FLUORINATION OF FLUORENE, DIBENZOFURAN AND THEIR OPEN ANALOGUES WITH CAESIUM FLUOROXYSULFATE AND RELATED FLUORINATING REAGENTS

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Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organofluorine chemistry.

Fluorination of fluorene (**1**) with caesium fluoroxysulfate (CFS), 2,6-dichloro-1-fluoropyridinium tetrafluoroborate (FP-B800) and 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]-octane bis(tetrafluoroborate) (Accufluor NFTh) occurred only on the aromatic ring in the position *ortho* and *para* to the biphenyl central bond with the ratio 2-fluoro- (**2a**) vs 4-fluorofluorene (**2b**) 1.7–2.4:1. Regioselectivity of fluorination of both open-chain analogues – diphenylmethane (**3a**) and biphenyl (**3b**) was different and more *ortho*-fluorinated product was formed. Furthermore, the reaction of diphenylmethane (**3a**) with CFS occurred also on central carbon forming benzophenone (**6**) and fluorodiphenylmethane (**7**), while fluorination with FP-B800 and Accufluor NFTh occurred only at the aromatic ring. Similar effect of the structure of fluorinating reagent on the regioselectivity was also observed with dibenzofuran (**8**) and its open-chain analogues diphenyl ether (**10**) and biphenyl (**3b**), where the regioselectivity of fluorination with CFS (1- (**9a**):2- (**9b**):3- (**9c**) = 27:46:27) was similar to fluorination with Selectfluor. Product distribution of fluorination of fluorene (**1**) and dibenzofuran (**8**) with CFS is similar to nitration and is in accordance with the calculated HOMO electron density, which indicates the presence of the electron transfer pathway.

Keywords: Fluorination; Mechanism; Electrophilic aromatic substitution; Electron transfer; Caesium fluoroxysulfate.

Introduction of a fluorine atom into an organic molecule could bring significant changes in its chemical and biological properties through special physicochemical properties of the fluorine atom and its bioisosterism with hydrogen and hydroxy group[1]. Therefore, selective introduction of fluorine

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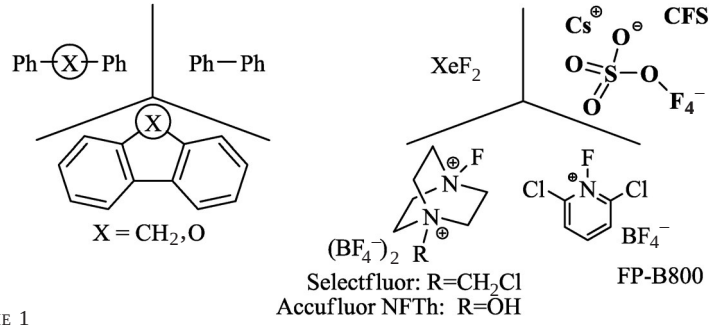
atom is an important and challenging task, especially when high reactivity of molecular fluorine is taken into consideration. One of the most important processes for selective introduction of fluorine atom into organic molecules is "electrophilic" fluorination where hydrogen atom is replaced by fluorine. However, selective fluorination with molecular fluorine as a basic fluorinating reagent is difficult to achieve due to a large difference in C–H and C–F bond energy leading to exothermic reactions. Furthermore, it is a dangerous and corrosive chemical. A very important breakthrough in this field was achieved by substitution of molecular fluorine for less reactive and easier-to-handle electrophilic fluorinating reagents, grouped into three major classes: xenon fluorides, fluoroxy reagents and N–F reagents[1e,2,3]. The fluoroxy reagents – perchloryl fluoride ($FClO_3$), acyl and alkyl hypofluorites (AcOF, MeOF) and metal fluoroxysulfate ($CsSO_4F$) – are strong fluorinating reagents and oxidants[4,5]. Caesium fluoroxysulfate was first prepared by the group of Appelman[6]. Although it was shown to be a powerful reagent for fluorination of aromatic molecules, little information is available on its mechanism of action[7].

