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N-FLUORINATION WITH CESIUM FLUOROXYSULFATE

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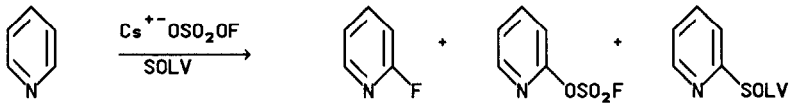
SUMMARY: *Cesium fluoroxysulfate was proved to be a N-fluorinating agent for some nitrogen compounds Yields of products obtained, mainly monofluoro-derivatives, depend on structures of initial nitrogen compounds The ability of cesium fluoroxysulfate for N-fluorination is much inferior to that of elemental fluorine and fluoromethylhypofluoride (CF_3OF), but superior to that of perchlorylfluoride ($FClO_3$)*

INTRODUCTION

Cesium fluoroxysulfate (CEFOX), $Cs^{+-}OSO_2OF$, a perspective electrophilic fluorinating agent, obtained for the first time in 1979[1], is being studied intensively now as the reagent for soft and selective fluorination of unsaturated, aromatic and elementorganic compounds[2]. In the course of these investigations a variety of C-fluoroderivatives have been obtained. CEFOX has also been shown to be a useful reagent for the synthesis of some fluoroelementorganic compounds with formation of fluorine-element bond, such as F-I, F-Si, etc[3].

At the same time, it has never been mentioned that CEFOX can be used to obtain N-fluoroderivatives, most of which are effective fluorinating agents themselves. Indeed, although many reactions of CEFOX with various nitrogen compounds have been studied, none of them has been found to give N-fluoroderivatives[3-5]. For example, the fluorination of anilines with CEFOX is accompanied by destructive processes[5], while the reaction of CEFOX with

pyridine give, to the authors' opinion[4], the mixture of products, among which 2-fluoropyridine, 2-pyridylfluorosulfate, and the solvolysis products prevail.



Other nitrogen heterocycles, i.e. substituted pyrimidines, uracil, barbituric acid, give C-fluoroderivatives[3].

All these results seem to be quite unexpected since CEFOX belongs to the class of hypofluorites, many of which are able for **N**- fluorination[6]. A question arise, if CEFOX is capable of **N**-fluorination or not?

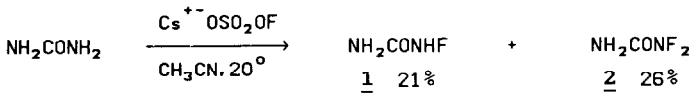
It is to resolve this ambiguity, that we have undertaken the present study. We have chosen a number of nitrogen compounds, different in their structures and reactivities, i.e. aliphatic and heteroaromatic amines, carbimides, sulfonamides and their salts, pyridine, so that a detailed estimation of **N**-fluorinating ability of CEFOX could be made.

For the preliminary communication see[7].

RESULTS AND DISCUSSION

We have started our investigation with several typical aliphatic amines, i.e. diethylamine, piperidine and morpholine. Their reaction with CEFOX in acetonitrile in a wide temperature range (-70^{o}- $+20^{o}$C) has not led to any noticeable amounts of **N**-fluoroderivatives, though CEFOX has been spent completely. We haven't studied this reactions in more detail.

In contrast to these amines, the less basic compounds containing amino-group, such as urea and butylcarbamate are **N**-fluorinated with CEFOX. Thus, urea reacts with CEFOX in acetonitrile at room temperature to give **N**-fluoro- 1 and **N,N**-difluoroureas 2 in moderate yields. It may be noted, that CEFOX acts in this reaction similarly to elemental fluorine, which gives the same products when interacts with urea[8].



