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Electrochemical Fluorination of Aromatic Compounds in Anhydrous HF

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Abstract—Electrochemical fluorination of anisole furnished 2- and 4-fluoroanisoles in a 3:1 ratio, guaiacol, and 4,4'-dimethoxydiphenyl ether. Phenylacetonitrile alongside the fluorination in the ring suffered the transformation of the cyano group into a trifluoromethyl. 4-Bromobenzamide was fluorinated to a high conversion mostly in the ring to afford predominantly 4-bromo-3,3,6,6-tetrafluoro-1,4-cyclohexadienecarboxamide. 4-Bromonitrobenzene in a low yield gave 4-bromofluoronitrobenzene and 3,4-dibromofluoronitrobenzene. 3-Bromo-nitrobenzene and 1,4-dichlorobenzene did not undergo fluorination. In the course of the electrolysis of the 4-bromobenzamide and 4-bromonitrobenzene in anhydrous HF apart the fluorination occurred also the bromination of the substrates.

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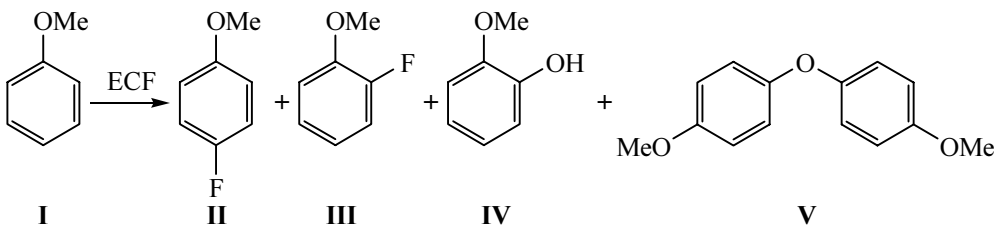
The fluorination of aromatic compounds with various fluorinating agents under different conditions already for a long time attracts the interest of researchers as a route to fluoroaromatic substances. Direct fluorination of various aromatic compounds with fluorine [1], and their oxidative fluorination with the higher metal fluorides (AgF_2, CoF_3 etc.) [2] is well documented. We formerly investigated the electrochemical fluorination (ECF) of some functionally-substituted aromatic compounds PhX (X = SO_2Me [3], AC [4], $CONH_2$, NHCOMe [5]) and demonstrated that the fluorination occurred exclusively in the aromatic ring with retention of the substituent.

In order to involve in the ECF process compounds with the other functional groups and in extension of our investigations in this field [3–6] we studied in this work the behavior of a series of aromatic substrates (anisole, 2-phenylacetonitrile, 4-bromo-benzamide, 3- and 4-bromonitrobenzenes, 1,4-dichlorobenzene) under ECF conditions in the anhydrous HF. One of the goals of the present study was the elucidation of the ECF process of aromatic compounds at the early stage and its further development with increased reaction time that might result in a partial or total saturation of the aromatic ring with the complete destruction of the benzene skeleton and formation in the limit of perfluoroalkanes. The processes we investigated proceeded to a moderate or low conversion with considerable tarring and formation of quite a number of products. Therefore, we did not isolate individual products of ECF from very complex reaction mixtures, but only analyzed them with the use of GLC, GC-MS, and ^1H, ^{13}C, and ^{19}F NMR spectroscopy.

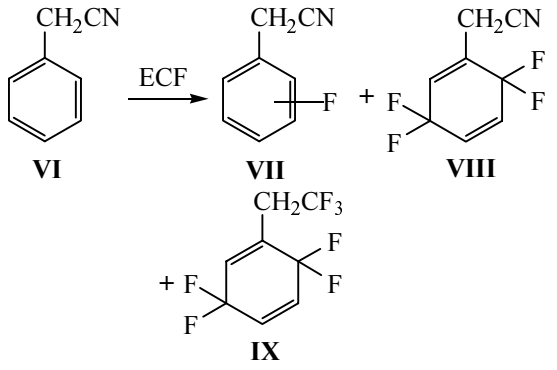
According to [7], the exhausted fluorination of anisole (**I**) afforded in a low yield the perfluorocyclohexyl trifluoromethyl ether $C_6F_{11}OCF_3$. We found that the fluorination of anisole in anhydrous HF for 15 h at 6.0–7.2 V occurred to ~35% conversion. By means of GC-MS and ^{19}F NMR spectroscopy we succeeded to identify in the reaction mixture alongside the initial anisole also 4- and 2-fluoroanisoles (**II**) and (**III**) in a ratio 3 : 1, guaiacol (**IV**), and 4,4'-dimethoxydiphenyl ether (**V**).



