NMR of 19 was in agreement with the literature values.[9a]

Bu_3SnH Reduction of 11. A solution of 11 (20 mg; 0.042 mmol) and Bu_3SnH (60 mg; 0.21 mmol) in benzene (3 mL) was refluxed for 1 day. Chromatography (SiO_2; 1:1 to 1:0 ether/hexane) yielded a fraction (10 mg; 66%), which was identified as 3β,17aβ-dihydroxy-17aα-methyl-*D*-homoandrost-5-en-17-one 13 by comparison of its ^1H NMR spectrum with that of the authentic sample.

Conversion of 18 to 20. A solution of 18 (30 mg; 0.06 mmol) in ether (10 mL) was refluxed with $BF_3{\cdot}OEt_2$ (0.5 mL; 4 mmol) for 1 h and allowed to stand overnight at room temperature. Workup and recrystallization of the crude product from ether afforded 18 mg (95%) of **3β-hydroxy-17-methyl-*D*-homoandrosta-5,16-dien-17a-one (20)** (recrystallized from ether): mp 205–207 °C; α^{25}_D −189° (*c* 3% in $CHCl_3$); UV (0.097 mg/mL EtOH) 236 nm (ε 7000); IR (KBr) 3500 (OH), 1660 (CO) cm^{-1}; ^1H NMR δ 1.01 (s, 2 CH_3), 1.76 (d, J = 1 Hz, $H_3CC(17)$), 3.45–3.60 (m, HC(3)), 5.36 (m, HC(6)), 6.62 (m, HC(16)). Anal. Calcd for $C_{21}H_{30}O_2$ (314.47): C, 80.21; H, 9.62. Found: C, 80.20; H, 9.71.

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Registry No. 1, 974-23-2; 2, 19454-86-5; 3, 97350-86-2; 4, 97373-99-4; 5, 97350-87-3; 6, 97374-00-0; 7, 97350-88-4; 8, 97374-01-1; 9, 97350-89-5; 10, 97350-90-8; 11, 97350-91-9; 12, 97350-92-0; 13, 2460-10-8; 14, 97350-93-1; 15, 21549-33-7; 16, 97374-02-2; 17, 97374-03-3; 18, 97350-94-2; 19, 1458-74-8; 20, 97350-95-3; $PhMe_2SiLi$, 3839-31-4; thiophenol, 108-98-5; diphenyl diselenide, 1666-13-3; 3β,17α-dihydroxypregn-5-en-20-one, 387-79-1; dimethylphenylsilyl chloride, 768-33-2; 1,1,2,2-tetramethyl-1,2-diphenyldisilane, 1145-98-8.

Notes

Fluorination with Cesium Fluoroxysulfate. Room-Temperature Fluorination of Benzene and Naphthalene Derivatives

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The introduction of fluorine into aromatic molecules is very important from the chemical and pharmaceutical point of view, but the problem differs considerably from those concerning other halogen atoms.[1] In the last two decades many efforts have been made to find a fluorinating agent which could introduce fluorine into organic molecules under mild conditions. Fluoroxytrifluoromethane was the most extensively studied reagent, with various success, in the introduction of a fluorine atom into aromatic molecules, while experimental conditions demanded safety precautions because of the high toxicity of the reagent and its high reactivity.[2] Recently, Rozen and co-workers have found that trifluoroacetyl hypofluorite[3] and acetyl hypofluorite[4,5] represent a new class of fluoroxy derivatives that could also be used for the introduction of fluorine into organic molecules, but reactions must usually be carried out at lower temperatures. The most easily handled fluorinating agent known up to now is xenon difluoride,[6-8] but its high price is a great disadvantage. The recent preparation and characterization of cesium and rubidium fluoroxysulfate,[9] and their oxidative properties and stability at room temperature, made them promising as mild fluorinating agents for organic substrates. Appelman and co-workers found that $CsSO_4F$ reacted with several benzene derivatives.[10] We ourselves found that various benzene and naphthalene derivatives reacted in the presence of boron trifluoride as a catalyst,[11] and detailed studies of the effect of various catalysts on the fluorination of toluene, nitrobenzene, and naphthalene have finally appeared.[12] We now report our investigations of boron trifluoride catalyzed room-temperature fluorinations of various benzene and naphthalene derivatives with cesium fluoroxysulfate.

