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Sodium dithionite initiated fluoroalkylation of trimethoxybenzenes, mesitylene and pyrroles with $BrCF_2CF_2Br$

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ABSTRACT

Sodium dithionite initiated reaction of 1,2-dibromotetrafluoroethane with 1,3,5-trimethoxybenzene (**1a**) in an acetonitrile–water mixture proceeded efficiently at ambient temperature to give 1-(2-bromotetrafluoroethyl)-2,4,6-trimethoxybenzene (**2**) almost quantitatively. Similar reaction with 1,2,3-trimethoxybenzene (**1b**) gave only reasonable yield of regioisomers of (2-bromotetrafluoroethyl)-trimethoxybenzenes **3** and **4** and small amount of a substitution product of the central trimethoxy group, 1-(2-bromotetrafluoroethyl)-2,6-dimethoxybenzene (**5**). The reaction with mesitylene (**6**) gave complex mixtures from which, depending on the temperature and a mesitylene/$BrCF_2CF_2Br$ ratio, the expected (2-bromotetrafluoroethyl)mesitylene (**8**) or a dimeric product, 4,4′-bis(2-bromo-1,1,2,2-tetrafluoroethyl)-1,3,5,1′,3′,5′-hexamethylbicyclohexyl-2,5,2′,5′-tetraene (**7**), were isolated in a yield of 18 and 13%, respectively. The reactions of $BrCF_2CF_2Br$ with pyrrole (**9**) and 1-methylpyrrole (**11**) gave the respective alkylated compounds, 2-(2-bromotetrafluoroethyl)pyrrole (**10**) and 2-(2-bromotetrafluoroethyl)-1-methylpyrrole (**12**) in over 70% yields; the former was found to be fairly unstable. The reactivity of the terminal bromine atom in 1-(2-bromotetrafluoroethyl)-2,4,6-trimethoxybenzene (**2**) was also investigated.

1. Introduction

Since many years it has been known that perfluoroalkylations of aromatic and heteroaromatic compounds, particularly when activated by electron donating substituents, with perfluoroalkyl iodides proceed readily in the presence of radical-anion sources like dithionites or hydroxymethanesulphinates. Thus, phenolates, anilines, amino-, methoxy- and methylbenzenes and pyrroles react readily with perfluoroalkyl iodides at ambient temperature in a water–acetonitrile, or water–dimethylsulphoxide solutions to give perfluoroalkylated derivatives with 40 to over 80% yields [1–4]. Similarly they react with pyridines [5], quinolines [4] and coumarines [6,7], however, in those cases, higher temperature is usually required and yields of alkylated products are somewhat lower. When more drastic reaction conditions were applied, i.e. water-free dimethylsulphoxide, temperature of 75 °C and prolonged reaction time, perfluoroalkylation of N, S and O heteroaromatics and activated benzenes with long chain perfluoroalkyl chlorides has also been reported [8]. In our laboratory, it has been found that the $Na_2S_2O_4$/acetonitrile/H_2O system is also able to promote addition of polyhaloalkanes, i.e.1-bromo-1-chloro-2,2,2-trifluoroethane (Halothane®) [9–12] and dibromodifluoromethane [13,14] to various electron-rich unsaturated compounds but most attempts to alkylate aromatic and heteroaromatic compounds with these reagents were unsuccessful. The only successful exceptions were reactions of 1-bromo-1-chloro-2,2,2-trifluoroethane with 1,3,5-trimethoxybenzene and with pyrroles, which resulted in coupling of one molecule of $CF_3CHClBr$ with two molecules of the aromatic compound to give, respectively, trifluoromethyl-bis(2,4,6-trimethoxyphenyl)methane [15] and 5-(trifluoromethyl)-dipyrromethanes [16] in a 38–50% yields. In those reactions both, Br and Cl atoms of $CF_3CHClBr$ were replaced with an aromatic moiety.