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

The structure of formed isomers of fluoroanisole **II** and **III** was confirmed by the chemical shifts in the ^{19}F NMR spectra {–125.94 (**II**) and –136.80 ppm (**III**); publ.: –125.2 and –136.1 ppm respectively [8]}, and also by the presence in the ^{13}C NMR spectra of characteristic doublets in the regions 115–116 ($^{2}J_{CF}$ ~ 8 Hz) and 161–163 ppm ($^{1}J_{CF}$ ~245 Hz). The fact of guaiacol (**IV**) and not 4-methoxyphenol formation is proved by the composition of fragment ions in the mass spectrum: in the mass spectrum of 4-methoxyphenol should appear with relatively high intensity a peak of ion with *m/z* 53 [*M* – CO – COMe]$^+$, whereas for guaiacol (**IV**) this peak is very weak (relative intensity in our case not exceeds 5%).

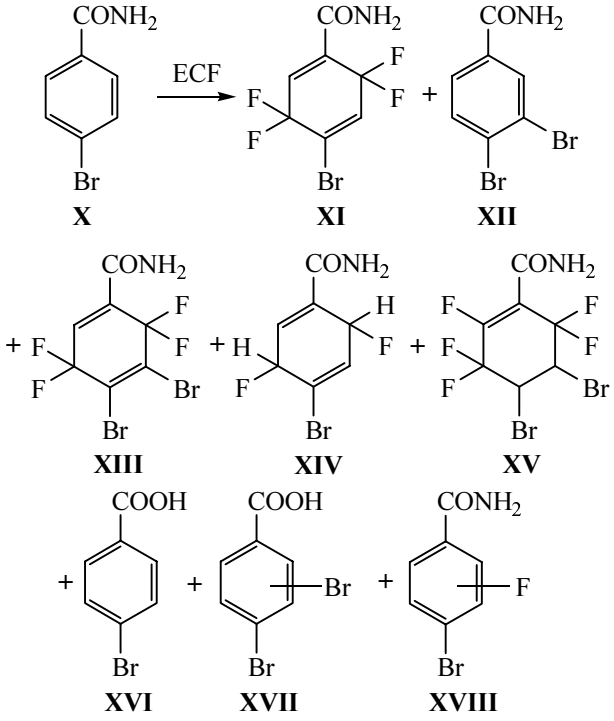
Formerly in ECF experiments with benzamide in acetonitrile we observed formation of benzonitrile and its monofluorinated products [5]. In this study we carried out the fluorination of benzonitrile homolog, phenylacetonitrile (**VI**). Inasmuch as the process is accompanied by strong tarring and gives rise to relatively low yield (25–30%) of fluorine-containing compounds, the reaction mixture was investigated only by means of GC-MS procedure. In contrast to benzamide and benzonitrile [5] where we did not found fluorination of the amide or cyano group in the course of the process, from nitrile **VI** alongside two isomers of (fluorophenyl)acetonitrile (**VII**) and a product of oxidative fluorination, (3,3,6,6-tetrafluoro-1,4-cyclo-hexadienyl)acetonitrile (**VIII**), formed to a small degree also 3,3,6,6-tetrafluoro-1-(2,2,2-trifluoroethyl)-1,4-cyclohexadiene (**IX**).



In the mixture several more volatile compounds are also present giving in the mass spectrum strong peaks of the ion $[CF_3]^+$ (*m/z* 69). These results indicate that the functional cyano group is partially fluorinated into trifluoromethyl one. This conversion apparently occurs by HF addition across the C≡N bond followed by exchange of amino group for a fluorine atom. The fragmentation of compounds **VIII** and **IX** under an electron impact is similar to the fragmentation of the other tetrafluorides of cyclohexadiennyl structure that we have formerly described in detail [4].

