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Fluorination of Bi- and Polycyclic Aromatic Hydrocarbons with *N*-Fluorobis(phenylsulfonyl)amine in the Absence of Solvent

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Abstract—Reactions of *N*-fluorobis(phenylsulfonyl)amine with naphthalene, 1-methylnaphthalene, phenanthrene, anthracene, and pyrene without solvent were investigated. Sometimes the fluorination of aromatic compounds with N-fluorobis(phenylsulfonyl)amine without solvent proceeded more selectively than at the use of fluorinating reagents in solution.

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In the last two decades the direct electrophilic fluorination of organic compounds is often performed with the use of NF-reagents: *N*-fluorobis(phenylsulfonyl)amine (NFSI), salts of N-fluoropyridinium, N-fluoroquinuclidinium, 1-R-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane (R = CH_2Cl, OH) etc. [1–20]. The solvents commonly used in the fluorination with these reagents are acetonitrile, dichloroethane, dichloromethane, and methanol. The replacement of toxic solvents or their exclusion from the process is an important task of the "green chemistry" [21–23].

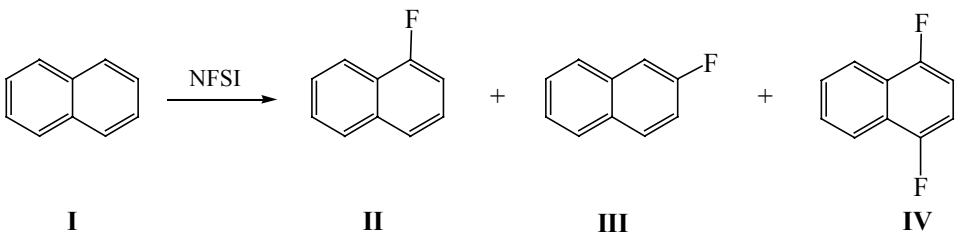
We showed formerly that the electrophilic fluorination of methyl-substituted benzenes, phenols, and their ethers could be performed with NFSI reagent in the absence of solvent, sometimes with a higher selectivity than in the presence of solvents [22].

The goal of this study was the investigation of the fluorination selectivity of bi- and polycyclic aromatic hydrocarbons with NFSI reagent in the absence of solvent. The problem of the selectivity of the electrophilic fluorination under these conditions is poorly understood (cf. [17, 22]).

We found that the naphthalene (**I**) fluorination with NFSI reagent in the absence of solvent provided prevailingly 1-fluoro- (**II**), 2-fluoro- (**III**), and 1,4-difluoronaphthalene (**IV**) (Scheme 1, Table 1).

The yield of the product of difluorination **IV** at 115°C and the ratio NFSI–ArH 1 : 1 grew with the growing reaction duration from 10 min to 1 h and afterwards remained practically constant. On increasing the ratio NFSI–ArH from 1 : 1 to 2 : 1 and the reaction time to 5 h the relative fraction of difluoride **IV** grew, but the further increase in this ratio resulted in reduction in the yield of the fluorination products apparently due to the oxidation

Scheme 1.



I **II** **III** **IV**

processes (cf. [5, 12, 24]). 1,4-Difluoronaphthalene evidently formed by the fluorination of arising in the reaction 1-fluoronaphthalene. The growth of the relative fraction of the difluoride in the mixture of the products with the increasing ratio NFSI–naphthalene is apparently caused by the greater reactivity of 1-fluoronaphthalene compared with naphthalene, in agreement with the electrophilic character of the reaction (cf. [25]). Practically in all events at the equimolar ratio of the substrate and the reagent a significant regioselectivity of the fluorination was observed: The ratio 1-fluoro-/2-fluoronaphthalene was in the range from 5 : 1 to 7 : 1. On decreasing the reaction temperature from 115 to 90°C this ratio increased. The use as solvent of acetonitrile, ethanol, or dichloroethane resulted in practically the same regioselectivity (at 115°C the regioselectivity of the fluorination characterized by the ratio 1-fluoronaphthalene–2-fluoro-naphthalene changed from 5 : 1 to 7 : 1), the overall yield of the fluorination products in EtOH and $ClCH_2CH_2Cl$ was lower than in the reaction without solvent.