1,2-Dibromotetrafluoroethane, which is readily prepared by bubbling of tetrafluoroethene into liquid bromine, has received considerable attention as fluoroalkylating agent. However, most of the reported examples involved halophilic reactions of phenolates and thiophenolates [17,18] or salts of heterocyclic amines [19,20] which resulted in O-, S- and N-alkylations. Reported reactions of $BrCF_2CF_2Br$ with free thiophenols under free-radical conditions (SO_2, pyridine) also lead exclusively to S-alkylation [21], however in the case of sterically hindered phenols, C-alkylation occurred [22]. Some of the obtained bromotetrafluoro derivatives were further funtionalized by nucleophilic replacement of the remaining bromine atom [18–20].

Our results of the reactions of $CF_3CHClBr$ with the most electron-rich aromatics, i.e. 1,3,5-trimethoxybenzene [15] and pyrroles [16] in the $Na_2S_2O_4/CH_3CN/H_2O$ system, however did not

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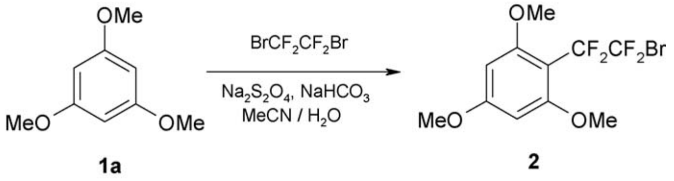
result in the expected CF_3CHCl-substituted aromatics, demonstrated ability of this reaction system to promote C-alkylation of the above-mentioned aromatics by fluorohaloalkanes other than the perfluoroalkyl iodides. On this basis, and considering the reported fact that even perfluoroalkyl chlorides are able to C-alkylate activated aromatics [8], we undertake studies on the reactions of polymethoxybenzenes, mesitylene and pyrroles with 1,2-dibromotetrafluoroethane, which hopefully should lead to C-alkylated product (2-bro-motetrafluoroethyl) aromatics.



Scheme 1.

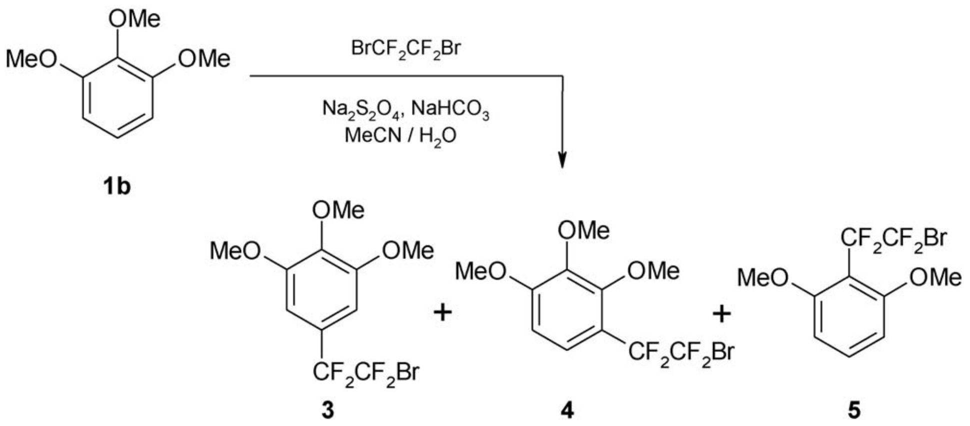
2. Results and discussion

1,2-Dibromotetrafluoroethane reacted readily with 1,3,5-trimethoxybenzene (**1a**) in the $Na_2S_2O_4/CH_3CN/H_2O$ system at ambient temperature to give the expected 1-(2-bromotetrafluoroethyl)-2,4,6-trimethoxybenzene (**2**) almost quantitatively (Scheme 1). The reaction proceeded cleanly, such that the crude crystalline **2** was pure enough to give correct elemental analysis without purification.