ECF of 4-bromobenzamide (**X**) proceeded fairly efficiently: the substrate conversion in 19 h exceeded 90%. The products were identified by means of GC-MS and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy after separating into fractions enriched with lighter and heavier products by column chromatography on silica gel. The products identification is simplified here by the presence in the mol-ecules of one or several bromine atoms giving in the mass spectrum peaks with a characteristic isotope composition. We also compared our mass spectra with the data on fragmentation under the electron impact of known compounds.

The fluorination result depended essentially on the throughput of current. When 17.4 A · h was passed on 20 g of substrate **X** the prevailing product of ECF (~ 40%) was 4-bromo-3,3,6,6-tetrafluoro-1,4-cyclohexadiene-1-carboxamide (**XI**). At the same time in considerable amounts formed also 3,4-dibromobenzamide (**XII**) (~20%) and 4,5-dibromo-3,3,6,6-tetrafluoro-1,4-cyclohexadiene-1-carboxamide (**XIII**) (~ 15%). The GC-MS method revealed also the presence in the reaction products in negligible quantities of 4-bromo-3,6-difluoro-1,4-cyclohexadiene-1-carboxamide (**XIV**), 4,5-dibromo-2,3,3,6,6-

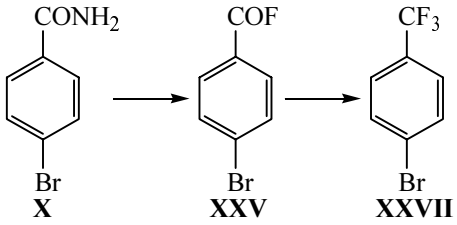


pentafluorocyclohexene-1-carboxamide (**XV**), 4-bromobenzoic acid (**XVI**), and isomers of dibromobenzoic acids (**XVII**). The presence in the ^{19}F NMR spectrum of the electrolysis products of signals in the region characteristic of compounds with a C_{Ar}–F bond (–107 to –108 ppm) demonstrated the formation of a mixture of monofluorinated products **XVIII**.

Tetrafluoride **XI** gave rise in the ^{19}F NMR spectrum to the signals with the maximum intensity in the region –93 to –95 ppm characteristic of these compounds [3–5]. The formation of just 3,4-dibromo-substituted benzamide **XII** is supported by the good agreement of aromatic protons signals in the ^{1}H NMR spectrum of the fraction enriched with compound **XII** with the corresponding simulated spectrum calculated using the program ACDLabs, whereas for the 2,4-dibromo-substituted benzamide the proton signals in positions *3* and *5* should appear significantly downfield and upfield respectively as compared to the observed range.

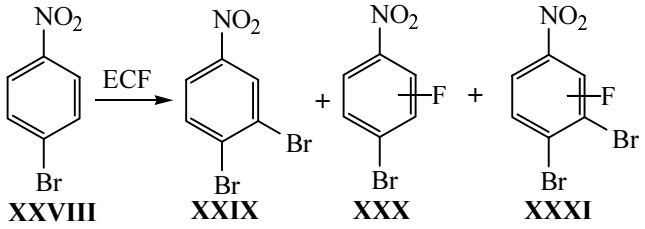
At the fractionation of the electrolysis products by column chromatography using methanol as eluent the main compounds obtained according to GC-MS were that resulting from the methanolysis of amide **XII**, methyl dibromobenzoate $Br_2C_6H_3CO_2Me$ (**XIX**), and also methyl 4-methoxybenzoate 4-$MeOC_6H_4CO_2Me$ (**XX**), methyl 4-bromobenzoate 4-$BrC_6H_4CO_2Me$ (**XXI**), and methyl benzoates fluorinated in the ring $FC_6H_4CO_2Me$ (**XXII**), $BrFC_6H_3CO_2Me$ (**XXIII**), $Br_2FC_6H_2CO_2Me$ (**XXIV**). The formation of compounds **XXII–XXIV** was confirmed by the presence in the ^{1}H NMR spectrum of several methoxy group signals in the region 3.8–3.9 ppm, and in the ^{19}F NMR spectrum of the signals from fluoro-aromatic compounds in the range 100–110 ppm with characteristic splitting [–98.62 d.d (*J* 8.3, 1.1 Hz), –107.57 d.d (*J* 8.9, 6.9 Hz), –108.16 d.d (*J* 9.6, 6.5 Hz), –110.25 d.d (*J* 10.0, 7.2 Hz)].