Results and Discussion

In 1979 Appelman and co-workers described the first synthesis of $CsSO_4F$, which was formed in the reaction of nitrogen diluted fluorine with Cs_2SO_4 in water.[9] During the synthesis of $CsSO_4F$ in our laboratory, we found that its instability in water reduced the isolation yield and thus, we only slightly modified the preparation procedures so that the precipitating $CsSO_4F$ was simultaneously removed from the reaction mixture every half hour. Finally, after a 5-h introduction of fluorine diluted with nitrogen, 65–75% of dry product was obtained, which can be stored in a polyethylene vessel at 0 °C for at least 14 days without a significant loss of activity. For our investigations we synthesized more than 200 g of the reagent. No explosion occurred, but any contact with a metallic spatula or any mechanical pressure must be avoided. In a typical experiment carried out in a glass vessel, to a stirred suspension of (0.5–5 mmol) $CsSO_4F$ in acetonitrile (3–15 mL) was added substituted benzene derivative (0.5–5 mmol in

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Table I. Effect of the Molar Ratio of $CsSO_4F$:7 and of the Group Magnitude on the Fluorination of 7

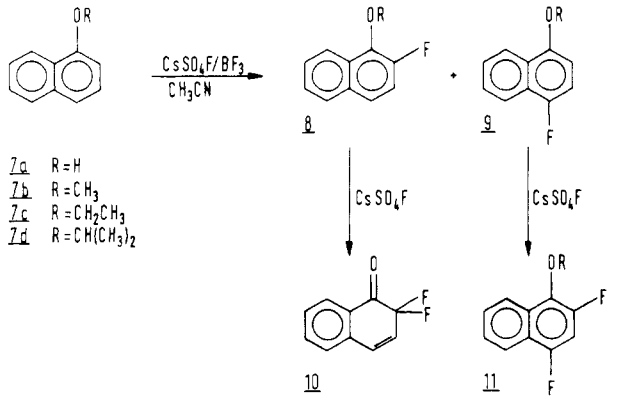
$CsSO_4F$:7	R	relative yields, % 8	9	10	11	8 + 10:9 + 11	convn of 7, %
0.7	H	89	11			89:11	51
	CH_3	78	22			78:22	50
	CH_2CH_3	75	25			75:25	50
	$CH(CH_3)_2$	65	35			65:35	51
1.2	H	75	13	12		87:13	80
	CH_3	73	19	3	5	76:24	85
	CH_2CH_3	73	18	2	7	75:25	80
	$CH(CH_3)_2$	65	9		26	65:35	83
1.6	H	62	10	21	7	83:17	>95
	CH_3	66	17	8	9	74:26	>95
	CH_2CH_3	69	10	6	15	75:25	>95
	$CH(CH_3)_2$	62	9	6	23	68:32	>95

0.5–5 mL of acetonitrile) at room temperature, and finally 0.5–1 mmol of gaseous BF_3 was introduced over the reaction mixture. The reaction mixture was stirred at room temperature for 0.5–6 h; methylene chloride was added, unsoluble residue was filtered off, the filtrate was washed with water and dried, and the solvent was evaporated under vacuum. The crude reaction mixture was analyzed by ^{19}F NMR spectroscopy and GLC. In the reactions where 1:1 molar ratio was used, 1–4% difluoro-substituted products were also observed. The regiospecificity of fluorine introduction into acetanilide (**1a**) is very simlar to that observed in the fluorination with acetyl hypofluorite.[4,5] The same high degree of ortho attack was also observed in the case of phenol (**1b**), while acetyl hypofluorite was found to be too reactive for the fluorination of phenol.[5] By replacing hydrogen with an alkyl group in **1b**, ortho–para regioselectivity was diminished, its degree depending on the size of group. Fluorination of aniline and (*N*,*N*-dimethylamino)benzene gave only tar, even when the temperature was lowered to −20 °C. The reaction with trifluoromethylbenzene, under the same reaction conditions mentioned above, gave only a small amount (2–3%) of a meta-substituted product. The reactions with nitrobenzene and methyl benzoate resulted in a very small converion of the starting material.