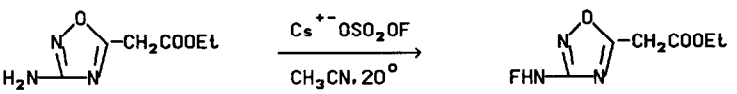
The fluorination of butylcarbamate with CEFOX in acetonitrile give

N-fluorobutylcarbamate **3** , though in poor yield. The synthesis of this compound was first reported to result from fluorination of butylcarbamate with elemental fluorine in water in 30% yield[9].

$$C_4H_9OCONH_2 \xrightarrow[CH_3CN,\,20^\circ]{Cs^{+-}OSO_2OF} C_4H_9OCONHF$$

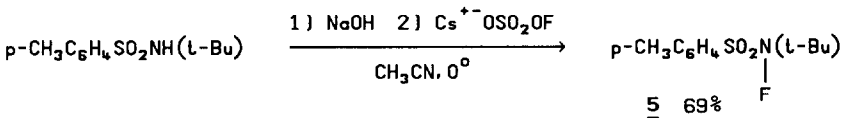
3 8,7%

Somewhat better are the results of CEFOX fluorination of 3-amino-5-carbethoxymethyl-1,2,4-oxadiazole, chosen as an example of low-basic heterocyclic amine. The main product of this reaction is monofluoro-derivative **4**.



4 63%

In contrast to the nitrogen compounds mentioned above, carbimides and sulfonamides do not react with CEFOX, but their salts are readily fluorinated to give desirable **N**-fluorination products. Thus, sodium **N**-t-butyl-p-toluenesulfonamide is selectively **N**-fluorinated with CEFOX in acetonitrile to give **N**-fluoroderivative **5** in high yield. The only by-product of this reaction is NH-sulfonamide, which may be separated from **5** by treatment of the reaction mixture with hexane.

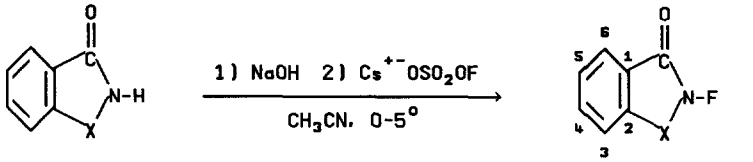


5 69%

Taking into account, that **5** is a useful fluorinating agent, the original synthesis of which is a quite complex one (the fluorination of the initial sulfonamide with elemental fluorine, yielding only 14% of **5**[10]), the proposed method may be of practical interest for a preparative synthesis of **5**.

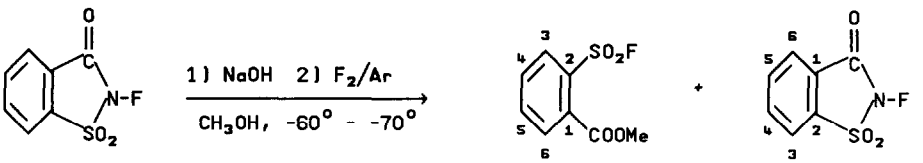
Similarly, the fluorination of saccharin and phthalimide salts leads to previously unknown **N**-fluorosaccharin **6** and **N**-fluorophthalimide **7**, respec-

tively, in good yields.



X = SO_2, **6** 69%
X = CO , **7** 48%

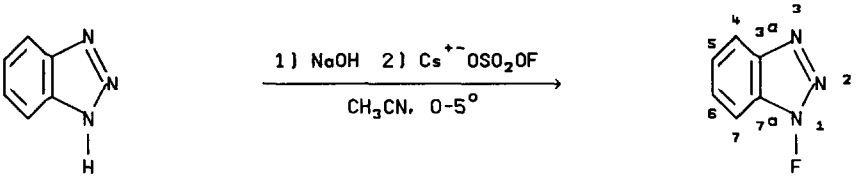
Considering **6** as a potent new fluorinating agent, we have undertaken an attempt to obtain it in greater amounts by fluorination of saccharin with elemental fluorine in methanol at a low temperature (MeOH has been chosen because of its good solving ability for saccharin sodium salt, as well as of its low freezing point). Unfortunately, unlike CEFOX, the elemental fluorine appeared to be a non-selective agent, that resulted in opening of the N-fluorosaccharin heterocyclic fragment with formation of flurosulfate derivative - the process well known for N-fluorosulfonamides[10].



8 28% **6** 15%

We have failed to obtain N-fluorosuccinimide on fluorination of succinimide sodium salt with CEFOX under the same conditions as used for phthalimide, although perfluoro-N-fluorosuccinimides have been synthesized successfully[11]. This failure may presumably be owed to the low hydrolytic stability of N-fluorosuccinimide.