On increasing the amount of passed current the character of fluorination suffered qualitative changes. Chromato-mass spectrometry reveals the presence of two main products with even values of *m/z* of molecular ions 202 (**XXV**) (1Br) and 280 (**XXVI**) (2Br). The presence of intensive fragment ion peaks with *m/z* 47 and overall pattern of molecular ions fragmentation, very similar for compounds **XXV** and **XXVI,** evidence that these are 4-bromobenzoyl (**XXV**) and dibromo-benzoyl (**XXVI**) fluorides. Besides a small amount of ECF products provides very strong peaks of ion CF_3 (*m/z* 69), and in the ^{19}F NMR spectrum of the electrolysis product appears a singlet at –80.6 ppm. These findings show that further fluorination occurred with conversion of the functional amide group first into the acyl fluoride C(O)F (**XXV**), and then into trifluoromethyl group (**XXVII**), in keeping with the following scheme by an example of 4-bromobenzamide (**X**).



X **XXV** **XXVII**

The fluorination of 4-bromonitrobenzene (**XXVIII**) proceeded with considerable tarring. On removing the tarred products on a column charged with silica gel the main components of the mixture according to GC-MS findings were substrate **XXVIII** (40%) and 3,4-dibromonitrobenzene (**XXIX**) (40%). The fluorinated products (~9%) contain two isomeric bromofluoronitrobenzenes (**XXX**) and dibromofluoronitrobenzenes (**XXXI**) with corresponding signals in the ^{19}F NMR spectra at –96.52 and –98.35 ppm respectively.



XXVIII **XXIX** **XXX** **XXXI**

The formation of dibromides **XII, XIII, XV, XVII, XIX, XXIV, XXVI, XXIX**, and **XXXI** at the ECF of 4-bromobenzamide (**X**) and 4-bromonitrobenzene (**XXVIII**) in anhydrous HF may occur either by elimination of bromine from the corresponding substrate by a cation-radical arising from the substrate oxidation on the anode, or by attack on the substrate of a bromine atom originating from the oxidation of bromide ion present in the solution as a result of bromine substitution by a fluorine atom.

No fluorination products were obtained after electrolysis of 3-bromonitrobenzene (**XXXII**) and 1,4-dichlorobenzene (**XXXIII**) solutions in anhydrous HF for 11–15 h. 3-Bromonitrobenzene (**XXXII**) suffered complete tarring, and the ^{19}F NMR spectrum lacked any signals, and the solution after electrolysis of 1,4- dichlorobenzene (**XXXIII**) contained only the initial substrate as showed the GC-MS data.

Thus the ECF of functionally-substituted aromatic compounds in anhydrous HF depending on conditions may involve the fluorination in the ring either with retention or with destruction of the aromatic system, fluorination of the functional group, and also the capture by a cation-radical of the substrate of other anions present in the solution, for instance, a bromide ion at ECF of the bromine-containing substrates leading to dibromo products.

EXPERIMENTAL

^1H, ^{13}C, and ^{19}F NMR spectra were registered on a spectrometer Bruker DPX 400 (at 400, 100, and 376 MHz respectively) from solution of substances in $CDCl_3$, internal reference HMDS, chemical shifts are given with respect to TMS (^1H, ^{13}C) and CCl_3F (^{19}F). Chromato-mass spectrometry was performed on Hewlett-Packard HP 5971A instrument (70 ev), chromatograph HP-5890, column Ultra-2 (5% of phenylmethylsilicone), vaporizer temperature 250°C, oven temperature 70–280°C. GLC analyses were carried out on a chromatograph LKhM-8MD, columns 2000×3 mm, stationary phase 15% of polyphenylmethylsilicone on Chromaton N-AW, detector katharometer, carrier gas helium.