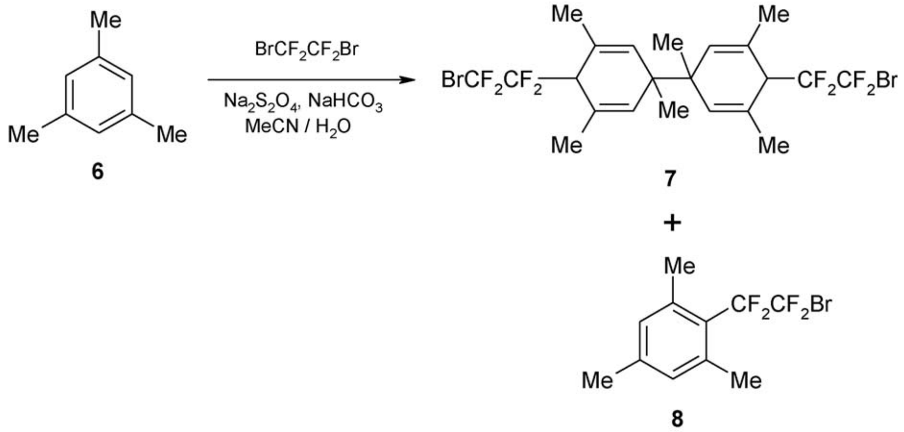
The reaction with 1,2,3-trimethoxybenzene (**1b**) was much less successful. Under the same conditions, and even when elevated temperature and prolonged reaction time were applied, only partial conversion of **1b** was achieved to give a mixture containing much of unreacted **1b** (ca. 58%), the expected 1-(2-bromotetrafluoroethyl)-3,4,5-trimethoxybenzene (**3**), 1-(2-bromotetrafluoroethyl)-2,3,4-trimethoxybenzene (**4**) and 1-(2-bromotetrafluoroethyl)-2,6-dimethoxybenzene (**5**) in a 4:3:1 ratio (NMR estimate) and some dark impurities (Scheme 2). Subjecting the crude reaction mixture to column chromatography allows to isolate colourless fraction containing only compounds **3**–**5** in the same ratio. It is worth to notice that formation of compound **5** involves substitution of the central methoxy group in **1b** by $BrCF_2CF_2$–, which was fairly unexpected process.

The ^1H and ^{19}F NMR analysis of a mixture obtained from the reaction of 1,2-dibromotetrafluoroethane with 1,4-dimethoxybenzene revealed mostly unreacted substrate and numerous signals difficult to be assigned to any expected product. No reaction at all occurred with anisole.

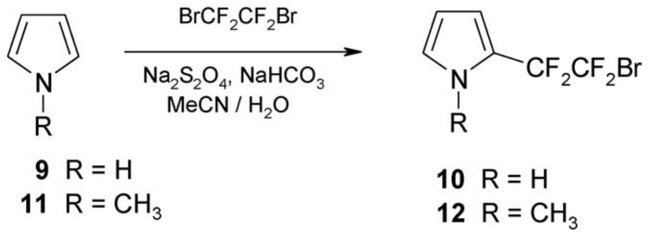
Results of the reaction of 1,2-dibromotetrafluoroethane with mesitylene (**6**) (Scheme 3) depended on the conditions applied. When it was carried out at ambient temperature with an excess of $BrCF_2CF_2Br$, the product consisted of a mixture of colourless oils and white crystalline precipitate. The precipitate was found by the ^1H and ^{19}F NMR spectra to be a dimeric product, 4,4′-bis(2-bromo-1,1,2,2-tetrafluoroethyl)-1,3,5,1′,3′,5′-hexamethyl-bicyclohexyl-2,5,2′,5′-tetraene (**7**) (13.3% isolated yield) and the oil consisted of unreacted mesitylene and (2-bromotetrafluoroethyl)mesitylene (**8**) in a 1:1 ratio. When an excess of mesitylene and elevated



Scheme 2.