Similar regioselectivity was formerly observed at the use of reagents XeF_2 and $CsSO_4F$ in the presence of BrØnsted or Lewis acids (Table 2). The use of reagent F-TEDA-BF_4 combined with BrØnsted acids led to a lower regioselectivity. A higher regioselectivity was obtained at the application of $CsSO_4F$ in MeCN, $(CF_3SO_2)_2NF$ and $CDCl_3$ and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bistetrafluoroborate (F-TEDA-BF_4) in a ionic liquid, 1-methyl-3-ethylimidazolium triflate [emim][CF_3SO_3] (Table 2).

Table 1. Fluorination of naphthalene and 1-methylnaphthalene with *N*-fluorobis(phenylsulfonyl)amine without solvent

Compound no.	NFSI–ArH	Temperature, °C	Time, h	Yield of reaction products, %[a]	Overall yield, %
I	1 : 1	115	0.17	**II** (13), **III** (2), IV (1)	16
I	1 : 1	115	0.5	**II** (20), **III** (4), IV (4)	28
I	1 : 1	115	1	**II** (21), **III** (4), IV (5)	30
I	1 : 1	115	2	**II** (23), **III** (4), IV (5)	32
I	1 : 1	115	3	**II** (22), **III** (4), **IV** (6)	32
I	1 : 1	115	5	**II** (22), **III** (4), **IV** (5)	31
I	1 : 1	115	21	**II** (22), **III** (4), **IV** (6)	32
I	1 : 1	90	1	**II** (10), **III** (1.5), **IV** (0.5)	12
I	1 : 1	90	5	**II** (19), **III** (3), **IV** (4)	26
I	1 : 2	115	4.5	**II** (33), **III** (6), **IV** (3)	42
I	1 : 4	115	4.5	**II** (37), **III** (6), **IV** (2)	45
I	2 : 1	115	0.17	**II** (16), **III** (3), **IV** (2)	21
I	2 : 1	115	5	**II** (8), **III** (2), **IV** (11)	21
I	4 : 1	115	5	**II** (0.2), **III** (0.2), **IV** (0.6)	1
I[b]	1 : 1	115	1	**II** (27), **III** (4), **IV** (3)	34
I[c]	1 : 1	115	1	**II** (8), **III** (1.5), **IV** (0.3)	10
I[d]	1 : 1	115	1	**II** (15), **III** (2), **IV** (0.7)	18
V	1 : 1	115	0.17	**VI** (3), **VII** (6), **VIII** (1), IX (1)	11
V	1 : 1	115	1	**VI** (4), **VII** (10), **VIII** (2) IX (2)	18
V	1 : 2	115	1	**VI** (5), **VII** (10), **VIII** (2) IX (2)	19
V	1 : 4	115	1	**VI** (5), **VII** (12), **VIII** (2) IX (2)	21
V[b]	1 : 1	115	1	**VI** (6), **VII** (13), **VIII** (2) IX (3)	24

[a] In all cases save the runs with deficit of NFSI the yields were determined with respect to the substrate, and at substrate excess, with respect to the reagent.
[b] In acetonitrile.
[c] In dichloroethane.
[d] In ethanol.

Table 2. Ratio of 1-fluoro- and 2-fluoronaphthalenes at the direct fluorination under various conditions

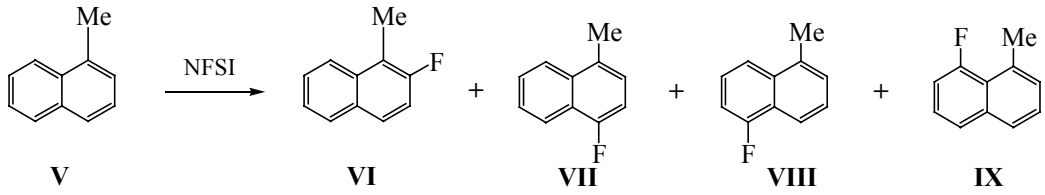
Reagent	Solvent (catalyst)	Temperature, °C	Molar ratio 1-fluoronaphthalene–2-fluoronaphthalene	Reference
$(CF_3SO_2)_2NF$	$CDCl_3$	22	11	[26]
F-TEDA-BF_4	[emim][CF_3SO_3]	80	13	[19]
F-TEDA-BF_4	CF_3COOH	70	3	[27]
F-TEDA-BF_4	CF_3SO_3H–CH_2Cl_2	boiling	1.5	[28]
$CsSO_4F$	MeCN	20	~40	[29]
$CsSO_4F$	MeCN (HF)	20	6	[29]
$CsSO_4F$	MeCN (H_2SO_4)	20	5	[29]
$CsSO_4F$	MeCN (BF_3)	20	4	[29]
$CsSO_4F$	MeCN (CF_3SO_3H)	20	4	[29]
$CsSO_4F$	MeCN (HSO_3F)	20	4	[29]
$CsSO_4F$	MeCN (BF_3)	20	5	[30]
XeF_2	CH_2Cl_2	–196–20	4.5	[31]