Electrochemical fluorination was carried out without addition of current-conducting salts in a steel electrolyzer of 130 cm^3 capacity with nickel electrodes of the overall surface 63 cm^2 equipped with cocks for input of HF and output of fluorination products and with a reflux condenser filled with a mixture acetone–ether, 1:1, and cooled with liquid nitrogen to –30°C.

Electrochemical fluorination of anisole. Into the cooled cell of the electrolyzed was charged 100 g of anhydrous HF and 10 g of anisole (**I**). The electrolysis was carried out for 14.7 h (17.6 A·h) at the anode current density 1.59 A/dm^2 and at voltage on the cell 6.0–7.2 V at the cell temperature ~ 5°C. After a short induction period the current grew from <1 A at 7.4 V to 1.2 A at 5.6 V. The fluorination proceeded with a considerable tarring, the yield of the fluorination products was ~ 35%. On completion of the electrolysis the reaction mixture was discharged, HF was evaporated, the residue was diluted with ethyl ether, NaOH was added to neutralize the residual HF till neutral pH, the solution was dried over $MgSO_4$, the ethyl ether was distilled off, and the mixture thus obtained was analyzed by means of ^1H, ^{13}C, and ^{19}F NMR spectroscopy and GC-MS procedure.

4-Fluoroanisole (II). ^{19}F NMR spectrum, δ, ppm: –125.94. Mass spectrum, *m/z* (I_{rel}, %): 126 (100) [*M*], 111 (65) [*M* – Me], 95 (18) [*M* – OMe], 83 (86) [*M* – COMe], 57 (12) [C_3H_2F].

3-Fluoroanisole (III). ^{19}F NMR spectrum, δ, ppm: –136.80. Mass spectrum was similar to that of 4-fluoroanisole.

Guaiacol (IV). Mass spectrum, *m/z* (I_{rel}, %): 124 (80) [*M*], 109 (100) [*M* – Me], 81 (59) [*M* – COMe], 53 (5) [*M* – CO – COMe].

4,4'-Dimethoxydiphenyl ether (V). Mass spectrum, *m/z* (I_{rel}, %): 230 (100) [*M*], 215 (20) [*M* – Me], 187 (10) [*M* – COMe], 172 (20) [*M* – Me – COMe], 159 (12) [*M* – CO – COMe], 144 (12) [*M* – 2COMe], 123 (44) [$MeOC_6H_4O$], 92 (38) [C_6H_4O], 77 (26) [Ph].

Electrochemical fluorination of phenylacetonitrile (VI) was carried out in the same fashion as described above for 16.8 h. On completion of the electrolysis the products were discharged, worked up as described above, and analyzed by GC-MS.

(Fluorophenyl)acetonitrile (VII). Mass spectrum, *m/z* (I_{rel}, %): 135 (100) [*M*], 134 (50) [*M* – H], 115 (22) [*M* – HF], 108 (46) [*M* – HCN], 107 (40) [*M* – H – HCN].

2-(3,3,6,6-Tetrafluoro-1,4-cyclohexadienyl)-acetonitrile (VIII). Mass spectrum, *m/z* (I_{rel}, %): 191 (40) [*M*], 171 (12) [*M* – HF], 164 (16) [*M* – HCN], 151 (100) [*M* – CH_2CN], 145 (52) [*M* – HCN – F], 132 (46) [$C_6H_3F_3$], 101 (52) [$C_5H_3F_2$], 75 (48) [C_3HF_2], 51 (32) [CHF_2], 31 (20) [CF].

3,3,6,6-Tetrafluoro-1-(2,2,2-trifluoroethyl)-1,4-cyclohexadiene (IX). Mass spectrum, *m/z* (I_{rel}, %): 234 (4) [*M*], 214 (5) [*M* – HF], 151 (100) [*M* – CH_2CF_3], 132 (54) [$C_6H_3F_3$], 113 (70) [$C_6H_3F_2$], 101 (58) [$C_5H_3F_2$], 82 (20) [C_5H_3F], 75 (45) [C_3HF_2], 69 (64) [CF_3], 51 (44) [CHF_2], 31 (25) [CF].