In addition, we also studied the regioselectivity of fluorine introduction into 1- and 2-hydroxy- and 1- and 2-alkoxy-substituted naphthalenes. Fluorination of 2-substituted naphthalenes resulted in the formation of 1-fluoro-substituted derivatives **5**, but further conversion of **5** to 1,1-difluoro-2-oxo-1,2-dihydronaphthalene (**6**) was observed. The amount of converted 1-fluoro-2-substituted naphthalene **5** depends on the structure of the alkoxy group. In separate experiments we found that pure 1-fluoro-2-alkoxy derivatives **5** are very quickly converted with $CsSO_4F$ to **6**.

Reactions with 1-hydroxy- and 1-alkoxy-substituted naphthalenes **7** resulted in the formation of 2- and 4-fluoro-substituted products (Scheme I). The effect of the substituent and the molar ratio of the substrate $CsSO_4F$ are presented in Table I. In separate experiments we also found that 1-hydroxy- or 1-alkoxy-2-fluoronaphthalene derivatives **8** readily reacted with $CsSO_4F$. They formed 2,2-difluoro-1-oxo-1,2-dihydronaphthalene (**10**), while 1-hydroxy and 1-alkoxy-4-fluoronaphthalenes **9** were converted to 2,4-difluoro derivatives **11**. The determination of regiospecificity of fluorine introduction into 1-alkoxy-substituted naphthalene **7** from ^{19}F NMR spectra represents a certain degree of difficulty, because only very small differences in ^{19}F chemical shifts for F-2 and F-4 were observed, both signals being very similar in shape. The exact determination of regioselectivity of fluorine introduction to the 1-substituted naphthalenes **7** was established in two ways; either by converting pure 1-alkoxy-2-

Scheme I



fluoronaphthalene **8** and 1-alkoxy-4-fluoronaphthalene **9** derivatives by hydrolysis, in the presence of HBr/CH_3COOH, to the corresponding fluoro-substituted naphthols **8a** and **9a**, which are already known and where chemical shifts for fluorine atoms differ by more than 10 ppm, or by converting **8b–d** to 2,2-difluoro-1-oxo-1,2-dihydronaphthalene (**10**) and 1-alkoxy-4-fluoro derivatives **9b–d** into the 1-alkoxy-2,4-difluoronaphthalenes **11**.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 727 B spectrometer and ^1H and ^{19}F NMR spectra on a JEOL JNM - PS 100 spectrometer, with Me_4Si or CCl_3F as an internal reference. Mass spectra and high resolution measurements were taken on a CEC-21-110 spectrometer. Gas–liquid partition chromatography was carried out on Varian Aerograph Models 2700 and 3700 chromatographs and TLC on Merck PSC-Fertigplatten Silicagel F-254.

Preparation of Cesium Fluoroxysulfate. In a 100-mL polyethylenic vessel containing 10 g of Cs_2SO_4 in 16 mL of water was introduced a 20% mixture of F_2 in nitrogen at 0 °C for 5 h (complete amount of F_2 introduced was approximately 40 mmol (1.5 g)). Ever half hour the insoluble $CsSO_4F$ was filtered off and washed with water (1 mL) and the combined precipitates were dried under vacuum at room temperature. Dry $CsSO_4F$ (4 g) was obtained, which must be stored in a polyethylenic vessel at 0 °C. The compound is stable for at least 14 d ays, but any contact with a metallic spatula or mechanical pressure must be avoided, since decomposition or even an explosion may take place.

Fluorination of Substituted Benzene Derivatives. $CsSO_4F$ (1 mmol) and 1.5 mL of acetonitrile were stirred at room temperature for 5 min, and after the introduction of BF_3 (0.5–1 mmol) over the reaction mixture, 1 mmol of a substituted benzene derivative (1) in 0.5 mL of acetonitrile was added. The reaction mixture was stirred at room temperature for 30 min, then 10 mL of methylene chloride was added, the insoluble residue was filtered off, the filtrate washed with water and dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The crude reaction mixture was analyzed by GLC and ^1H and ^{19}F NMR

spectroscopy, and the pure products were isolated by GLC or TLC. Yields of the isolated products were based on the reacted starting material.

Fluorination of Acetanilide (1a). The obtained crude reaction mixture (130 mg, 71% conversion of **1a**) was separated by preparative TLC (SiO_2, CH_2Cl_2:CH_3OH, 9.5:0.5).

2-Fluoro-1-(acetylamino)benzene[14] **(2a)**: 80 mg (74.5%); mp 76–78 °C (lit.[13] mp 80 °C; NMR δF −129.6 (m), δCH_3 2.2 (3 H, br s), δH 7.15–8.4 (4 H, m); MS, *m/e* (relative intensity) 153 (M^+, 50), 111 (100), 84 (10), 83 (15).