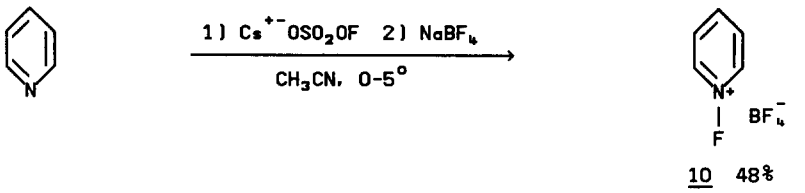
CEFOX appears to be the effective fluorinating agent not only for sulfonimides and carbimides salts, but also for some heterocyclic compounds salts such as sodium benzo-1,2,3-triazole. Thus, the latter is readily fluorinated with CEFOX in acetonitrile at room temperature to give 1-fluorobenzo-1,2,3-triazole **9** , a colorless oil, stable at room temperature.



9 25%

Another heterocycle, pyridine, readily reacts with CEFOX under the same

conditions to give **N**-fluoroderivative, isolated as the stable tetrafluoroborate **10** .



10 48%

Quite different results, obtained by the authors, who had studied this reaction earlier[4] may be attributed, to our opinion, to the secondary transformations of the initially formed **N**-fluoropyridinium sulfate. Transformation of this kind, leading to 2-substituted pyridines are typical for this class of activated heterocyclic structures[12].

All the structures obtained have been elucidated by means of multinuclear NMR (^1H, ^{13}C, ^{14}N, ^{15}N, ^{17}O, ^{19}F) and confirmed with the microanalysis data. Special attention has been paid to prove the structures of the first time synthesized **N**-fluoroderivatives.

Thus, the presence of NHF group in the 3-fluoroamino-5-carbethoxymethyl-1,2,4-oxadiazole **4** molecule has been confirmed by the presence of a doublet of doublets with $^1J(NH)=73.3$ Hz and $^1J(NF) = 67.5$ Hz at -181.67 ppm in the ^{15}N NMR spectrum, as well as of a doublet with $^2J(HF)=51.3$ Hz at 10.20 ppm in the ^1H NMR spectrum, and also by the magnitude of $^2J(CF)=2.8$ Hz observed for for the C^3 resonance line of the oxadiazole cycle in the ^{13}C NMR spectrum. The presence of an additional triplet with $^3J(NCH_2)=2.1$ Hz at -153.8 ppm in the ^{15}N NMR spectrum of **4** makes it evident, that, on the contrary to the conclusions of[13], the initial oxadiazole, synthesized by the method[13] is the 3-amino-, but not the 5-amino-1,2,4-oxadiazole.

The **N**-fluorophthalimide **7** structure has been confirmed by observation in its ^{13}C NMR spectrum two-, three-, four-, and five-bonded coupling constants between ^{13}C and ^{19}F, equal to 6.6; 2.8; 2.4 and 1.9 Hz respectively.

The saccharin fluorination products (**6** and **8**) structure has been proved by, besides its ^{17}O, ^{19}F, and ^{13}C NMR data, comparison of simulated and observed ^1H NMR spectrum, that allowed also to determine the values, as well as the signs of all of the coupling ^1H, ^1H constants.

In conclusion, CEFOX has been proved to be a useful reagent for **N**-fluorination. Moreover, in some cases it has been shown to be more selective, than elemental fluorine, although yields of the products obtained with CEFOX do not exceed those obtained using F_2. Clear evidence of the higher selectivity of CEFOX has been shown by the facts of preferential

formation of monofluoroderivatives when using CEFOX and absence of N-S bond cleavage in the process of formation of N-fluorosulfonamide 5 and N-fluorosaccharin 6. These and some other data[7] on the behavior of CEFOX as a fluorinating agent allow us to conclude that CEFOX is much inferior in its activity to the elemental fluorine as well as to the majority of hypofluorites of R_fOF-type, but is much superior to such a well-known fluorinating agent as $FClO_3$.

Thus, the possibility of N-fluorination should always be kept in mind when carrying out the reactions of nitrogen compounds with CEFOX.