The fluorination of 1-methylnaphthalene (**V**) with NFSI reagent without solvent occurs nonselectively affording 1-methyl-2-fluoro- (**VI**), 1-methyl-4-fluoro- (**VII**), 1-methyl-5-fluoro- (**VIII**), and 1-methyl-8-fluoronaphthalenes (**IX**) (Scheme 2). The yield of fluorination products somewhat grows at the ratio NFSI–1-methylnaphthalene decreased from 1 : 1 to 1 : 4 (Table 1). The isomers ratio (**VI**) : (**VII**) : (**VIII**) : (**IX**) in the fluorination of the 1-methylnaphthalene with the NFSI reagent without solvent was close to this ratio observed in acetonitrile (Table 1) and also at the use of F-TEDA-BF_4 reagent in ionic liquid [bmim]PF_6 (21 : 53 : 11 : 15) [19].

In the fluorination of phenanthrene (**X**) with NFSI reagent without solvent formed predominantly 9-fluorophenanthrene (**XI**) (Scheme 3, Table 3). Alongside this compound in small quantities formed 1-fluoro-, 3-fluoro-, 4-fluorophenanthrenes (**XII–XIV** respectively), and also 9,10-difluorophenanthrene (**XV**).

The variation of the ratio NFSI–substrate and the temperature weakly affected the isomer ratio in the product. The maximum yield of the fluorination products was obtained at 115°C and the ratio NFSI–substrate 1 : 2. As expected, the relative amount of 9,10-difluorophenanthrene decreased with the decreasing ratio NFSI–substrate. The prevailing formation of 9-fluorophenanthrene in the phenanthrene fluorination was also observed at

Scheme 2.



Scheme 3.

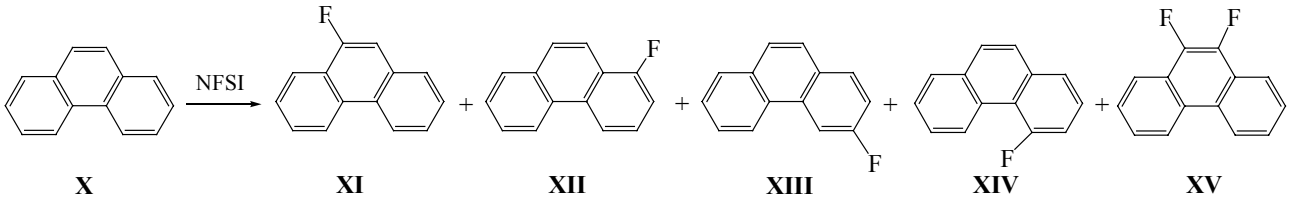


Table 3. Fluorination of polycyclic arenes with *N*-fluorobis(phenylsulfonyl)amine without solvent

