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Synthesis and Pummerer reaction of 2-*F*-alkyl-2-hydroxyethylphenyl sulfoxides

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Abstract

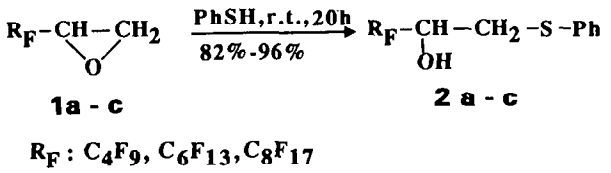
The synthesis of new 2-*F*-alkyl-2-hydroxyethylphenyl sulfoxides **3** and their 2-methyl ethers **4** is reported. They undergo the Pummerer rearrangement to yield 2-*F*-alkyl-1,2-diacetoxyethylphenyl sulfides **7** and 2-*F*-alkyl-1-acetoxy-2-methoxyethylphenyl sulfides **8**, respectively.

Keywords: Synthesis; Pummerer reaction; *F*-Alkylhydroxyethylphenyl sulfoxides; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

The ring-opening reactions of *F*-alkyl oxiranes **1a–c** [1] by reagents with labile hydrogens have been largely investigated in our laboratories [2–5]. The reactions of compounds **1a–c** are highly regioselective; in all cases we obtained a secondary alcohol as the end-product. We have prepared 2-*F*-alkyl-2-hydroxyethyl sulfides **2a–c** in this way and have reported previously [2] the synthesis and characterization of **2b** according to Scheme 1.

In this paper we describe the reactivity of the sulfides **2a–c** which was previously unknown. Initially we attempted to oxidize them to the sulfoxides **3a–c** and **4a–c**, and then studied the Pummerer rearrangement of the latter into sulfides **7a–c** and **8a–c** as shown in Scheme 2. In the hydrocarbon series, of the preparative methods for sulfoxides described in the literature [6–14] that involving oxidation of the sulfides is most employed.



Scheme 1.

Unfortunately, this reaction is not always selective and generally yields a mixture of sulfoxide and sulfone. In the fluorocarbon series, the synthesis of perfluoroalkyl sulfoxides has not been studied to any great extent; nevertheless Bravo et al. have succeeded in condensing methyl *p*-tolyl sulfoxide and the lithium salts of perfluoroalkyl acids [15] to produce 2-oxopropyl sulfoxides which may be reduced into β-hydroxyl β-fluorosulfoxides [16]. The same process has been used by Yamazaki et al. [17] to give α,β-unsaturated β-fluoro sulfoxides. Other works describe the preparation of α-fluoro sulfoxide according to a fluoro-Pummerer rearrangement reaction using *m*-chloroperbenzoic acid [18–20].

2. Results and discussion

In our present work, the oxidation of 2-*F*-alkyl-2-hydroxyethylphenyl sulfides **2a–c** into 2-*F*-alkyl-2-hydroxyethyl sulfoxides **3a–c** has been achieved by the use of hydrogen peroxide in the presence of titanium chloride in methanol [21] (Scheme 2). The sulfoxides **3a–c** were isolated in very good yield (Table 1). However, whereas such oxidation reactions occur within several hours, oxidation of the sulfide **5b** which was obtained in good yield (Table 1) by treating the sulfide **2b** with methyl iodide and silver oxide gave a mixture of sulfoxide **4b** and sulfone **6b** virtually immediately (Scheme 3). Hence the presence of the hydroxy group appears to