Scheme 3.



Scheme 4.

temperature (70 °C) were applied, the resulting oil contained, besides unreacted mesitylene, compound **8** (isolated by distillation, 18.5% yield) and complex mixture of higher molecular weight compounds. The NMR analysis of the residual oil obtained after removal of mesitylene and **8** (distillation) suggested that it consisted of diastereo- and geometric-isomers of dimers of the type **7**. Mechanism of the formation of **7** and similar dimerization of unsubstituted benzene [5] and 2,5-dimethylfurane [23] involves direct coupling of intermediate fluoroalkylaryl radicals and is somewhat different from that reported by us for the reactions of $CF_3CHClBr$ with trimethoxybenzene and pyrroles [15,16]; in the latter, the coupling is proceeded by elimination of HCl from one of the interacting primary aryl radical.

Pyrrole (**9**) and N-methylpyrrole (**11**) reacted with $BrCF_2CF_2Br$ under standard conditions to give 2-(2-bromotetrafluoroethyl)-substituted pyrroles **10** and **11** in good yields (Scheme 4). Compound **10** was very unstable and quickly getting dark on contact with the air and after storing overnight at the refrigerator totally decomposed to form black tar. In contrast, N-methyl analog **12** was stable enough to be stored for a couple of weeks in the refrigerator but also slowly decomposed at ambient temperature. Both compounds, **11** and **12**, could be distilled under reduced pressure without decomposition.

The most stable and easy to prepare with high yield compound **2** was chosen to study the reactivity of its terminal bromine atom. In contrast to the reported easy funtionalization of similar compounds [18,20,21], compound **2** was found to be fairly unreactive. The attempted substitution of bromine with fluorine by treatment with 20% KOH/Bu_4NBF_4 in a water–benzene system failed. Sulfinatodehalogenation of **2** in the presence of large excess of 1,3,5-trimethoxybenzene did not give the expected 1,2-diaryltetrafluoroethane. Also, sulfinatodehalogenation did not occurred in the presence of ethyl vinyl ether, which is very susceptible to attack by free radicals [9]. However, when compound **2** was refluxed in an acetonitrile–water system with large excess of $Na_2S_2O_4$, reduction of the bromine atom or elimination of both Br and F radicals occurred to give a mixture of 1-(1,1,2,2-tetrafluoroethyl)-2,4,6-trimethoxybenzene (**13**) and 1-(trifluoroethenyl)-2,4,6-trimethoxybenzene (**14**) in a 1:3 ratio and 70% total yield (Scheme 5). Low reactivity of the bromine atom in **2** is probably due to high steric hindrance created by the neighboring methoxy groups.

In conclusion, our experiments have shown that the $Na_2S_2O_4/CH_3CN/H_2O$ system, in general, is able to promote C-alkylation of aromatics with $BrCF_2CF_2Br$ but this method could be applied only to the most electron-rich compounds like polymethoxybenzenes, pyrroles and mesitylene.

3. Experimental

Melting points were determined in a capillary and are uncorrected. ^1H NMR, and ^{19}F NMR spectra were recorded with a Varian 400 spectrometer in $CDCl_3$ solutions. Chemical shifts are quoted in p.p.m. from internal TMS for ^1H and from internal $CFCl_3$ for ^{19}F nuclei. Coupling constants (*J*) values are in Hz. Mass spectra were obtained with an AMD-604 spectrometer.