Compound no.	NFSI–ArH	Temperature, °C	Time, h	Yield of reaction products, %[a]	Overall yield, %
X	1 : 1	115	0.33	**XI** (27), **XII** (2), **XIII** (1), **XIV** (1), **XV** (5)	36
X	1 : 1	105	1	**XI** (29), **XII** (2), **XIII** (1), **XIV** (1), **XV** (5)	38
X	1 : 2	115	0.33	**XI** (40), **XII** (3), **XIII** (1), **XIV** (2), **XV** (2)	48
X	1 : 4	115	0.33	**XI** (27), **XII** (2), **XIII** (1), **XIV** (1), **XV** (0.5)	32
X	2 : 1	115	0.33	**XI** (30), **XII** (3), **XIII** (1), **XIV** (1), **XV** (6)	41
X	4 : 1	115	0.33	**XI** (23), **XII** (3), **XIII** (1), **XIV** (1), **XV** (5)	33
X[b]	1 : 1	115	0.33	**XI** (21), **XII** (2), **XIII** (1), **XIV** (2), **XV** (2)	28
XVI	1 : 1	115	1	**XVII** (5), **XVIII** (4)	9
XVI	1 : 1	115	5	**XVII** (4), **XVIII** (3)	7
XVI	1 : 1	90	1	**XVII** (3), **XVIII** (2)	5
XVI	1 : 1	140	1	**XVII** (9), **XVIII** (4)	13
XVI	2 : 1	115	1	**XVIII** (1)	1
XVI	1 : 2	115	1	**XVII** (10), **XVIII** (3)	13
XVI	1 : 4	115	1	**XVII** (11), **XVIII** (3)	14
XVI[b]	1 : 1	115	1	**XVII** (30), **XVIII** (12)	42
XIX	1 : 1	115	1	**XX** (25), **XXI** (4)	29
XIX	1 : 1	90	1	**XX** (23), **XXI** (4)	27
XIX	1 : 1	105	1	**XX** (19), **XXI** (4)	23
XIX	1 : 1	140	1	**XX** (23), **XXI** (6)	29
XIX	1 : 2	115	1	**XX** (36), **XXI** (5)	41
XIX	1 : 4	115	1	**XX** (41), **XXI** (5)	46
XIX	2 : 1	115	1	**XX** (7), **XXI** (3)	10
XIX[b]	1 : 1	115	1	**XX** (32), **XXI** (9)	41
XIX[c]	1 : 1	105	25	**XX** (32), **XXI** (8)	40
XIX[d]	1 : 1	115	1	**XX** (24), **XXI** (6)	30

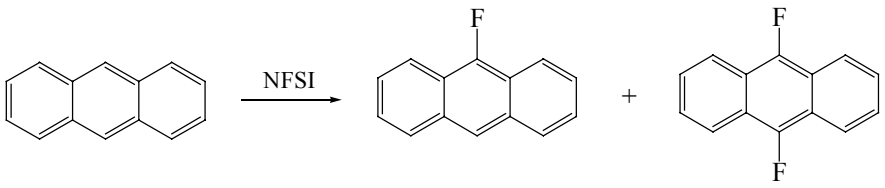
[a] In all cases save the runs with deficit of NFSI the yields were determined with respect to the substrate, and at substrate excess, with respect to the reagent . [b]In acetonitrile. [c]In dichloroethane. [d]In ethanol.

the use of acetonitrile as solvent (Table 3), and also at the application of other reagents: F-TEDA-BF_4 [27], XeF_2 [31–33], XeF_6 [34], $CsSO_4F$ [30], therewith the products formed of deeper fluorination and oxidation, 9,9,10-trifluoro-9,10-dihydrophenanthrene [32, 34], 9,9,10,10-tetrafluoro-9,10-dihydro-phenanthrene [34], and 9,9-difluoro-10-keto-9,10-dihydrophenanthrene [30].

The fluorination of anthracene (**XVI**) with the NFSI reagent without solvent at the equimolar ratio NFSI–substrate and 115°C led to the formation predominantly of 9-fluoroanthracene (**XVII**) and 9,10-difluoroanthracene (**XVIII**) in low yields (Scheme 4, Table 3). At the temperature increased to 140°C grew the relative fraction of the monofluorination product **XVII**.

The decreased ratio NFSI–substrate also resulted in the growth of the relative fraction of the monofluorina-

Scheme 4.



XVI **XVII** **XVIII**

tion product **XVII** whereas at the increase in this ratio formed only 9,10-difluoroanthracene in a low yield. The ratio of compounds **XVII** and X**VIII** weakly depended on the temperature variation. This ratio is sometimes higher than at the application of N-fluoro-2,4-dinitroimidazole in CH_2Cl_2 [35] or of N-fluoropyridinium triflate in $ClCH_2CH_2Cl$ [36]. At the use of the reagent F-TEDA-BF_4 in CF_3COOH the fluorination products did not form at all, and the main product was 9-trifluoroacetoxyanthracene [27].

The fluorination of pyrene (**XIX**) with the NFSI reagent at the molar ratio NFSI–substrate 1 : 1 in the absence of solvent led to predominant formation of 1-fluoro- (**XX**) and 4-fluoropyrene (**XXI**) (Scheme 5, Table 3).