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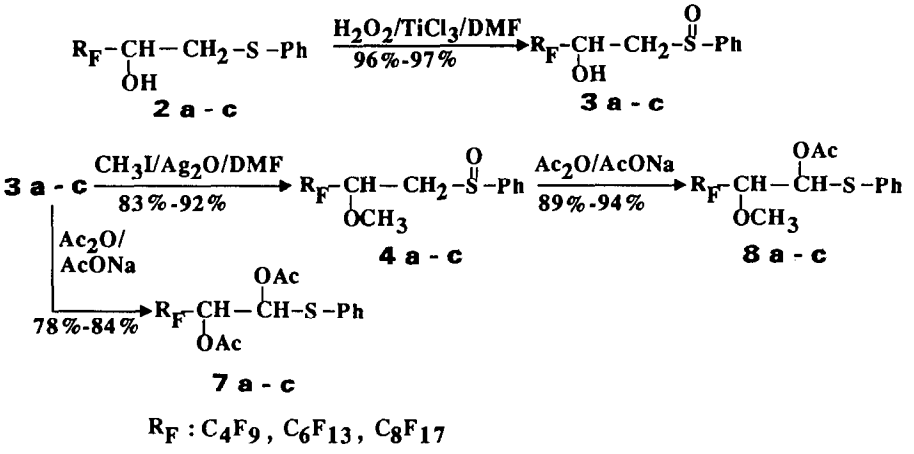


Scheme 2.

Table 1
Reaction conditions and product yields in oxidation reactions studied

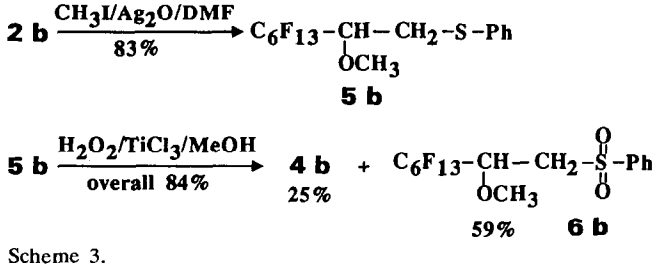
Product	Reaction time (h)	Yield (%)[a]	B.p. (°C/Torr) or m.p. (°C)[b]
3a	3	96	93/0.35
3b	5	97	86
3c	5.5	97	106
4a	6	83	79/0.3
4b	6	91	107/0.2
4c	6	92	57
5b	–	83	118/4
6b	–	59	74

[a]Yield of isolated product. [b]Uncorrected.

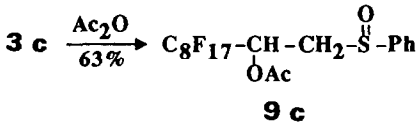
Table 2
Products and yields in Pummerer rearrangements studied

Product	Yield (%)[a]	B.p. (°C/Torr) or m.p. (°C)[b]
7a	78	73/0.3
7b	83	36
7c	84	68
8a	89	68/0.25
8b	91	118/0.60
8c	94	125/0.40
9c	63	71

[a]Yield of isolated product. [b]Uncorrected.



Scheme 3.



Scheme 4.

slow down the reaction and stop the oxidation at the sulfoxide stage.

To prepare the methoxylated analogues of 2-*F*-alkyl-2-hydroxyethyl sulfoxides **3a–c**, we also treated the latter with methyl iodide and silver oxide and obtained the corresponding 2-*F*-alkyl-2-methoxyethyl sulfoxides **4a–c** (Scheme 2). Methylation of the hydroxy function was accomplished in excellent yield (Table 1). Finally, according to Scheme 2, when sulfoxides **3a–c** and **4a–c** are treated with acetic anhydride in the presence of sodium acetate the 2-*F*-alkyl-1,2-diacetoxyethylphenyl sulfides **7a–c** and 2-*F*-alkyl-1-acetoxy-2-methoxyethylphenyl sulfides **8a–c** are obtained in satisfactory yield (Table 2).

These results accord with those found in the hydrocarbon series [22]. In the case of simple 2-hydroxy sulfoxides, the addition of sodium acetate is necessary to induce the previous acetylation reaction and to avoid the formation of α,β-unsaturated sulfides. With 2-*F*-alkyl-2-hydroxy sulfoxide **3c**, the action of acetic anhydride alone does not lead to the Pummerer product **7c** but generates the monoacetoxy sulfoxide **9c** according to Scheme 4, with no side-products such as α,β-unsaturated sulfides.

3. Experimental

The structures of the compounds synthesized in this work were determined from spectroscopic and elemental analysis data.