One of the results of the present study which should be mentioned is the synthesis for the first time of N-fluorophthalimide 7 and N-fluorosaccharin 6. Both of these products deserve special attention as new potent electrophilic fluorinating reagents. The study is in progress now.

EXPERIMENTAL

^1H and ^{19}F NMR spectrum were obtained on a **Bruker WM-250** spectrometer with TMS and $CFCl_3$ as internal standards, respectively. ^{13}C, ^{14}N, ^{15}N, and ^{17}O NMR spectrum were obtained on a **Bruker AM-300** spectrometer with TMS (internal), CH_3NO_2 , $CH_3{}^{15}NO_2$, and D_2O as (external) standards, respectively. ^{14}N and ^{15}N downfield chemical shifts are quoted as positive, ^{19}F as negative. Numeration of atoms is given in the text.

IR spectra were recorded on a **Specord UR-20** spectrometer.

Starting cesium fluoroxysulfate (CEFOX) was synthesized according to[1], 3-amino-5-carbethoxymethyl-1,2,4-oxadiazole obtained according to[13], being isolated from the mixture of isomers by crystallization from CCl_4. Other reagents used are commercially available. Chromatographic separation was carried out on L 40/100 silica gel (**Chemapol**, CSFR). Reactions were monitored by TLC on standard silica gel plates of the same company; the components were detected by 5% solution of KI at elevated temperature.

Fluorination of urea with CEFOX. Synthesis of N-fluoro- and N,N-difluoroureas (1 and 2).

To a stirred solution of urea (0.6 g, 10 mmol) in dry CH_3CN (10 ml) at 20^oC was added portionwise over 5 min, CEFOX (3.0 g, 12 mmol), and the

mixture left to stir at this temperature for 20 min. The precipitate of inorganic salts was filtered off, and the solvent evaporated under reduced pressure. The residue was separated chromatographically (200\35 mm column, $CHCl_3$) to give **N**-fluorourea 1 (0.16 g, 21%) and **N,N**-difluorourea 2 (0.25 g, 26%). For 1 : Mp 55-56°C. ^1H NMR (CD_2Cl_2): δ 10.15 (br.s, 1H, NHF); 6.25 (br.s, 2H, NH_2). ^{13}C NMR (CD_2Cl_2): δ 161.46 (C=O). ^{15}N NMR (CD_2Cl_2): δ -154.35 (d.d, $^1J_{N-H}$=7.9 Hz, $^1J_{N-F}$=35 Hz, NHF); -296.98 (t, $^1J_{N-H}$=90 Hz, NH_2). Lit. [4]: Mp 56-57°C. ^1H NMR (TGF-D_8): δ 10.66 (br.s, 1H, NHF); 6.67 (br.s, 2H, NH_2). For 2: Mp 40-42°C. ^1H NMR (CD_2Cl_2): δ 6.83 (br.s, NH_2). ^{13}C NMR (DMSO-D_6): δ 152.44 (t, $^2J_{C-F}$=74 Hz, C=O). ^{14}N NMR (DMSO-D_6): δ -50.0 (br.s, $\Delta\nu_{1/2}$=300 Hz, 1H, NF_2); -300.05 (t, $^1J_{N-H}$=92.0 Hz, 1H, NH_2). Lit. [4]: for 2: Mp 41-41.5°C.

Fluorination of n-butyl carbamate with CEFOX. Synthesis of N-fluorobutyl carbamate 3.

To a stirred solution of n-butyl carbamate (1.2 g, 10 mmol) in dry CH_3CN (10 ml) at 20°C was added portionwise over 5 min, CEFOX (3.0 g, 12 mmol), and the mixture left to stir at room temperature for 2 h. The precipitate of inorganic salts was removed by filtration, the filtrate evaporated under reduced pressure and separated chromatographically (200\35 mm column, $CHCl_3$) to give N-fluorocarbamate 3 (0.12 g, 8.7%). ^1H NMR ($CDCl_3$): δ 9.45 (d, $^3J_{H-F}$=55.2 Hz, 1H, NHF); 4.28 (t, 2H, CH_2O); 1.7 (m, 4H, CH_2CH_2); 0.97 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$): δ -114.62 (d, $^3J_{H-F}$=55.6 Hz, NHF). Lit. [8]: ^1H NMR ($CDCl_3$): δ 9.42 (d, $^3J_{H-F}$=55.5 Hz, 1H, NHF); 4.26 (t, 2H, CH_2O); 1.6 (m, 4H, CH_2CH_2); 0.94 (t, 3H, CH_3); ^{19}F NMR ($CDCl_3$): δ -114.88 (d, ^3J=55.1 Hz, NHF).