Electrochemical fluorination of 4-bromobenzamide (X) was carried on for 17.4 h at the voltage 5.8–6.2 V. The electrolysis products were worked up as above, the mixture obtained was separated by column chromatography on silica gel at successive elution with solvents of growing polarity (petroleum ether; petroleum ether–ethyl ether, 3:1; petroleum ether–ethyl ether, 1:1; ethyl ether). As a result three fractions were obtained which were subjected to analysis by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and GC-MS. For all bromine-containing ions the presented values of *m/z* correspond to the isotope ^{79}Br.

4-Bromo-3,3,6,6-tetrafluoro-1,4-cyclohexadiene-1-carboxamide (XI). ^{19}F NMR spectrum, δ, ppm:

–95.56 m (F^3), –93.97 m (F^5). Mass spectrum, *m/z* (I_{rel}, %): 273 (46) [*M*], 257 (6) [*M* – NH_2], 253 (6) [*M* – HF], 210 (26) [*M* – F – $CONH_2$], 178 (48) [257 – Br], 150 (32) [178 – CO], 131 (22) [210 – Br], 81 (30) [C_5H_2F], 44 (100) [$CONH_2$].

2,4-Dibromobenzamide (XII). Mass spectrum, *m/z* (I_{rel}, %): 279 (72) [*M*], 263 (100) [*M* – NH_2], 235 (30) [263 – CO], 154 (10) [235 – Br], 75 (38) [154 – Br], 44 (34) [$CONH_2$].

3,3,6,6-Tetrafluoro-2,4-dibromo-1,4-cyclohexadiene-1-carboxamide (XIII). ^{19}F NMR spectrum, δ, ppm: –89.82 m (F^3), –90.45 m (F^5). Mass spectrum, *m/z* (I_{rel}, %): 353 (100) [*M*], 337 (5) [*M* – NH_2], 290 (28) [*M* – F –$CONH_2$], 258 (24) [337 – Br], 230 (18) [258 – CO], 211 (10) [290 – Br], 177 (9) [258 – Br], 149 (12) [230 –Br], 130 (14) [209 – Br], 80 (10) [Br], 44 (90) [$CONH_2$].

4-Bromo-3,6-difluoro-1,4-cyclohexadiene-1-carboxamide (XIV). Mass spectrum, *m/z* (I_{rel}, %): 237 (24) [*M*], 217 (12) [*M* – HF], 182 (100) [*M* – HF – F – NH_2], 103 (24) [182 – Br], 75 (78) [C_6H_3].

4,5-Dibromo-2,3,3,6,6-pentafluorocyclohexene-1-carboxamide (XV). Mass spectrum, *m/z* (I_{rel}, %): 295 (14) [*M*], 277 (5) [*M* – NH_2], 214 (14) [*M* – Br], 194 (20) [214 – HF], 170 (14) [214 – $CONH_2$], 151 (10) [170 – F], 119 (12) [151 – CHF], 101 (18) [151 – CF_2], 44 (100) [$CONH_2$].

4-Bromobenzoic acid (XVI). Mass spectrum, *m/z* (I_{rel}, %): 220 (46) [*M*], 202 (100) [*M* – H_2O], 185 (80) [202 – OH], 155 (40) [*M* – CH_2COOH], 75 (60) [155 – HBr].

3,4-Dibromobenzoic acid (XVII). Mass spectrum, *m/z* (I_{rel}, %): 278 (50) [*M*], 261 (28) [*M* – OH], 233 [14, *M* – COOH], 154 (12) [233 – Br], 75 (33) [C_6H_3], 74 (35) [C_6H_2].

Methyl dibromobenzoate $Br_2C_6H_3CO_2Me$ (XIX). Mass spectrum, *m/z* (I_{rel}, %): 292 (15) [*M*], 261 (30) [*M* – OMe], 233 (12) [*M* – COOMe], 75 (95) [C_6H_3], 74 (100) [C_6H_2].