4-Fluoro-1-(acetylamino)benzene[14] **(3a)**: 12 mg (11%); mp 152–153 °C (lit.[15] mp 148 °C); NMR δF −119(m), δCH_3 2.2 (3 H, s), δH 6.9–7.35 (4 H, m); MS, *m/e* (relative intensity) 153 (M^+, 25), 111 (100), 84 (8), 83 (15).

Fluorination of Phenol (1b). The obtained crude reaction mixture (100 mg, 61% conversion of **1b**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 215 °C).

2-Fluorophenol[14] **(2b)**: 38 mg (56%) of liquid product; NMR δF −143.3 (m), δH 6.8–7.2 (m); MS, *m/e* (relative intensity) 112 (M^+, 100), 92 (20), 83 (20), 64 (60), 63 (25).

4-Fluorophenol[14] **(3b)**: 7 mg (10.5%) of crystalline product; mp 43–45 °C (lit.[15] mp 46 °C); NMR δF −123 (m), δH 6.8–7.4 (m); MS, *m/e* (relative intensity) 112 (M^+, 100), 92 (30), 83 (33), 64 (95), 63 (50).

Fluorination of Methoxybenzene (1c). The obtained crude reaction mixture (110 mg, 73% conversion of **1c**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 125 °C).

2-Fluoro-1-methoxybenzene[14] **(2c)**: 45 mg (49%) of oily product; NMR δF −135.3 (m), δCH_3 3.7 (3 H, s), δH 6.5–6.9 (4 H, m); MS, *m/e* (relative intensity) 126 (M^+, 100), 112 (21), 111 (54), 83 (80), 57 (30).

4-Fluoro-1-methoxybenzene[14] **(3c)**: 15 mg (16%) of oily product; NMR δF −125 (m), δCH_3 3.7 (3 H, s), δH 6.5–6.9 (4 H, m); MS *m/e* (relative intensity) 126 (M^+, 100), 111 (70), 83 (80), 57 (30).

Fluorination of Ethoxybenzene (1d). The obtained crude reaction mixture (130 mg, 73% conversion of **1d**) was separated by preparative GLC (FFAP 30%, Chrom W H/P, 80–100, *T* 125 °C).

2-Fluoro-1-ethoxybenzene[14] **(2d)**: 42 mg (41%) of oily product; NMR δF −135 (m), δCH_3 1.25 (3 H, t), δCH_2 4.1 (2 H, q), δH 6.7–7.2 (4 H, m); MS, *m/e* (relative intensity) 140 (M^+, 35), 112 (100), 64 (20), 63 (10).

4-Fluoro-1-ethoxybenzene[14] **(3d)**: 10 mg (10%) of oily product; NMR δF −125 (m), δCH_3, 1.3 (3 H, t), δCH_2 4.0 (2 H, q), δH 6.7–7.0 (4 H, m); MS, *m/e* (relative intensity) 140 (M^+, 40), 112 (100), 83 (20), 64 (30).

Fluorination of Isobutoxybenzene (1e). The crude reaction mixture (170 mg, 62% conversion of **1e**) was obtained. We were unable to separate the isomers **2e** and **3e** individually, but after GLC purification 62 mg (59.5%) of the mixture **2e**:**3e** = 1.7:1 was isolated: NMR δF −134.6 (m) for 2-fluoro isomer (**2e**) and δF −125.3 (m) for 4-fluoro isomer (**3e**); mass spectrum calcd for $C_{10}H_{13}OF$ *m/e* 168.0950, found *m/e* 168.0955; MS, *m/e* (relative intensity) 168 (M^+, 5), 112 (100), 83 (7), 64 (7). A mixture, containing **2e** and **3e** in the ratio 1.27:1, was heated in HBr (47%)/CH_3COOH and after workup the presence of 2-fluorophenol and 4-fluorophenol in the ratio 1.17:1 was established.