The 2-*F*-alkyl-2-hydroxyethylphenyl sulfides **2a–c** were prepared from *F*-alkyloxiranes and thiobenzene according to the reported procedure [2] ($R_F = C_4F_9$, yield 82%, b.p. 81 °C/0.2 Torr; $R_F = C_6F_{13}$, yield 84%, m.p. 52 °C; $R_F = C_8F_{17}$, yield 96%, m.p. 62 °C). All reagents and solvents were purchased from the Aldrich Chemical Co. and used as received. Melting points were taken using a Tottoli apparatus and are uncorrected.

Thin layer chromatography (TLC) was carried out with plates precoated with silica gel 60 F254 (Merck). Microanalysis was performed by the Central Laboratory for Analysis, CNRS, Lyon (France). The following instruments were used to record the spectroscopic data. MS: Nermag Ribermag R10-10C spectrometer (70 eV); IR: Brucker IFS 45 spectrophotometer; ^{1}H NMR: Brucker W-80 spectrometer at 80 MHz with TMS as internal standard; ^{19}F NMR: Brucker AC-200 spectrometer at 188.3 MHz with $CFCl_3$ as internal standard.

Compounds **3a–c** and **4a–c** which possess one chiral centre exist as diastereoisomeric mixtures of the form **3a–c/3′a–c/3a–c** and **4a–c/4′a–c** in an approximately 3:1 ratio. Spectroscopic data are given for the most abundant diastereoisomers **3a–c**. Compounds **7a–c** and **8a–c** were also obtained as diastereoisomeric mixtures of the form **7a–c/7′a–c** and **8a–c/8′a–c** in an approximately 1.5:1 ratio. ^{1}H NMR and 19F NMR spectroscopic data are given for each diastereoisomer of compounds **7a–c** and **8a–c**.

3.1. Preparation of 2-F-butyl-2-hydroxyethylphenyl sulfoxide (3a): typical procedure

A solution of sulfide **2a** (4.46 g, 12 mmol) in MeOH (180 ml) and water (36 ml) was stirred at 0 °C while $TiCl_3$ (17 ml) was added dropwise. Then 30% H_2O_2 (5.52 ml) in MeOH (28 ml) was added portionwise. After 30 min at 0 °C, the mixture was stirred at room temperature until completion of the reaction was indicated by TLC ($CHCl_3$/AcOEt, 80:20). The mixture was then poured into ice water (300 ml) and extracted with $CHCl_3$ (2×100 ml). The extracts were combined, dried over Na_2SO_4 and evaporated under reduced pressure. The resulting crude sulfoxide **3a** was purified by distillation under vacuum. Yield, 4.38 g (96%); b.p. 93 °C/0.35 Torr.

Analysis: $C_{12}H_9F_9O_2S$ (388.25) requires: C, 37.12; H, 2.33; F, 44.03; S, 8.25%. Found: C, 36.81; H, 2.48; F, 43.54; S, 7.90%. ^{1}H NMR ($CDCl_3$/TMS) δ: 3.39 (m, 2H, CH_2); 4.90 (m, 1H, CH); 7.69 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3/CFCl_3$) δ: −81.5 (3F, CF_3); −119.7 to −127.0 (2F, 1-CF_aF_b, J_{ab} = 282 Hz); −122.9 (2F, 2-CF_2); −126.7 (2F, 3-CF_2) ppm. IR (film) ν (cm^{-1}): 3213 (CH arom.); 1448 (C=C); 1250–1100 (C−F); 1020 (S=O). MS (70 eV) *m/z* (%): 388 (M^+, 10); 219 (2); 119 (3); 125 (100); 77 (59); 69 (22); 51 (37).

3.2. Preparation of 2-F-hexyl-2-hydroxyethylphenyl sulfoxide (3b)

Sulfide **2b** (5.66 g, 12 mmol) was converted according to the previous typical procedure into sulfoxide **3b** and purified by recrystallization from a mixture of hexane/chloroform. Yield 5.68 g (97%); m.p. 86 °C.