Valuable information about the role of the structure of fluorinating reagent on the fluorination process could be obtained by studying model molecules under comparable reaction conditions. Interesting model compounds are dibenzofuran, fluorene and their open-chain analogues – biphenyl, diphenylmethane and diphenyl ether that were used many times in studies of the effect of geometry, electronegativity, conjugation and strain on the electrophilic aromatic substitution[8]. Furthermore, comparison of the results of fluorination of these substrates with those of other electrophilic substitution reactions would bring further insight into the mechanism of fluorination of aromatic molecules with F–L reagents (where L represents ligand part of reagent). Studies on the fluorination of fluorene, dibenzofuran and their open analogues with Selectfluor (F-TEDA, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)) and xenon difluoride have already provided an interesting insight into the mechanism of fluorination of aromatics in the light of the dichotomy between the polar and electron transfer mechanisms[9].

In this article, we present a study of the effect of the fluorinating reagent structure on the fluorination of fluorene, dibenzofuran and their open-chain analogues diphenylmethane, biphenyl and diphenyl ether with the emphasis on the fluorination with caesium fluoroxysulfate (CFS, $CsSO_4F$), *N*-fluoropyridinium salt (FP-B800, 2,6-dichloro-1-fluoropyridinium tetrafluoroborate) and Accufluor NFTh (1-fluoro-4-hydroxy-1,4-diazoniabicyclo-[2.2.2]octane bis(tetrafluoroborate)), while comparison with literature data

about fluorination with Selectfluor and xenon difluoride and other electrophilic processes (nitration, bromination etc.) will also be presented (Scheme 1).



SCHEME 1

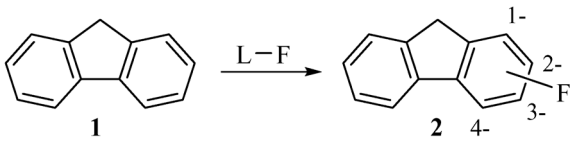
RESULTS

Fluorination of fluorene (**1**) with caesium fluoroxysulfate ($CsSO_4F$, CFS) at 30 °C in acetonitrile yielded 15% of 2-fluoro- (**2a**) and 4-fluorofluorene (**2b**) in a 71:29 ratio (Table I, entry 1). No functionalization of the methylene group of **1** was observed, although CFS is known to react with alkyl-substituted benzenes in the side chain (i.e. the reaction of 1,2,4,5-tetra-alkylbenzene occurs exclusively in the side chain)[10]. Yield of fluorinated products is not optimized, however, we were interested in the ratio of the products formed in order to get an insight into the course of fluorination. Hence, only one equivalent of fluorinating reagent was used to minimize side-product formation. Decomposition of fluorinating reagent under the reaction conditions also contributes to the lower yield of fluorination[11]. Reagents of the N–F group (FP-B800 and Accufluor NFTh) reacted in a similar manner giving only products fluorinated in the aromatic ring (entries 2, 3). The regioselectivity was similar to fluorination with Selectfluor and XeF_2, being in accordance with the calculated electron density of fluorene[12]. A comparison of regioselectivity of other electrophilic reagents reveals that fluorination and nitration (entry 6) are very similar[13], while bromination and chlorination occurs mainly in the position 2 (entry 7)[14].

A similar study on the effect of reagent structure on the course of fluorination was performed with both open analogues of fluorene (**1**), namely diphenylmethane (**3a**) and biphenyl (**3b**). The major reaction site in the reaction of **3a** with CFS is the CH_2 group, where the formation of two products was observed; benzophenone (**6**) as the main product in 71% yield and

fluorodiphenylmethane (**7**) in a yield of 11%. Ring fluorination was a side reaction and occurred only in the *ortho* position giving **4a** in 18% yield (Table II, entry 1). The yield of fluorination can be enhanced by taking higher amount of CFS and performing reaction in an inert atmosphere, nevertheless, the ratio between CH_2 functionalization and ring fluorination remains almost the same (82% (**6** and **7**):18% (**4a**) vs 85%:15% [15], respectively). A different course of fluorination was observed with *N*-fluoropyridinium salt FP-B800 where **3a** was fluorinated only in the aromatic ring and formation of 2-(fluorophenyl)phenylmethane (**4a**) prevailed over the *para* derivative **5a** (entry 2). Similar reactivity was also observed with Accufluor NFTh where *ortho*- and *para*-fluorodiphenylmethanes **4a** and **5a** were formed in the ratio 71:29 (entry 3). Although similar in structure to Selectfluor, Accufluor NFTh did not show any reactivity on the CH_2 group, while XeF_2 was the only reagent that formed a higher amount of the *para*-substituted product **5a** than of the *ortho* **4a** (entry 5).