*3.1. 1-(2-Bromotetrafluoroethyl)-2,4,6-trimethoxybenzene (**2**)*

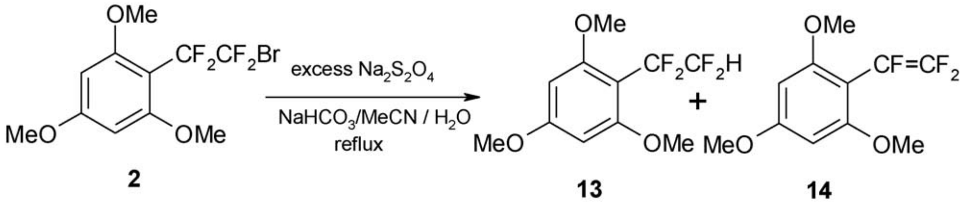
Sodium dithionite (4.0 g [85%], 20 mmol), sodium hydrogen carbonate (3.5 g, 40 mmol), 1,3,5-trimethoxybenzene (**1a**, 3.36 g, 20 mmol) and $BrCF_2CF_2Br$ (7.2 g, 30 mmol) were added one by one to an acetonitrile–water solution (1:1, 30 ml) at ambient temperature (22 °C). The reaction mixture was vigorously stirred and after few minutes slow gas evolution occurred (CO_2 formed by the reaction of SO_2 with $NaHCO_3$). No exothermic effect was observed but thick precipitate of NaBr was formed. After 4.5 h the reaction mixture was poured into water (200 ml), insoluble crystalline precipitate was filtered off and dried at ambient temperature under vacuum to give white crystals. Yield: 6.5 g (18.7 mmol, 93.7%). M.p. 81–83 °C. Analysis—found: C, 38.0; H, 3.3; Br, 23.1; F, 22.0%. Calculated for $C_{11}H_{11}BrF_4O_3$ (347.11): C, 38.1; H, 3.2; Br, 23.0; F, 21.9%. ^1H NMR: 3.80 (s, 2× CH_3); 3.84 (s, CH_3); 6.14 (s, $2H_{arom}$). ^{19}F NMR: −64.2 (t, $^3J_{FF}$ = 5.3 Hz, CF_2); −99.7 (t, $^3J_{FF}$ = 5.3 Hz, CF_2). MS (EI): *m*/*z* (rel. int., ion): 348, 346 (12, 12, M^+); 267 [11, $(M-Br)^+$]; 217 [100, $(M-CF_2Br)^+$]; 139 (21, $C_7H_7O_3)^+$.

*3.2. Reaction of $BrCF_2CF_2Br$ with 1,2,3-trimethoxybenzene (**1b**)*

The reaction was carried out as described above (Section 3.1) using the same amounts of reactants. Pouring the reaction mixture into water resulted in precipitation of an oil, which was extracted with diethyl ether and the extract was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave dense, yellowish oil (6.4 g) which was found by the ^1H NMR analysis to consist of unreacted **1b** (58%), compounds **3** (21%), **4** (15%) and **5** (5%) and some impurities. A part of the crude product (2.0 g) was subjected to column chromatography to give colourless fraction (0.75 g, yield 34.5%) containing only **3–5**. Identical results were obtained when the reaction was carried out in a sealed ampoule for 22 h at 74 °C (to avoid high pressure of evolved CO_2, $NaHCO_3$ was replaced with NaH_2PO_4).

1-(2-*Bromotetrafluoroethyl*)-3,4,5-*trimethoxybenzene* (**3**): ^1H NMR: 3.62 (s, 2× CH_3); ca. 3.6 (CH_3); 6.79 (s, $2H_{arom}$). ^{19}F NMR: −65.0 (t, $^3J_{FF}$ = 4.9 Hz, CF_2); −107.7 (t, $^3J_{FF}$ = 4.9 Hz, CF_2).

1-(2-*Bromotetrafluoroethyl*)-2,3,4,-*trimethoxybenzene* (**4**): ^1H NMR: ca. 3.5–3.7 (broad, 3× CH_3); 6.72 (d, $^3J_{HH}$ = 9.0 Hz, $1H_{arom}$); 7.22 (d, $^3J_{HH}$ = 9.0 Hz, $1H_{arom}$). ^{19}F NMR: −64.0 (t, $^3J_{FF}$ = 5.0 Hz, CF_2); −104.1 (t, $^3J_{FF}$ = 5.0 Hz, CF_2).