The ratio of products **XX–XXI** and the yield grew at the reduction of the molar ratio NFSI–substrate from 1 : 1 to 1 : 4. The increase in the relative content of the NFSI reagent resulted in the reverse effect apparently due to the oxidation processes. At the ratio NFSI–substrate 4 : 1 compounds **XX** and **XXI** were not detected in the reaction products. The regioselectivity of the fluorination is somewhat higher in the process without solvent than at the use the NFSI reagent with solvents (Table 3), and it increases at lowering the temperature: 140°C (3.8), 105°C (4.8), and 90°C (5.8). Analogous temperature effect was observed at the pyrene fluorination with 1-hydroxy-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bistetrafluoroborate in MeCN: 80°C (3), 60°C (4), 22°C (8), 5°C (13) [37].

Thus the exclusion of the solvent from the fluorination process of bi- and polycyclic aromatic hydrocarbons with NFSI reagent does not considerably affects the reaction selectivity, but the fluorination regioselectivity of polycyclic hydrocarbons increases.

EXPERIMENTAL

^1H and ^{19}F NMR spectra were registered on a spectrometer Bruker AV-300 [operating frequencies 300 (^1H), 282.4 MHz (^{19}F)]. As internal references served $CHCl_3$ (δ 7.24 ppm) for ^1H and $PhCF_3$ (δ –63.73 ppm, calculated from $CFCl_3$) for ^{19}F. GC-MS measurements were performed on an instrument Hewlett Packard G1800A including a gas chromatograph HP 5890 series II and mass-selective detector HP 5971. The structure of compounds obtained was confirmed by ^1H and ^{19}F NMR spectra and GC-MS data. The spectral characteristics were consistent with the published data for 1-fluoro-, 2-fluoro-, 1,4-difluoronaphthalene [26, 38, 39], 1-methyl-2-fluoro-, 1-methyl-4-fluoro-, 1-methyl-5-fluoro-, 1-methyl-8-fluoronaphthalene [19], 1-fluoro-, 3-fluoro-, 4-fluoro-, 9-fluoro-, 9,10-difluorophenanthrene [32, 34, 40], 9-fluoro-, 9,10-difluoroanthracene [35], 1-fluoro-, 4-fluoropyrene [35, 40].

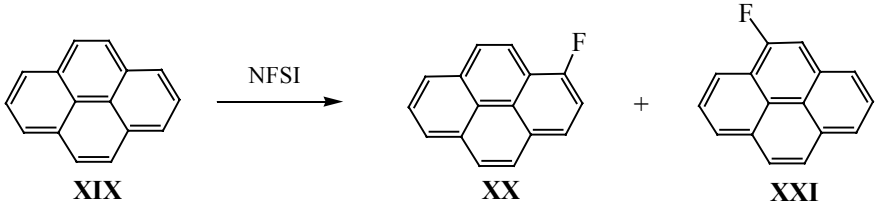
The following reagents were used in the study: 97% N-fluorobis(phenylsulfonyl)amine (Aldrich), naphthalene of "pure for analysis" grade, distilled 1-methyl-naphthalene of "pure" grade, anthracene of "pure for analysis" grade, phenanthrene of "pure" grade, pyrene (>95%) (Fluka), 99.9% MeCN (Panreac), EtOH (rectified), distilled $ClCH_2CH_2Cl$ of "pure" grade, $CDCl_3$ with deuterium content 99.8 at%.

General procedure of fluorination with NFSI reagent. To 0.2 mmol of an aromatic substrate was added a desired amount of NFSI reagent in a glass ampule (molar ratios ArH–NFSI are indicated in Tables 1, 3). The reaction mixture was maintained at definite temperature, cooled, 1 ml of $CDCl_3$ or of a mixture $CDCl_3$–$(CH_2Cl)_2$, 1 : 1, and a weighed amount of $PhCF_3$ were added, and the NMR spectra were registered, The yield and the ratio of the fluorination products were determined from ^{19}F NMR spectra.

The maintaining the solutions of aromatic hydrocarbons and NFSI reagent in solvents MeCN, EtOH, and $(CH_2Cl)_2$ was performed in sealed ampules. The concentration of substrate solutions was 0.3–1.7 mol l^{-1}.

The study was carried out under a financial support of the Russian Foundation for Basic Research (grant

Scheme 5.



XIX **XX** **XXI**

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