TABLE I
The effect of reagent structure on the regioselectivity of fluorination of fluorene (**1**)

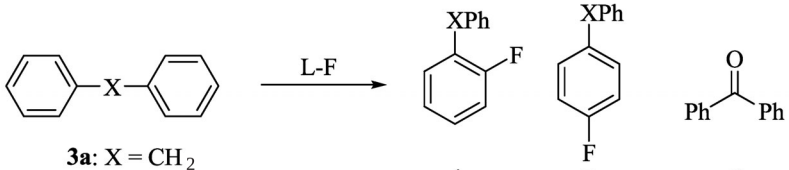


Entry	Reagent	Reaction conditions	Yield %[a]	Regioselectivity[a]		Ref.
				2- (**2a**)	4- (**2b**)	
1	CFS	MeCN, 30 °C, 3 h	15	71	29	
2	FP-B800	MeCN, 80 °C, 4 h	25	68	32	
3	Accuflor NFTh	MeCN, 80 °C, 4.5 h	19	63	37	
4	Selectfluor	MeCN, 80 °C, 4.5 h	27	67	33	9c
5	XeF_2[b]	DCM, r.t., 3 h	23	65	35	9b
6	HNO_3	Ac_2O		67	33	13
7	Br_2	AcOH		>97		14a
8	Cl_2	AcOH		89		14b

[a] Yield and regioselectivity were determined by ^{19}F NMR spectroscopy with octafluoronaphthalene as internal standard. [b] One drop of $BF_3 \cdot OEt_2$ was used as a catalyst.

TABLE II

The effect of reagent structure on the regioselectivity of fluorination of diphenylmethane (**3a**) and biphenyl (**3b**)



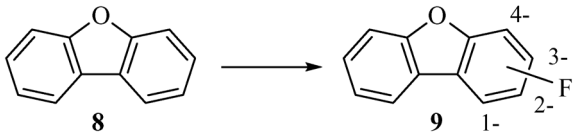
3a: X = CH_2
3b: X = nil

4 **5** **6**

Entry	Substrate	Reagent	Reaction conditions	Yield %[a]	Regioselectivity[a]			Ref.
					2- (**4**)	4- (**5**)	(**6**)	
1	X = CH_2	CFS	MeCN, 30 °C, 3 h	45	18		71[c]	
2	**3a**	FP-B800	MeCN, 80 °C, 24 h	23	61	39		
3		Accuflor NFTh	MeCN, 80 °C, 24 h	31	71	29		
4		Selectfluor	MeCN, 80 °C, 48 h	45	22	7	71	9c
5		XeF_2[b]	DCM, r.t., 3 h	20	45	55		9b
6	X = nil	$CsSO_4F$	MeCN, 40 °C, 3 h	20	70	30		
7	**3b**	FP-B800	MeCN, 70 °C, 24 h	53	60	40		9a
8		Accuflor NFTh	MeCN, 70 °C, 97 h	50	77	23		9a
9		Selectfluor	MeCN, 70 °C, 97 h	77	78	22		9b
10		XeF_2[b]	DCM, r.t., 3 h	46	53	47		9b

[a] Yield and regioselectivity were determined by ^{19}F NMR spectroscopy with octafluoronaphthalene as internal standard. [b] One drop of $BF_3 \cdot OEt_2$ was used as a catalyst. [c] 11% (3%) of fluorodiphenylmethane **7** was also formed.

TABLE III
The effect of reagent structure on fluorination of dibenzofuran (**8**)



8 **9**

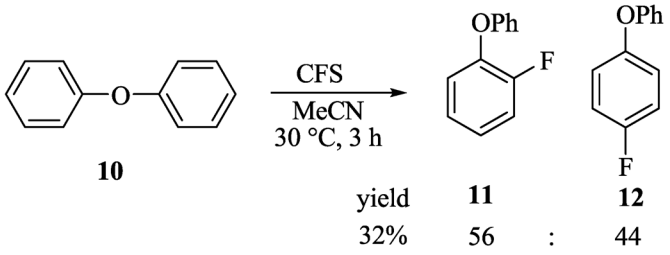
Entry	Reagent	Reaction conditions	Yield %[a]	Regioselectivity of 2[a]				Ref.
				1-	2-	3-	4-	
1	$CsSO_4F$	MeCN, 40 °C, 3 h	10	27	46	27	<1	
2	Selectfluor	MeCN, 70 °C, 27 h	35	27	42	31	<1	9a
3	Accuflor NFTh	MeCN, 70 °C, 24 h	35	26	42	32	<1	9a
4	FP-B800	MeCN, 70 °C, 24 h	38	18	53	29	<1	9a
5	XeF_2[b]	DCM, r.t., 4 h	30	26	21	53	<1	9b
6	HNO_3	TFA		3	4	93	1	16
7	NO_2BF_4	$EtNO_2$		22	43	33	2	16
8	ICN	MeOH, hν		32	23	24	21	17
9	PhCOCl	$AlCl_3$, $PhNO_2$		1	92	7	<1	16
10	Br_2	AcOH			100			18