Methyl 4-methoxybenzoate $4\text{-}MeOC_6H_4CO_2Me$ (XX). Mass spectrum, *m/z* (I_{rel}, %): 166 (35) [*M*], 135 (100) [*M* – OMe], 107 (25) [*M* – COOMe], 92 (30) [107 – Me], 77 (35) [Ph].

Methyl 4-bromobenzoate $4\text{-}BrC_6H_4CO_2Me$ (XXI). Mass spectrum, *m/z* (I_{rel}, %): 214 (35) [*M*], 183 (25) [*M* – OMe], 155 (45) [*M* – COOMe], 213 (5) [*M* – Br], 135 (15) [*M* – Br], 104 (20) [183 – Br], 76 (70) [C_6H_4], 75 (80) [C_6H_3], 50 (100) [C_4H_2].

Methyl fluorobenzoate $FC_6H_4CO_2Me$ (XXII). Mass spectrum, *m/z* (I_{rel}, %): 154 (30) [*M*], 123 (100) [*M* – OMe], 95 (60) [*M* – COOMe], 75 (40) [95 – HF].

Methyl bromofluorobenzoate $BrFC_6H_3COOMe$ (XXIII). Mass spectrum, *m/z* (I_{rel}, %): 232 (35) [*M*], 201 (100) [*M* – OMe], 173 (50) [*M* – COOMe], 153 (15) [*M* – Br], 122 (15) [201 – Br], 94 (90) [173 – Br], 75 (40) [95 – HF].

Methyl dibromofluorobenzoate $Br_2FC_6H_2COOMe$ (XXIV). Mass spectrum, *m/z* (I_{rel}, %): 310 (25) [*M*], 279 (50) [*M* – OMe], 251 (20) [*M* – COOMe], 172 (35) [251 – Br], 93 (100) [172 – Br], 74 [50, 93 – F].

4-Bromobenzoyl fluoride $4\text{-}BrC_6H_4C(O)F$ (XXV). Mass spectrum, *m/z* (I_{rel}, %): 202 (40) [*M*], 183 (13) [*M* – F], 174 (100) [*M* – CO], 155 (22) [*M* – COF], 123 (10) [*M* – Br], 79 (50) [Br], 47 (30) [COF].

Dibromobenzoyl fluoride $Br_2C_6H_3C(O)F$ (XXVI). Mass spectrum, *m/z* (I_{rel}, %): 280 (45) [*M*], 261 (15) [*M* – F], 252 (60) [*M* – CO], 233 (15) [*M* – COF], 201 (21) [*M* – Br], 173 (40) [*M* – CO – Br], 94 (40) [M – CO –2Br], 79 (68) [Br], 47 (58) [COF].

Electrochemical fluorination of 4-bromonitrobenzene took 15.4 h. After the above described workup the reaction mixture was analyzed by GLC and GC-MS.

3,4-Dibromonitrobenzene $Br_2C_6H_3NO_2$ (XXIX). Mass spectrum, *m/z* (I_{rel}, %): 281 (75) [*M*], 251 (20) [*M* – NO], 235 (45) [*M* – NO_2], 223 (32) [*M* – CNO_2], 170 (5) [253 – Br], 154 (25) [235 – Br], 153 (20) [154 – H], 128 (5) [154 – C_2H_2], 75 (100) [156 – Br], 74 (85) [75 – H].

4-Bromofluoronitrobenzene $BrFC_6H_3NO_2$ (XXX). Mass spectrum, *m/z* (I_{rel}, %): 221 (45) [*M*], 205 (5) [*M* – O], 191 (25) [*M* – NO], 173 (40) [*M* – NO_2], 153 (5) [173–HF], 161 (18) [173 – C], 94 (100) [175 – Br], 74 (26) [94 – HF], 68 (24) [94 – C_2H_2], 50 (32) [C_4H_2].

3,4-Dibromofluoronitrobenzene $Br_2FC_6H_2NO_2$ (XXXI). Mass spectrum, *m/z* (I_{rel}, %): 299 (74) [*M*], 269 (25) [*M* – NO], 253 (43) [*M* – NO_2], 241 (35) [253 – C], 172 (55) [253 – Br], 93 (100) [174 – Br], 74 (38) [93 – F], 61 (28) [74 – CH].

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