Fluorination of 2-Substituted Naphthalene Derivatives. $CsSO_4F$ (1.3 mmol) and 1.5 mL of acetonitrile were stirred at room temperature for 5 min, and after the introduction of BF_3 (0.5–1 mmol) over the reaction mixture, 1 mmol of 2-substituted naphthalene derivative (**4**), dissolved in 0.5 mL of acetonitrile, was added. The reaction mixture was stirred at room temperature for 30 min and then 10 mL of methylene chloride was added, the insoluble residue was filtered off, the filtrate was washed with water and dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The crude reaction mixture was analyzed by GLC and the pure products were isolated by preparative TLC. Yields of isolated products were based on the reacted starting material.

Fluorination of 2-Hydroxynaphthalene (4a). The obtained crude reaction mixture (160 mg, 77.5% conversion of **4a**) was separated by preparative TLC (SiO_2, CH_2Cl_2:CH_3OH 9.5:0.5).

1-Fluoro-2-hydroxynaphthalene (5a): 80 mg (50%); mp 73–74 °C (lit.[16] mp 74–76 °C; NMR δF −154 (d, *J* = 7 Hz), δH 7.05–7.9 (m); MS, *m/e* (relative intensity) 162 (M^+, 100), 133 (25), 114 (43), 81 (10).

1,1-Difluoro-2-oxo-1,2-dihydronaphthalene (6): 25 mg (13%); mp 50 °C (lit.[16] mp 53–54 °C), NMR δF −102 (broad s), δH_3 6.2 (1 H, dt, $^3J_{H_3H_4}$) = 9 Hz, $^4J_{H_3F}$ = 1.5 Hz), δH 7.3–7.9 (5 H, m); MS, *m/e* (relative intensity) 180 (M^+, 25), 162 (10), 161 (100), 152 (43), 151 (55), 133 (35), 114 (40), 81 (12); IR ν_{CO} 1690 cm^{-1}.

Fluorination of 2-Methoxynaphthalene (4b). The obtained crude reaction mixture (160 mg, 79.5% conversion of **4b**) was separated by preparative TLC (SiO_2, cC_6H_{12}:$CHCl_3$ 7:3) and 35 mg (18.6%) of product **6** and 90 mg (51%) of liquid 1-fluoro-2-methoxynaphthalene (**5b**)[5] were isolated.

Spectroscopic data of **5b**: NMR δF −148 (d, *J* = 7 Hz), δCH_3 3.9 (3 H, s), δH 7.2–7.9 (6 H, m); mass spectrum calcd for $C_{11}H_9OF$ *m/e* 176.0637, found *m/e* 176.0634; MS, *m/e* (relative intensity) 176 (M^+, 75), 161 (22), 134 (10), 133 (100).

Fluorination of 2-Ethoxynaphthalene (4c). The obtained crude reaction mixture (175 mg 79.5% conversion of **4c**) was separated by preparative TLC (SiO_2, cC_6H_{12}:$CHCl_3$ 7:3) and 35 mg (18.6%) of product **6** and 95 mg (50%) of liquid 1-fluoro-2-ethoxynaphthalene (**5c**) were isolated.

Spectroscopic data of **5c**: NMR δF −147 (d, *J* = 7 Hz), δCH_3 1.5 (3 H, t, *J* = 6 Hz), δCH_2 (2 H, q, *J* = 6 Hz), δH 7.2–8.2 (6 H, m); mass spectrum calcd for $C_{12}H_{11}OF$ *m/e* 190.0794, found *m/e* 190.0790; MS, *m/e* (relative intensity) 190 (M^+, 37), 163 (11), 162 (100), 133 (28), 114 (22).

Fluorination of 2-Isopropoxynaphthalene (4d). The obtained crude reaction mixture (180 mg, 85% conversion of **4d**) was separated by preparative TLC (SiO_2, cC_6H_{12}:$CHCl_3$ 7:3) and 40 mg (21%) of product **6** and 100 mg (49%) of liquid 1-fluoro-2-isopropoxynaphthalene (**5d**) were obtained.

Spectroscopic data of **5d**: NMR δF −145 (d, *J* = 7 Hz), δCH_3 1.35 (6 H, d, *J* = 6 Hz), δCH 4.6 (1 H, hept, *J* = 6 Hz), δH 7.1–8.1 (6 H, m); mass spectrum calcd for $C_{13}H_{13}OF$ *m/e* 204.0950, found *m/e* 204.0953; MS (relative intensity) 204 (M^+, 24), 163 (12), 162 (100), 133 (36), 114 (23).