[a] Yield and regioselectivity were determined by ^{19}F NMR spectroscopy with octafluoronaphthalene as internal standard. [b] One drop of $BF_3{\cdot}OEt_2$ was used as a catalyst.

Regioselectivity of fluorination of biphenyl (**3b**) was similar to that of **3a**. CFS fluorinated **3b** preferentially in the *ortho* position giving 2-fluorobiphenyl (**4b**) and 4-fluorobiphenyl (**5b**) in the ratio 7:3 (Table II, entry 6). *Ortho* regioselectivity was less pronounced than with Accufluor NFTh and Selectfluor but more than with FP-B800 and XeF_2.

Dibenzofuran (**8**) was taken as a testing substrate for investigation on the course of fluorination with CFS, as it is characteristic by affording different products depending on the reaction mechanism (Table III). Thus, nitration proceeds through the electron transfer mechanism (HNO_3 in TFA) and the reaction with **8** occurs predominantly in position 3, an ionic reaction (Friedel–Crafts acylation and bromination) in position 2, while a radical process does not show any regioselectivity (Table III, entries 6–10). In fluorination of dibenzofuran (**8**) with CFS no 4-fluorodibenzofuran was formed, indicating the absence of a radical mechanism in the fluorination with CFS (entry 1). However, product distribution is very similar to that in nitration (entry 7)[16] for which a pronounced electron-transfer character was suggested, and also to the fluorination with Selectfluor[9a]. A comparison of the regioselectivity in fluorination of **8** with various fluorinating reagents shows a similarity between CFS, Selectfluor and Accufluor NFTh, while *N*-fluoropyridinium salt (FP-B800) gave the highest ratio of 2-fluorodibenzofuran (**9b**) among the studied fluorinating reagents[9a]. In contrast, XeF_2 showed a slightly different regioselectivity[9b] and 3-fluorodibenzofuran (**9c**) was the product that was formed in the highest yield.

Fluorination of an open-chain analogue – diphenyl ether (**10**) with CFS was also studied. Reaction of **10** with CFS at 30 °C yielded 32% of *ortho*- (**11**) and *para*- (**12**) fluorinated products in the ratio 56:44 (Scheme 2). Both open analogues of dibenzofuran **3b** and **10** showed a preference in the fluorination to position *ortho*, while this is not reflected in the fluorination of dibenzofuran (**8**) where reaction proceeded mainly in the position *para* to ether and biphenyl bond. Of the F–L reagents studied, CFS was the only



SCHEME 2

one that reacted with diphenyl ether (**10**) preferentially in position *ortho*, while XeF_2 had the highest ratio of *para* substitution (*ortho*:*para* 38:62)[9b]. A similar effect was observed also in the case of biphenyl (**3b**). Fluorination occurred predominantly in the *ortho* position (*ortho*:*para* 70–78:30–22) while FP-B800 and XeF_2 were less regioselective (*ortho*:*para* 60:40 and 53:47, respectively).

CONCLUSION

Regioselectivity of reaction of fluorene (**1**), dibenzofuran (**8**) and their open analogues diphenylmethane (**3a**), biphenyl (**3b**) and diphenyl ether (**10**) shows interesting insights into the mechanism of fluorination with caesium fluoroxysulfate and other fluorinating reagents. Purely radical fluorination of aromatic ring could be ruled out due to the regioselectivity of fluorination. However, in diphenylmethane (**3a**), whose low reactivity of benzene rings prevents the fluorination, the functionalization of CH_2 group became the main reaction channel in reaction with CFS. This reactivity is very similar to the Selectfluor reagent. On the other hand, *N*-fluoropyridinium salt (FP-B800) and Accufluor NFTh reacted only at the aromatic ring. Regioselectivity of fluorination of fluorene (**1**) and dibenzofuran (**8**) with all the studied fluorinating reagents shows a very good agreement with that of nitration, in contrast to reagents with a less pronounced oxidative power (bromination, Friedel–Crafts acylation). Product distribution is similar also to the HOMO electron density of **1** and **8** and this could point to the involvement of the electron transfer mechanism in the fluorination with studied reagents.