Analysis: $C_{14}H_9F_{13}O_2S$ (488.26) requires: C, 34.43; H, 1.85; F, 50.58; S, 6.56%. Found: C, 34.01; H, 1.90; F, 49.79; S, 5.92%. ^{1}H NMR ($CDCl_3$/TMS) δ: 3.20 (m, 2H, CH_2); 4.83 (m, 1H, CH); 7.68 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3/CFCl_3$) δ: −81.0 (3F, CF_3); −119.3 to −126.4 (2F, 1-CF_aF_b, J_{ab} = 280 Hz); −121.5 (2F, 2-CF_2); −122.4 (2F, 3-CF_2); −124.7 (2F, 4-CF_2); −127.0 (2F, 5-CF_2) ppm. IR (KBr) ν (cm^{-1}): 3310 (CH arom.); 1445 (C=C); 1250–1100 (C−F); 1035 (S=O). MS (70 eV) *m/z* (%): 488 (M^+, 4); 169 (2); 125 (100); 119 (2); 109 (7); 77 (11).

3.3. Preparation of 2-F-octyl-2-hydroxyethylphenyl sulfoxide (3c)

Sulfide **2c** (6.86 g, 12 mmol) treated as above led to the formation of sulfoxide **3c**. Yield, 6.84 g (97%); m.p. 106 °C. Analysis: $C_{16}H_9F_{17}O_2S$ (588.28) requires: C, 32.66; H, 1.54; F, 54.90; S, 5.45%. Found: C, 32.44; H, 1.57; F, 54.68; S, 4.71%. ^{1}H NMR (DMSO-d_6/TMS) δ: 3.21 (m, 1H, CH_2); 4.84 (m, 1H, CH); 7.75 (m, 5H, Ph) ppm. ^{19}F NMR (DMSO-$d_6/CFCl_3$) δ: −81.3 (3F, CF_3); −119.6 to −125.9 (2F, 1-CF_aF_b, J_{ab} = 295 Hz); −121.9 (2F, 2-CF_2); −122.4 (6F, 3,4,5-CF_2); −123.3 (2F, 6-CF_2); −126.7 (2F, 7-CF_2) ppm. IR (KBr) ν (cm^{-1}): 3026 (CH arom.); 1448 (C=C); 1250–1100 (C−F); 1016 (S=O). MS (70 eV) *m/z* (%): 588 (M^+, 19); 554 (7); 169 (6); 126 (75); 125 (100); 109 (18); 77 (51); 69 (25).

3.4. Preparation of 2-F-butyl-2-methoxyethyl sulfoxide (4a): typical procedure

To a solution of sulfoxide **3a** (3.1 g, 8 mmol) in DMF (30 ml) was added methyl iodide (3.4 g, 24 mmol) and silver oxide (1.86 g, 8 mmol). When TLC (PhH/AcOEt, 98:2) indicated completion of the reaction (6 h at room temperature), the solvent was evaporated and the resulting residue chromatographed on a silica gel column using a mixture of PhH/AcOEt (70:30) as eluent. The solvents were removed under reduced pressure and the compound **4a** obtained was purified by distillation under vacuum. Yield, 2.67 g (83%); b.p. 79 °C/0.3 Torr.

Analysis: $C_{13}H_{11}F_9O_2S$ (402.28) requires: C, 38.81; H, 2.75; F, 42.50; S, 7.97%. Found: C, 38.56; H, 2.76; F, 42.02; S, 8.25%. ^{1}H NMR ($CDCl_3$/TMS) δ: 3.25 (m, 2H, CH_2); 3.35 (s, 3H, CH_3); 4.34 (m, 1H, CH); 7.75 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/TMS) δ: −81.5 (3F, CF_3); −117.1 to −122.3 (2F, 1-CF_aF_b, J_{ab} = 286

Hz); −124.6 (2F, 2-CF_2); −126.9 (2F, 3-CF_2) ppm. IR (film) ν (cm^{-1}): 1443 (C=C); 1250–1150 (C−F); 1038 (S=O). MS (70 eV) *m/z* (%): 402 (M^+, 2); 387 (8); 385 (36); 125 (100); 119 (3); 77 (35); 69 (13).

