**): $\delta_{\text{F}} = -132.4$ ppm (dddd).

The crude reaction mixture obtained after fluorination of DBF was separated by preparative GLC (FFAP 30%, 180°C) and 5% of 1-fluorodibenzofuran (**3**) was isolated as a white crystalline product: mp $30.5\text{--}32^\circ\text{C}$; NMR $\delta_{\text{F}} = -118.8$ ppm (ddd, $J = 12, 6, 1$ Hz), $\delta_{\text{H}} = 6.7\text{--}8.1$ ppm (m); HRMS calcd for $\text{C}_{12}\text{H}_7\text{FO}$ m/z 186.0481, found m/z 186.0485; MS m/z 186 (M^+ , 100), 157 (35), 93 (12); elem. anal. calc. for $\text{C}_{12}\text{H}_7\text{FO}$: C 77.41% H 3.79%, found C 77.47% H 3.46%;

Under the above mentioned conditions the 2-fluoro and 3-fluoroisomers were not separated but their structure determined using independently synthesised products: 2-fluorodibenzofuran (**4**): m.p. $86\text{--}88^\circ\text{C}$ (lit.³⁷ $88.5\text{--}88.8^\circ\text{C}$) $\delta_{\text{F}} = -121.0$ ppm (ddd, $J = 9, 9, 5$ Hz), 3-fluorodibenzofuran (**5**): m.p. $88\text{--}89^\circ\text{C}$ (lit.³⁷ $88.5\text{--}88.8^\circ\text{C}$) $\delta_{\text{F}} = -113.7$ ppm (ddd, $J = 9, 9, 5$ Hz).

Kinetic Measurements of Reactions of Aromatic Molecules with F-TEDA:

To 25 mL of a thermostated solution of 1 mmol of substrate (2, 6) in CH₃CN, a thermostated solution of F-TEDA in CH₃CN (25 mL 0.02M) was added and stirred at 65°C. After various times 10 mL aliquots were mixed with 20 mL ice cold 0.02M KI and the liberated iodine titrated with 0.05M Na₂S₂O₃. The results are presented in Figure.

Acknowledgment: The financial support of the Ministry of Science and Technology of the Republic of Slovenia is acknowledged. We are indebted to Dr. G. A. Shia from Allied Signal Chemicals, Buffalo, for free samples of NFTh and NFS, to Dr. K. Nukui from New Field Research Lab., Chichibu Onoda Cement Corp., Japan, for free samples of FPD-B, to Dr. B. Kralj for MS and HRMS spectral measurements and to Mrs. M. Kastelic and Professor Dr. B. Stanovnik for elemental analysis.

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b) Accufluor, NFTh (1b), 1-hydroxy-4-fluoro-1,4-diazoniabicyclo-[2,2,2]octane bis(tetrafluoroborate), N-fluorobis(phenylsulfonyl)amine, Allied Signal Inc., Buffalo, New York;
c) FPD-B (2), N-fluoro-2,6-dichloropyridinium tetrafluoroborate, New Field Research Lab., Chichibu Onoda Cement Corp., Japan.
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(Received in UK 17 June 1996; accepted 11 July 1996)