EXPERIMENTAL

Materials

Caesium fluoroxysulfate was synthesized by a known procedure[19]. 2,6-Dichloro-1-fluoropyridinium tetrafluoroborate (FP-B800, Chichibu Onoda Cement Corp.), 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane tetrafluoroborate (Accufluor NFTh, Allied Signal Chemicals), fluorene (Janssen Chimica), dibenzofuran (Matheson Coleman), diphenylmethane (Fluka), biphenyl (Fluka), diphenyl ether (Fluka) and BF_3-OEt_2 (Merck) were obtained from commercial sources. ^1H and ^{19}F NMR spectra (δ, ppm; *J*, Hz) were recorded by a Varian EM360L spectrometer at 60 or 56.45 MHz with Me_4Si or CCl_3F as internal standards. Gas chromatography was carried out on Varian Models 3799 and 3300, and TLC on a Merck PSC-Fertigplatten silica gel F-254.

Fluorination with $CsSO_4F$. General Procedure

To a solution of 0.5 mmol of fluorene (**1**) (83 mg) in 5 ml of acetonitrile, 0.5 mmol of $CsSO_4F$ (124 mg) was added within 15 min and the mixture was stirred at 30 or 40 °C for additional 3 h. The reaction mixture was poured into water and organic products were extracted three times with 10 ml of CH_2Cl_2. The combined organic extracts were washed with 10 ml of water, 10 ml of a saturated solution of $NaHCO_3$, dried with anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure. The crude reaction mixture was analyzed by ^1H and ^{19}F NMR spectroscopy. The yields of fluorinated products were determined using octafluoronaphthalene as internal standard.

Fluorination of Fluorene (**1**) and Diphenylmethane (**3a**) with Accufluor NFTh and FP-B800

A solution of 1.0 mmol of substrate (**1**, **3a**) and 1.0 mmol of reagent (Accufluor NFTh or FP-B800) in 10 ml of MeCN was stirred at 80 °C for 4–24 h (consumption of reagent was followed by KI-starch strips). The solvent was partially removed under reduced pressure, the residue was diluted with 30 ml of CH_2Cl_2, washed with water (10 ml) and a saturated solution of $NaHCO_3$ (10 ml) (in reactions with FP-B800, the organic phase was washed with 15 ml of 0.5 M HCl) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude reaction mixture was analyzed by ^1H and ^{19}F NMR spectroscopy and the yields of fluorinated products were determined using octafluoronaphthalene as internal standard.

Pure products were isolated by preparative GC (FFAP 30% on Chromosorb W A/W 80/100) and the structures were determined on the basis of their spectroscopic data compared with the known data or with those of independently prepared samples. ^{19}F NMR (56.45 MHz, $CDCl_3$) of: 2-fluorofluorene[20] (**2a**) –116.2, ddd; 4-fluorofluorene[20] (**2b**) –120.8, m; (2-fluorophenyl)phenylmethane[21] (**4a**) –118.5, m; (4-fluorophenyl)phenylmethane[22] (**5a**) –117.7, dd; 2-fluorobiphenyl[23] (**4b**) –116.0, m; 4-fluorobiphenyl[23] (**5b**) –118.2, m; 1-fluorodibenzofuran[9a] (**9a**) –118.8, ddd; 2-fluorodibenzofuran[24] (**9b**) –121.0, ddd; 3-fluorodibenzofuran[24] (**9b**) –113.7, ddd; 2-fluorodiphenyl ether[25] (**11**) –130.5, m; 4-fluorodiphenyl ether[25] (**12**) –120.0, m.

In fluorination of diphenylmethane (**3a**) with CFS, fluorodiphenylmethane (**7**) was isolated by preparative TLC (SiO_2, petroleum ether), 6 mg (3%)[26], oil. ^1H NMR (60 MHz, $CDCl_3$): 6.4 (d, J = 47, 1 H); 7.2–7.4 (m, 10 H). ^{19}F NMR (56.45 MHz, $CDCl_3$): –168 (d, J = 47).

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