Fluorination of 3-amino-5-carbethoxymethyl-1,2,4-oxadiazole. Synthesis of 3-fluoroamino-5-carbethoxymethyl-1.2.4-oxadiazole 4 .

To a stirred solution of 3-amino-5-carbethoxymethyl-1,2,4- oxadiazole (1.7 g, 10 mmol) in dry CH_3CN (15 ml) at 20°C was added portionwise over 10 min, CEFOX (3.0 g, 12 mmol). The mixture was left to stir at this temperature for 30 min, diluted with $CHCl_3$ (40 ml), the resultant

precipitate filtered off, and the filtrate evaporated under reduced pressure. The residue was separated chromatographically (70\30 mm column, $CHCl_3$) to afford 3-fluoroamino-5-carbethoxymethyl-1,2,4-oxadiazole 4 (1.2 g, 63%) as a yellowish oil. Found: C, 39.14; H, 4.54; N, 21.83 %. $C_6H_8N_3O_3F$ requires: C, 38.71; H, 4.23; N, 22.22%. ^1H NMR ($CDCl_3$): δ 10.20 (d, $^3J_{H-F}$=51.2 Hz, 1H, NHF); 4.20 (t, J=7.1 Hz, 2H, CH_2O); 3.95 (s, 2H, CH_2); 1.24 (t, J=7.1 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 174.06 (s, C^5); 169.50 (d, $^3J_{C-F}$=2.8 Hz, C^3); 165.34 (t, $^2J_{C-CH_2}$=4.5 Hz, $^3J_{C-CH_2O}$=1.9 Hz, C=O); 62.48 (t.q, $^1J_{C-H}$=148.7 Hz, $^2J_{C-H}$=4.5 Hz, CH_2O); 33.29 (t, $^1J_{C-H}$=133.6 Hz, CH_2); 13.88 (q.t, $^1J_{C-H}$=127.6 Hz, $^2J_{C-H}$=2.4 Hz, CH_3). ^{19}F NMR ($CDCl_3$): δ -104.21 (d, $^2J_{F-H}$=51.4 Hz, NHF).

Fluorination of N-t-butyl-p-toluenesulfonamide sodium salt. Synthesis of N-fluoro-N-t-butyl-p-toluenesulfonamide 5 .

N-t-Butyl-p-toluenesulfonamide (2.3 g, 10 mmol) and carefully powdered NaOH (0.4 g, 10 mmol) were stirred at room temperature in dry CH_3CN (15 ml) over 3 h until the dissolution of NaOH was complete. To the rapidly and efficiently stirred suspension at 0-5°C was added portionwise over 5 min, CEFOX (3.0 g, 12 mmol). The reaction mixture was left to stir for 30 min at the same temperature and for 30 min more at room temperature, then diluted with ether (50 ml). The resultant precipitate was filtered off, filtrate washed with water (3×50 ml). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The residue (2.2 g) was treated with hexane (10 ml) and left overnight in a refrigerator. Precipitated NH-sulfonamide was removed by filtration, and the filtrate chromatographed on a short column (70/30 mm, hexane-ether, 3:1) to afford N-fluoro-N-t-butyl-p-toluenesulfonamide 5 (1.4 g, 69%, based on spent sulfonamide). Mp 61-62°C. ^1H NMR ($CDCl_3$): 7.86 (d, $^3J_{H-H}$=8.2 Hz, 2H, $H^{2(6)}$), 7.32 (d, $^3J_{H-H}$=8.2 Hz, 2H, $H^{3(5)}$); 2.43 (s, 3H, CH_3); 1.44 (d, $^4J_{H-F}$=1 8 Hz, 9H, $C(CH_3)_3$). ^{19}F NMR ($CDCl_3$): δ -62.78 (N-F).