Fluorination of 1-Fluoro-2-substituted-naphthalene Derivatives 5. $CsSO_4$ (0.36 mmol) and 0.75 mL of acetonitrile were stirred at room temperature for 5 min and after the introduction of BF_3 (0.2–0.4 mmol) over the reaction mixture, 0.3 mmol of 1-fluoro-2-substituted-naphthalene derivative **5** dissolved in 0.3 mL of acetonitrile was added. The reaction mixture was stirred for 30 mn at room temperature and after the usual workup the crude reaction mixture was purified by preparative TLC (SiO_2, $CHCl_3$:CH_3OH 9:1), and 1,1-difluoro-2-oxo-1,2-dihydronaphthalene in 90–92% yield was obtained.

Fluorination of 1-Substituted-naphthalene Derivatives 7. $CsSO_4F$ (0.7 mmol) and 1.5 mL of acetonitrile were stirred at room temperature for 5 min and after the introduction of BF_3 (0.5–1 mmol) over the reaction mixture, 1 mmol of 1-substituted-naphthalene derivative **7** dissolved in 0.5 mL of acetonitrile was added. The reaction mixture was stirred for 20 min at room temperature and after the usual workup the pure product was isolated by preparative GLC or TLC. Yields of isolated products are based on the reacted starting material. The effect of the molar ratio of 7:$CsSO_4F$ on the product distribution is presented in Table I.

Fluorination of 1-Hydroxynaphthalene (7a). The obtained crude reaction mixture (160 mg, 51% conversion of **7a**) was separated by preparative TLC (SiO_2, CH_2Cl_2:CH_3OH 9.5:0.5).

2-Fluoro-1-hydroxynaphthalene (8a):[16] 65 mg (78.5%); mp 71 °C (lit.[16] mp 71–73 °C; NMR δF −144.6 (dd, *J* = 10 Hz, 6 Hz), δH 7.2–8.3 (m); MS, *m/e* (relative intensity) 162 (M^+, 100), 134 (18), 133 (65), 114 (35), 81 (13), 63 (10), 57 (13).

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4-Fluoro-1-hydroxynaphthalene (9a): 8 mg (10%); mp 120–122 °C (lit.[17] mp 127–128 °C); NMR δF −134.8 (dm), δH_2 6.7 (1 H, dd), δH_3 7.0 (1 H, dd), δH 7.5–8.3 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; MS, *m/e* (relative intensity) 162 (M^+, 100), 134 (10), 133 (40), 114 (20).

Fluorination of 1-Methoxynaphthalene (7b). The obtained crude reaction mixture (165 mg, 50% conversion of **7b**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 220 °C).

2-Fluoro-1-methoxynaphthalene (8b): 42 mg (48%) of liquid product; NMR δF −135.7 (dm, $^3J_{FH_3}$ = 10 Hz), δCH_3 4.0 (3 H, d, *J* = 2 Hz), δH 7.2–8.2 (6 H, m); mass spectrum calcd for $C_{11}H_9OF$ *m/e* 176.0637, found *m/e* 176.0639; MS, *m/e* (relative intensity) 176 (M^+, 80), 161 (56), 134 (10), 133 (100).

4-Fluoro-1-methoxynaphthalene (9b):[17] 12 mg (14%) of liquid product; NMR δF −135.4 (dm), δCH_3 3.9 (3 H, s), δH_2 6.55 (1 H, dd), δH_3 7.0 (1 H, dd), δH 7.5–8.3 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; MS, *m/e* (relative intensity) 176 (M^+, 100), 161 (54), 133 (90).

Fluorintion of 1-Ethoxynaphthalene (7c). The obtained crude reaction mixture (180 mg, 50% conversion of **7c**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 220 °C).

2-Fluoro-1-ethoxynaphthalene (8c): 44 mg (46% of liquid product; NMR δF −134.3 (ddm), δCH_3 1.5 (3 H, t, *J* = 6 Hz), δCH_2 4.3 (2 H, qd, *J* = 6 Hz, 1 Hz), δH 7.1–8.1 (6 H, m), $^3J_{FH_3}$ = 10 Hz, $^4J_{FH_4}$ = 5 Hz; mass spectrum calcd for $C_{12}H_{11}OF$ *m/e* 190.0794, found *m/e* 190.0795; MS, *m/e* (relative intensity) 190 (M^+, 37), 163 (11), 162 (100), 134 (15), 133 (57), 114 (14).