Scheme 5.

1-(2-*Bromotetrafluoroethyl*)-2,6-*dimethoxybenzene* (**5**): ^{1}H NMR: ca. 3.5–3.7 (broad, 2× CH_3); 6.15 (d, $^{3}J_{HH}$ = 8.4 Hz, $2H_{arom}$); 7.40 (t, $^{3}J_{HH}$ = 8.4 Hz, $1H_{arom}$). ^{19}F NMR: −64.1 (t, $^{3}J_{FF}$ = 5.2 Hz, CF_2); −100.1 (t, $^{3}J_{FF}$ = 5.2 Hz, CF_2).

3.3. Reactions of $BrCF_2CF_2Br$ with mesitylene (**6**)

3.3.1. With an excess of $BrCF_2CF_2Br$ at ambient temperature

Sodium dithionite (4.0 g [85%], 20 mmol), sodium hydrogen carbonate (2.0 g, 24 mmol), mesitylene (**6**, 2.4 g, 20 mmol) and $BrCF_2CF_2Br$ (10.4 g, 40 mmol) were added one by one to an acetonitrile–water solution (1:1, 30 ml) and the reaction mixture was vigorously stirred at ambient temperature (23 °C) for 20 h, then poured into water (100 ml). The organic oily layer was extracted with Et_2O, the extract was washed with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a mixture of colourless oil and fine, white precipitate. The precipitate was filtered off, washed with ethanol and dried under vacuum to give 4,4′-bis(2-bromo-1,1,2,2-tetrafluoroethyl)-1,3,5,1′,3′,5′-hexamethylbicyclohexyl-2,5,2′,5′-tetraene (**7**) as white powder. Yield: 0.81 g (2.7 mmol, 13.3%). M.p. 107 °C (rapid decomposition). Analysis—found: C, 44.0; H, 4.1; Br, 26.6; F, 25.6%. Calculated for $C_{22}H_{24}Br_2F_8$ (600.23): C, 44.15; H, 4.0; Br, 26.4; F, 25.4%. ^{1}H NMR: 0.99 (s, 2× CH_3); 1.82 (s, 4× CH_3); 3.34 (t, $^{3}J_{HF}$ = 10.0 Hz, 2H); 5.76 (s, 4H). ^{19}F NMR: −62.4 (s, CF_2); −99.0 (d, $^{3}J_{HF}$ = 10.0 Hz).

The oil was found by the NMR analysis to be a 1:1 mixture of unreacted mesitylene (**6**) and (2-bromotetrafluoroethyl)mesitylene (**8**) which were not separated.

3.3.2. With an excess of mesitylene at elevated temperature

Sodium dithionite (4.0 g [85%], 20 mmol), disodium hydrogen phosphate (4.3 g, 30 mmol), mesitylene (**6**, 7.2 g, 60 mmol), $BrCF_2CF_2Br$ (5.2 g, 20 mmol) and acetonitrile–water solution (1:1, 30 ml) were placed in a firmly closed reaction flask (the stopcock was wired). The reaction mixture was vigorously stirred at 70 °C for 2 h (all inorganic salts dissolved), then for 22 h at ambient temperature. Addition of water (100 ml) to the reaction mixture caused formation of bottom organic layer which was separated and the water layer was extracted with ether (2× 30 ml). The extract and the main organic layer were combined, washed with brine (2× 70 ml) and dried over anhydrous $MgSO_4$. Vacuum distillation of an oil (8.4 g) obtained after evaporation of the ether allowed to isolate (2-bromotetrafluoroethyl)mesitylene (**8**) (1.1 g, 3.7 mmol, 18.5% in respect to $BrCF_2CF_2Br$) as colourless oil. B.p. 54–56 °C/2 mmHg. Analysis—found: C, 44.5; H, 3.7; Br, 26.3; F, 25.2%. Calculated for $C_{11}H_{11}BrF_4$ (299.11): C, 44.15; H, 4.0; Br, 26.4; F, 25.4%. ^{1}H NMR: 2.28 (s, CH_3); 2.42 (t, $^{5}J_{HF}$ = 4.7 Hz, 2× CH_3); 6.91 (narrow m, $2H_{arom}$). ^{19}F NMR: −63.0 (t, $^{3}F_{FF}$ = 4.2 Hz, CF_2); −95.5 (nonet, average $J_{HF\ and\ FF}$ = 4.4 Hz, CF_2). MS (EI): *m*/*z* (rel. int., ion): 300, 298 (36, 36, M^+); 219 [17, $(M-Br)^+$]; 169 [100, $(M-CF_2Br)^+$]; 119 [12, $(M-C_2F_4Br)^+$].