Fluorination of sodium saccharin with CEFOX. Synthesis of N-fluorosaccharin 6 .

Saccharin (0.9 g, 5 mmol) and NaOH (0.2 g, 5 mmol) were dissolved in

small amount of MeOH, the resultant solution filtered and evaporated to dryness under reduced pressure. The dry residue of sodium saccharin (1.0 g, 5 mmol) was suspended with dry CH_3CN (10 ml), and to the resultant suspension stirred at 0-5°C was added portionwise over 5 min, CEFOX (1.5 g, 6 mmol). The mixture was left to stir at this temperature for 30 min and diluted with ether (20 ml). The resultant precipitate was filtered, and the filtrate evaporated under reduced pressure. The residue was chromatographed on a short column (70\30 mm, $CHCl_3$) to give N-fluorosaccharin 6 (0.8 g, 69%). Mp 71-72°C. Found: C, 41.26; H, 2.05; N, 6.60%. $C_7H_4NO_3FS$ requires: C, 41.79; H, 1.99; N, 6.97%. ^1H NMR (C_6D_6): δ 7.10 (d.d.d, $^3J_{H^2-H^3}$=7.2 Hz, $^4J_{H^2-H^4}$=1.2 Hz, $^5J_{H^2-H^5}$=0.6 Hz, 1H, H^2); 6.81 (d.d.d, $^3J_{H^4-H^5}$=7.3 Hz, $^4J_{H^3-H^5}$=1.3 Hz, $^5J_{H^2-H^5}$=0.6 Hz, 1H, H^5); 6.66 (d.d.d, $^3J_{H^3-H^4}$=7.3 Hz, $^3J_{H^4-H^5}$=7.3 Hz, $^4J_{H^2-H^4}$=1.2 Hz, 1H, H^4); 6.61 (d.d.d, $^3J_{H^2-H^3}$=7.2 Hz, $^3J_{H^3-H^4}$=7.3 Hz, $^4J_{H^3-H^5}$= 1.3 Hz, 1H, H^3). ^{13}C NMR ($CDCl_3$): δ 160.02 (d.d, $^2J_{C-F}$=2.0 Hz, $^3J_{C-H^5}$=2.68 Hz, C=O); 137,56 (d.d, $^1J_{C-H}$=168.0 Hz, $^3J_{C-H}$=7.3 Hz, C^4); 136.90 (d.m, $^3J_{C-F}$=4.7 Hz, C^6); 136.22 (d.d, $^1J_{C-H}$=168.0 Hz, $^3J_{C-H}$=6.7 Hz, C^3); 126.69 (d.d.d, $^1J_{C-H}$=172.4 Hz, $^3J_{C-H}$=7.6 Hz, $^4J_{C-F}$=2.0 Hz, C^5); 124.41 (d.m, $^3J_{C-F}$=5.1 Hz, C^1). ^{17}O NMR ($CDCl_3$): δ 173.40 ($\Delta\nu_{1/2}$=300 Hz, SO_2); 395.80 ($\Delta\nu_{1/2}$=460 Hz; C=O). ^{19}F NMR ($CDCl_3$): δ -77.70 (NF). IR (KBr): 456, 496, 528, 576, 592, 672, 688, 736, 752, 792, 900, 944, 1116, 1165, 1200, 1288, 1376, 1410, 1464, 1528, 1584, 1768, 2280, 3096 cm^{-1}.

Fluorination of potassium phthalimide with CEFOX. Synthesis of N-fluorophthalimide 7 .

To a rapidly and efficiently stirred suspension of potassium phthalimide (0.9 g, 4.9 mmol) in dry CH_3CN (10 ml) at 0-5°C was added in small portions over 5 min , CEFOX (1.5 g, 6 mmol). The mixture was left to stir at this temperature for 30 min, then diluted with ether (20 ml). The precipitate was filtered, and the filtrate evaporated under reduced pressure. The resultant residue was treated with $CHCl_3$ (30 ml), and the extract washed with water (3×50 ml). The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to afford N-fluorophthalimide 7 (0.4 g, 48%). Mp 81-82°C. Found: C, 57.85; H, 2.31; N, 8.29; F, 11.13 %. $C_8H_4NO_2F$ requires: C, 58.18; H, 2.42; N, 8.48; F, 11.51 %. ^{13}C NMR (CD_2Cl_2): δ 155.2 (d, $^2J_{C-F}$= 6.6 Hz, C=O); 131.2 (d.d.d.d,