4-Fluoro-1-ethoxynaphthalene (9c): 14 mg (15%) of liquid product; NMR δF −135.2 (dm) δH_2 6.6 (1 H, dd), δH_3 7.0 (1 H, dd), δCH_3 1.5 (3 H, t, *J* = 6 Hz), δCH_2 4.1 (2 H, q, *J* = 6 Hz), δH 7.55–8.3 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; mass spectrum calcd for $C_{12}H_{11}OF$ *m/e* 190.0794, found *m/e* 190.0800; MS, *m/e* (relative intensity) 190 (M^+, 40), 162 (100), 133 (56), 114 (15).

Fluorination of 1-Isopropoxynaphthalene (7d). The obtained crude reaction mixture (190 mg, 51% conversion of **7d**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 225 °C).

2-Fluoro-1-isopropoxynaphthalene (8d): 41 mg (40%) of liquid product; NMR δF −133.8 (dd), δCH_3 1.3 (6 H, d, *J* = 6 Hz), δCH 4.5 (1 H, hept, *J* = 6 Hz), δH 7.2–8.0 (6 H, m), $^3J_{FH_3}$ = 10 Hz, $^4J_{FH_4}$ = 5 Hz; mass spectrum calcd for $C_{13}H_{13}OF$ *m/e* 204.0950, found *m/e* 204.0955; MS, *m/e* (relative intensity) 204 (M^+, 10), 163 (12), 162 (100), 133 (30), 114 (10).

4-Fluoro-1-isopropoxynaphthalene (9d): 22 mg (21%) of liquid product; NMR δF −135.4 (dm), δCH_3 1.4 (6 H, d, *J* = 6 Hz), δCH 4.7 (1 H, hept, *J* = 6 Hz), δH_2 6.7 (1 H, dd), δH_3 7.1 (1 H, dd), δH 7.65–8.4 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; mass spectrum calcd for $C_{13}H_{13}OF$ *m/e* 204.0950, found *m/e* 204.0955, MS, *m/e* (relative intensity) 204 (M^+, 15%), 163 (12), 162 (100), 133 (25), 114 (10).

Fluorination of 2-Fluoro-1-substituted-naphthalene Derivatives 8. $CsSO_4F$ (0.36 mmol) and 0.75 mL of acetonitrile were stirred at room temperature for 5 min and after the introduction of BF_3 (0.2–0.4 mmol) over the reaction mixture, 0.3 mmol of 2-fluoro-1-substituted-naphthalene derivative **8**, dissolved in 0.3 mL of acetonitrile, was added and the reaction mixture was stirred for 30 min at room temperature. After the usual workup procedure and purification by preparative TLC (SiO_2, $CHCl_3$:CH_3OH 9:1), 2,2-difluoro-1-oxo-1,2-dihydronaphthalene[16] (**10**) in 90–92% yield was obtained: mp 40–42 °C; NMR δF −105.5 (d, *J* = 7 Hz), δH_3 6.3 (1 H, td), δH_4 6.9 (1 H, d), δH 7.3–8.5 (4 H, m), $^3J_{FH_3}$ = 7 Hz, $^3J_{H_3H_4}$ = 10.5 Hz; mass spectrum calcd for $C_{10}H_6OF_2$ *m/e* 180.0387, found *m/e* 180.0389; MS, *m/e* (relative intensity) 180 (M^+, 86), 152 (74), 151 (100), 133 (17), 75 (10), 63 (10), 51 (11), 50 (11); IR ν_{CO} 1705 cm^{-1}.

Fluorination of 4-Fluoro-1-substituted-naphthalene Derivatives 9. $CsSO_4F$ (0.24 mmol) and 0.5 mL of acetonitrile were stirred at room temperature for 5 min and after the introduction of BF_3 (0.1–0.3 mmol) over the reaction mixture, 0.2 mmol of 4-fluoro-1-substituted-naphthalene derivative **9**, dissolved in 0.2 mL of acetonitrile, was added. The reaction mixture was stirred at room temperature for 30 min and after the usual workup procedure and purification by preparative TLC (SiO_2, petroleum ether:$CHCl_3$ 9:1), 2,4-difluoro-1-substituted-naphthalene derivatives **11** were isolated.