3.4. 2-(2-Bromotetrafluoroethyl)pyrrole (**10**)

Sodium dithionite (1.0 g [85%], 5 mmol), sodium hydrogen carbonate (3.5 g, 42 mmol), freshly distilled pyrrole (**9**, 1.34 g, 20 mmol,) and $BrCF_2CF_2Br$ (7.2 g, 30 mmol) were added one by one to an acetonitrile–water solution (1:1, 30 ml) at ambient temperature (22 °C). The reaction mixture was vigorously stirred and after few minutes the CO_2 evolution occurred with slight exothermic effect. The gas evolution ceased after 3 h, then the reaction mixture was diluted with water (100 ml) and worked up as in Section 3.3.2. Vacuum distillation of an oil (5.0 g) obtained after evaporation of the ether gave 2-(2-bromotetrafluoroethyl)-pyrrole (**10**) as colourless liquid. Yield: 3.6 g (14.6 mmol, 73%). B.p. 32–36 °C/6 mmHg. Analysis—found: C, 29.8; H, 1.8; Br, 32.2; F, 30.6; N, 5.9%. Calculated for $C_6H_4BrF_4N$ (246.00): C, 29.3; H, 1.6; Br, 32.5; F, 30.9; N, 5.7%. ^{1}H NMR: 6.30 (m, H-4); 6.62 (m, H-3); 6.95 (m, H-5); 8.57 (broad m, H-1). ^{19}F NMR: −66.0 (t, $^{3}J_{FF}$ = 7.2 Hz, CF_2); −105.3 (t, $^{3}J_{FF}$ = 7.2 Hz, CF_2). MS (EI): *m*/*z* (rel. int., ion): 247, 245 (18, 18, M^+); 166 [13, $(M-Br)^+$]; 147 [12, $(M-BrF)^+$]; 116 [100, $(M-CF_2Br)^+$]; 89 (12, $C_4H_3F_2^+$).

3.5. 2-(2-Bromotetrafluoroethyl)-1-methylpyrrole (**12**)

Sodium dithionite (1.0 g [85%], 5 mmol), sodium hydrogen carbonate (3.5 g, 40 mmol), 1-methylpyrrole (**11**, 1.62 g, 20 mmol,) and $BrCF_2CF_2Br$ (7.2 g, 30 mmol) were added one by one to an acetonitrile–water solution (1:1, 30 ml) at ambient temperature (22 °C). The reaction was carried out and worked up as in Section 3.5. Vacuum distillation of an oil (4.4 g) obtained after evaporation of the ether gave 2-(2-bromotetrafluoroethyl)-1-methylpyrrole (**12**) as colourless liquid. Yield: 3.75 g (14.4 mmol, 72%). B.p. 46 °C/6 mmHg. Analysis—found: C, 32.3; H, 2.2; Br, 30.7; F, 39.5; N, 5.3%. Calculated for $C_7H_6BrF_4N$ (260.03): C, 32.3; H, 2.3; Br, 30.7; F, 39.2; N, 5.4%. ^{1}H NMR: 3.73 (s, CH_3); 6.15 (t, *J* = 3.3 Hz, H-4); 6.57 (m, H-3); 6.73 (narrow m, H-5). ^{19}F NMR: −64.1 (t, $^{3}J_{FF}$ = 6.8 Hz, CF_2); −101.5 (t, $^{3}J_{FF}$ = 6.8 Hz, CF_2). MS (EI): *m*/*z* (rel. int., ion): 261, 259 (12, 12, M^+); 180 [9, $(M-Br)^+$]; 161 [7, $(M-BrF)^+$]; 130 [100, $(M-CF_2Br)^+$].