J_{C-H}=166.0, 6.3, 1.7 Hz, $^5J_{C-F}$=1.9 Hz, $C^{3(4)}$); 123.3 (d, $^3J_{C-F}$=2.8 Hz, $C^{1(6)}$); 120.0 (d.d.d.d, J_{C-H}=169.0, 5.4, 2.5 Hz, $^4J_{C-F}$=2.4 Hz, $C^{2(5)}$). ^{19}F NMR (CD_2Cl_2): δ -87,6 (s, NF).

Fluorination of saccharin with elemental fluorine. Synthesis of o-fluorosulfonylmethylbenzoate 8 and N-fluorosaccharin 6.

Saccharin (1.83 g, 10 mmol) and NaOH (0.4 g, 10 mmol) were stirred at room temperature in dry MeOH (15 ml) until dissolution was complete. Through the rapidly and efficiently stirred solution of the resultant saccharin sodium salt at -60 - -75°C was passed over 1 h 1:10 (v/v) fluorine-argon mixture (2.5 l, 11 mmol F_2). The reaction mixture was then allowed to warm, diluted with $CHCl_3$ (40 ml), washed with water (3\30 ml), then with a saturated sodium bicarbonate solution until the gas evolution stopped, and again with water. The organic layer was dried over $MgSO_4$, then evaporated under reduced pressure. The resultant residue was recrystallized from small amount of $CHCl_3$ to give O-fluorosulfonylmethylbenzoate 8 (0,51 g, 28%). The filtrate was chromatographed on a short column (70\30 mm, $CHCl_3$) to give N-fluorosaccharin 6 (0,32 g, 15%). For 8: Mp 88-89°C. Found: C, 43.57; H, 3.22%. $C_8H_7O_4F$ requires: C, 44 04; H, 3.21%. ^1H NMR (acetone-D_6): δ 8.38 (d.d.d.d, $^3J_{H^6-H^5}$=8.5 Hz, $^4J_{H^6-H^4}$=1.6 Hz, $^5J_{H^6-H^3}$=0.5 Hz, $^5J_{H^6-F}$=0.9 Hz, 1H, H^6); 8.06 (d.d.d.d, $^3J_{H^3-H^4}$=8.1 Hz, $^4J_{H^3-H^5}$=1.6 Hz, $^4J_{H^3-F}$=0.5 Hz, 1H, H^3); 7.91 (d.d.d.d, $^3J_{H^5-H^4}$=7.4 Hz, $^3J_{H^5-H^6}$=8.5 Hz, $^4J_{H^5-H^3}$=1.6 Hz, $^6J_{H^5-F}$=0 7 Hz, 1H, H^5); 7.43 (d.d.d.d, $^3J_{H^4-H^3}$=8.1 Hz, $^3J_{H^4-H^5}$=7.4 Hz, $^4J_{H^4-H^6}$=1.2 Hz, $^5J_{H^4-F}$=1,2 Hz, 1H, H^4). ^{13}C NMR ($CDCl_3$): δ 153.23 (q, J=4.1 Hz, C=O); 138.31 (t, J=9.2 Hz, C^1); 137.23 (d.d, J=162.4 Hz, 8.0 Hz, C^5); 130.35 (d.d.d, J=168.0 Hz, 8 4 Hz, 2.8 Hz, C^3); 123.02 (d.d, J=167.2 Hz, 8.2 Hz, C^4); 121.24 (d.d.d, J=169.6 Hz, 5.0 Hz, 2.4 Hz, C^6); 119 08 (d.t, $^2J_{C-F}$=22.6 Hz, J=9.0 Hz, C^2); 52,89 (q, J=147.5, CH_3). ^{17}O NMR ($CDCl_3$): δ 253.30 ($\Delta\nu_{1/2}$=300 Hz, 1 0, C=O); 182.60 ($\Delta\nu_{1/2}$=200 Hz, 2 0, SO_2F); 105.40 ($\Delta\nu_{1/2}$=400 Hz, 1 0, OCH_3). ^{19}F ($CDCl_3$): -65.36 (SO_2F). IR (KBr): 512, 575, 592, 704, 744, 768, 784, 1056, 1080, 1168, 1200, 1232, 1256, 1300, 1400, 1440, 1462, 1536, 1584, 1720, 3360 cm^{-1}.