3.5. Preparation of 2-F-hexyl-2-methoxyethylphenyl sulfoxide (4b)

Sulfoxide **3b** (3.9 g, 8 mmol) was converted according to the previous typical procedure into compound **4b**. Yield, 3.66 g (91%); b.p. 107/0.2 Torr. Analysis: $C_{15}H_{11}F_{13}O_2S$ (502.29) requires: C, 35.86; H, 2.20; F, 49.17; S, 6.38%. Found: C, 35.20; H, 2.25; F, 48.80; S, 6.82%. ^1H NMR ($CDCl_3$/TMS) δ: 3.23 (m, 2H, CH_2); 3.30 (s, 3H, CH_3); 4.35 (m, 1H, CH); 7.72 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.4 (3F, CF_3); −116.7 to −121.7 (2F, 1-CF_aF_b, J_{ab}=289 Hz); −121.5 (2F, 2-CF_2); −122.4 (2F, 3-CF_2); −122.9 (2F, 4-CF_2); −126.7 (2F, 5-CF_2) ppm. IR (film) ν (cm^{-1}): 1445 (C=C); 1250–1100 (C−F); 1048 (S=O). MS (70 eV) *m/z* (%): 502 (M^+, 3); 487 (3); 485 (33); 125 (100); 119 (2), 77 (39).

3.6. Preparation of 2-F-octyl-2-methoxyethylphenyl sulfoxide (4c)

Sulfoxide **3c** (4.7 g, 8 mmol) treated as above led to the formation of compound **4c** which was purified by recrystallization from hexane. Yield, 4.82 g (92%); m.p. 57 °C. Analysis: $C_{17}H_{11}F_{17}O_2S$ (602.31) requires: C, 33.90; H, 1.84; F, 53.62; S, 5.32%. Found: C, 33.69; H, 1.98; F, 52.88; S, 5.97%. ^1H NMR ($CDCl_3$/TMS) δ: 3.21 (m, 2H, CH_2); 3.30 (s, 3H, CH_3); 4.34 (m, 1H, CH); 7.69 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.5 (3F, CF_3); −119.9 to −122.6 (2F, 1-CF_aF_b, J_{ab}=292 Hz); −122.5 (8F, 2,3,4,5-CF_2); −123.4 (2F, 6-CF_2); −126.8 (2F, 7-CF_2) ppm. IR (KBr) ν (cm^{-1}): 1442 (C=C); 1250–1100 (C−F); 1040 (S=O). MS (70 eV) *m/z* (%): 602 (M^+, 1); 587 (2); 169 (1); 126 (51); 125 (100); 109 (13); 77 (32); 69 (16); 63 (35).

3.7. Preparation of 2-F-hexyl-2-methoxyethylphenyl sulfide (5b)

Sulfide **2b** (2.98 g, 8 mmol) was converted according to the typical procedure for sulfoxide **4a** into compound **5b**. Yield, 3.23 g (83%); b.p. 118 °C/4 Torr. Analysis: $C_{15}H_{11}F_{13}OS$ (486.29) requires: C, 37.04; H, 2.27; F, 50.78; S, 6.59%. Found: C, 37.21; H, 2.31; F, 51.01; S, 6.90%. ^1H NMR ($CDCl_3$/TMS) δ: 3.20 (m, 2H, CH_2); 3.63 (s, 3H, CH_3); 3.86 (m, 1H, CH); 7.39 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.4 (3F, CF_3); −118.2 to −123.3 (2F, 1-CF_aF_b, J_{ab}=282 Hz); −121.9 (2F, 2-CF_2); −122.6 (2F, 3-CF_2); −123.3 (2F, 4-CF_2); −126.7 (2F, 5-CF_2) ppm. IR ($CHCl_3$) ν (cm^{-1}): 1440 (C=C); 1350–1200 (C−F). MS (70 eV) *m/z* (%): 487 (M+1, 5.79); 123 (60.32); 119 (1.16); 109 (18.60); 77 (3.01); 69 (3.26); 45 (100.00).