2,4-Difluoro-1-hydroxynaphthalene (11a): 32 mg (89%); mp 97–99 °C (lit.[16] mp 99–100 °C; NMR δF_2 −144 (d), δF_4 −130.7 (d), δH_3 7.1 (1 H, t, *J* = 11 Hz), δH 7.5–8.3 (4 H, m); *m/e* (relative intensity) 180 (M^+, 100), 151 (100), 152 (40).

2,4-Difluoro-1-methoxynaphthalene (11b): 30 mg (77%); mp 30 °C; NMR δF_2 −132.2 (dm), δF_4 −126 (dm), δH_3 6.8 (1 H, t, *J* = 11 Hz), δH 7.5–8.0 (4 H, m), δCH_3 4.1 (3 H, s); mass spectrum calcd for $C_{11}H_8OF_2$ *m/e* 194.0543, found *m/e* 194.0545; MS, *m/e* (relative intensity) 194 (M^+, 90). 180 (30), 179 (95), 162 (60), 152 (16), 151 (100), 150 (10), 133 (34).

2,4-Difluoro-1-ethoxynaphthalene (11c): 35 mg (85%) of liquid product; NMR δF_2 −131.2 (dm), δF_4 −126.2 (dm), δH_3 6.9 (1 H, t, *J* = 11 Hz), δCH_3 1.4 (3 H, t, *J* = 6 Hz), δCH_2 4.1 (2 H, q, *J* = 6 Hz), δH 7.5–8.3 (4 H, m); mass spectrum calcd for $C_{12}H_{10}OF_2$ *m/e* 208.0699, found *m/e* 208.0695; MS, *m/e* (relative intensity) 208 (M^+, 40), 181 (10), 180 (100), 179 (11), 151 (50), 131 (10).

2,4-Difluoro-1-isopropoxynaphthalene (11d): 38 mg (86%) of liquid product; NMR δF_2 −131.1 (dm), δF_4 −126.2 (dm), δH_3 6.95 (1 H, t, *J* = 11 Hz), δCH_3 1.3 (6 H, d, *J* = 6 Hz) δCH 4.5 (1 H, hept, *J* = 6 Hz), δH 7.5–8.2 (4 H, m); mass spectrum calcd for $C_{13}H_{12}OF_2$ *m/e* 222.0856, found *m/e* 222.0860; MS, *m/e* (relative intensity) 222 (M^+, 8), 181 (11), 180 (100), 151 (33), 132 (10).

Registry No. **1a**, 103-84-4; **1b**, 108-95-2; **1c**, 100-66-3; **1d**, 103-73-1; **1e**, 1126-75-6; **2a**, 399-31-5; **2b**, 367-12-4; **2c**, 321-28-8; **2d**, 451-80-9; **2e**, 97295-03-9; **3a**, 351-83-7; **3b**, 371-41-5; **3c**, 459-60-9; **3d**, 459-26-7; **3e**, 97295-04-0; **4a**, 135-19-3; **4b**, 93-04-9; **4c**, 93-18-5; **4d**, 15052-09-2; **5a**, 51417-63-1; **5b**, 27602-71-7; **5c**, 78649-26-0; **5d**, 78649-27-1; **6**, 51417-64-2; **7a**, 90-15-3; **7b**, 2216-69-5; **7c**, 5328-01-8; **7d**, 20009-27-2; **8a**, 56874-95-4; **8b**, 88288-00-0; **8c**, 97295-05-1; **8d**, 97295-07-3; **9a**, 315-53-7; **9b**, 10471-09-7; **9c**, 97295-06-2; **9d**, 97295-08-4; **10**, 97295-09-5; **11a**, 56874-96-5; **11b**, 97295-10-8; **11c**, 97295-11-9; **11d**, 97295-12-0; Cs_2SO_4, 10294-54-9; F_2, 7782-41-4; $CsSO_4F$, 70806-67-6.

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Solid-State Aromatic S_N2 Reactions: Displacement of the Nitro Moiety in Arenediazonium Salts

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Displacement reactions of the aromatic S_N2 type under neat conditions to our knowledge have not been reported. While screening for reagents that couple with the bile pigment bilirubin,[1] we unexpectedly encountered a spontaneous reaction of this type. It has been previously reported that in various solvent systems displacement of substituents can occur and that it is the strongly electron-withdrawing diazonium group that activates such displacements.[2] Displaced groups are generally nitro or halo substituents which are situated ortho and/or para to the diazonium group.[3] We herein report the displacement

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