Fluorination of benzo-1,2,3-triazole with CEFOX. Synthesis of 1-fluorobenzo-1,2,3-triazole 9 .

Benzo-1,2,3-triazole (1.2 g, 10mmol) and NaOH (0.4 g, 10 mmol) were stirred in dry CH_3CN (20 ml) at 50-60°C up to complete dissolution. The reaction mass was then cooled to 0-5°C, and to the resultant suspension of triazole sodium salt was added portionwise, over 5 min, CEFOX (3.0 g, 12 mmol). The reaction mixture was stirred for 20 min more at the same temperature and then for 1 h at room temperature, diluted with $CHCl_3$ (40 ml), washed seven times with water. The chloroform extract was separated, dried over anhydrous $MgSO_4$, evaporated under reduced pressure. The resultant residue was chromatographed on a short column (70\ 30 mm, hexane-ether 3:1) to give 1-fluorobenzo-1,2,3-triazole 9 (0.34 g, 25%) as colorless oil. Found: C, 52.96; H, 3.14; N, 30.12%. $C_6H_4N_3F$ requires: C, 52.55; H, 2.92; N, 30.66%. ^1H NMR ($CDCl_3$): δ 8.03 (d.d.t, J=8.5, 2.7, 1.0 Hz, 1H, H^{ar}); 7.62 (m, 1H, H^{ar}); 7.48 (m, 2H, H^{ar}) ^{13}C NMR ($CDCl_3$): δ 129.39 (d.d, $^1J_{C-H}$=163 2 Hz, $^3J_{C^6-H^4}$=7.7 Hz, C^6); 127.56 (d.m, $^3J_{C-F}$=3.6 Hz, C^{3a}); 125.76 (d d, $^1J_{C-H}$=155.4 Hz, $^3J_{C^5-H^7}$=7.8 Hz, C^5); 123.53 (d.d, $^1J_{C-H}$=161,1 Hz, $^3J_{C^4-H^6}$=6.5 Hz, C^4); 117.96 (m, C^{7a}); 108.01 (d.d, $^1J_{C-H}$=173.2 Hz, $^3J_{C^7-H^5}$=9.1 Hz, C^7). ^{19}F NMR ($CDCl_3$): δ -18,41 (br.s, NF).

Fluorination of pyridine with CEFOX. Synthesis of N-Fluoropyridinium tetrafluoroborate 10.

To a efficiently stirred solution of pyridine (0.8 g, 10 mmol) in dry CH_3CN (15 ml) at 0 - +5°C was added in small portions over 15 min, CEFOX (3.0 g, 12 mmol). The light-yellow mixture was stirred additionally for two hours at this temperature, then for 1 h at ambient temperature. The precipitate of inorganic salt was filtered off, the filtrate was evaporated under reduced pressure. Residue obtained was recrystallized twice from small amount of hot CH_3CN (for better result a portion of CH_2Cl_2 was added to the solution after chilling in refrigerator) to give N-fluoropyridinium tetrafluoroborate 10 (0.9 g, 48%).^1H NMR (CH_3CN-D_3): δ 9.23 (d.d, $^3J_{H-F}$=15 Hz, $^3J_{H-H}$=7.5 Hz, 2H, $H^{2(6)}$), 8.68 (m, 1H, H^4), 8.27 (m, 2H, $H^{3(5)}$). Lit[14]: ^1H NMR (CD_3CN): δ 9.33 (d.d, $^3J_{H-F}$=16 Hz, 2H, $H^{2(6)}$); 8.77 (m, 1H, H^4), 8.32 (m, 2H, $H^{3(5)}$).

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Supplementary Material Available: ^{1}H NMR observed and simulated (PANIC) spectra for compounds 6 and 8.