3.6. Reaction of 1-(2-bromotetrafluoroethyl)-2,4,6-trimethoxybenzene (**2**) with an excess of $Na_2S_2O_4$

Compound **2** (3.47 g, 10 mmol), sodium dithionite (10.0 g [85%], 50 mmol), sodium hydrogen carbonate (4.5 g, 54 mmol), acetonitrile (20 ml) and water (40 ml) were refluxed for 9 h. Acetonitrile was removed on a rotary evaporator and the insoluble white solid was filtered off, washed with large amount of cold water (removal of inorganic salts) and dried over NaOH under vacuum. The NMR, GC–MS and HMRS analyses have shown that the solid consist of 1-(1,1,2,2-tetrafluoroethyl)-2,4,6-trimethoxybenzene (**13**) 1-(trifluoroethenyl)-2,4,6-trimethoxybenzene (**14**) in a 1:3 ratio. Total yield: 2.0 g (7 mmol, 70%).

1-(1,1,2,2-*Tetrafluoroethyl*)-2,4,6-*trimethoxybenzene* (**13**): ^{1}H NMR: 3.82 (s, 2× CH_3); 3.83 (s, CH_3); 6.15 (s, $2H_{arom}$); 6.31 (tt, $^{2}J_{HF}$ = 54.1 Hz, $^{3}J_{HF}$ = 5.5 Hz, CF_2H). ^{19}F NMR: −110.6 (td, $^{3}J_{FF}$ = 9.5 Hz and 5.5 Hz, $-CF_2-$); −137.7 (dt, $^{2}J_{HF}$ = 54.1 Hz, $^{3}J_{FF}$ = 9.5 Hz, CF_2H). GC–MS (EI): *m*/*z* (rel. int., ion): 268 (25, M^+); 217 [100, $(M-HF-OCH_3)^+$]; 139 (40, $C_7H_7O_3^+$); 101 (6, $C_2F_2H^+$); 51 (4, CF_2H)$^+$. HRMS: 268.07153. Calculated for $H_{11}H_{12}F_4O_3$: 268.07226.

1-(*Trifluoroethenyl*)-2,4,6-*trimethoxybenzene* (**14**): ^{1}H NMR: 3.82 (s, 2× CH_3); 3.84 (s, CH_3); 6.11 (s, $2H_{arom}$). ^{19}F NMR: −103.1 (dd, $^{2}J_{FF}$ = 74.4 Hz, $^{3}J_{FF}$ = 26.5 Hz, $=CF_2$); −117.9 (dd, $^{2}J_{FF}$ = 74.4 Hz, $^{3}J_{FF}$ = 117.0 Hz, $=CF_2$); −163.8 (dd, $^{3}J_{FF}$ = 117.0 Hz, $^{3}J_{FF}$ = 26.5 Hz, $-CF=$). GC–MS (EI): *m*/*z* (rel. int., ion): 248 (70, M^+); 233 [100, $(M-CH_3)^+$]; 218 [10, $(M-2CH_3)^+$]; 203 [20, $(M-3CH_3)^+$]; 139 (40, $C_7H_7O_3^+$); 81 (20, $C_2F_3^+$). HMRS: 248.06649. Calculated for $C_{11}H_{11}F_3O_3$: 248.06603.

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