3.8. Preparation of 2-F-hexyl-2-methoxyethylphenyl sulfone (6b)

Compound **5b** (5.83 g, 12 mmol) was converted according to the typical procedure for compound **3a** into compound **6b**. This was isolated from the mixture of **4b**/**6b** and purified by recrystallization from petroleum ether. Yield, 3.67 g (59%); m.p. 74 °C. Analysis: $C_{15}H_{11}F_{13}O_3S$ (518.29) requires: C, 34.76; H, 2.13; F, 47.65; S, 6.18%. Found: C, 34.65; H, 2.04; F, 48.11; S, 6.63%. ^1H NMR ($CDCl_3$/TMS) δ: 3.00 (d, 2H, CH_2); 3.76 (s, 3H, CH_3); 4.38 (m, 1H, CH); 7.56 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.5 (3F, CF_3); −117.0 to −122.1 (2F, 1-CF_aF_b, J_{ab}=287 Hz); −121.8 (2F, 2-CF_2); −122.7 (2F, 3-CF_2); −123.0 (2F, 4-CF_2); −126.6 (2F, 5-CF_2) ppm. IR ($CHCl_3$) ν (cm^{-1}): 1440 (C=C); 1250–1200 (C−F); 1145 (SO_2). MS (70 eV) *m/z* (%): 518 (M^+, 1.3); 519 (M+1, 1.1); 517 (2.2); 485 (84.3); 377 (24.8); 141 (14.3); 78 (48.0); 77 (100.00); 69 (29.2); 63 (47.9); 51 (41.9); 43 (44.5).

3.9. Preparation of 2-F-butyl-1,2-diacetoxyethylphenyl sulfide (7a): typical procedure

A mixture of sulfoxide **3a** (0.66 g, 1.7 mmol), sodium acetate (1 g, 1.2 mmol) and acetic anhydride (8 ml) was stirred, progressively heated to 140 °C and kept at this temperature for 5 h. After evaporation of acetic anhydride and excess acetic acid, the residue obtained was chromatographed on a silica gel column using a mixture of PhH/AcOEt (70:30) as eluent. The solvents were removed under reduced pressure and compound **7a** obtained was purified by distillation under vacuum. Yield, 0.63 g (78%); b.p. 73 °C/0.3 Torr.

Analysis: $C_{16}H_{13}F_9O_4S$ (472.32) requires: C, 40.68; H, 2.77; F, 36.20; S, 6.78%. Found: C, 41.34; H, 2.41; F, 36.99; S, 6.41%. ^1H NMR ($CDCl_3$/TMS) δ: 2.06, 2.11, 2.15, 2.20 (s, 12H, $2CH_3$ for each diastereoisomer **7a** and **7'a**); 5.94 (m, 1H, C_2H); 6.47 (d, 1H, C_1H for diastereoisomer **7a**, J=4.8 Hz); 6.53 (d, 1H, C_1H for the other diastereoisomer **7'a**, J=4.9 Hz); 7.26–7.82 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.5 (3F, CF_3); −117.1 to −121.2 (2F, 1-CF_aF_b, J_{ab}=290 Hz for diastereoisomer **7a**); −117.8 to −122.4 (2F, 1-$CF_{a'}$,$F_{b'}$, $J_{a'b'}$=290 Hz for the other diastereoisomer **7'a**); −124.0 (2F, 2-CF_2); −126.5 (2F, 3-CF_2) ppm. IR (film) ν (cm^{-1}): 1772 (C=O); 1483 (C=C); 1250–1100 (C−F). MS (70 eV) *m/z* (%): 472 (M^+, 0.25); 152 (4); 110 (38); 109 (8); 69 (1); 43 (100).

3.10. Preparation of 2-F-hexyl-1,2-diacetoxyethylphenyl sulfide (7b)

Sulfoxide **3b** (0.83 g, 1.7 mmol) was converted according to the previous typical procedure into compound **7b** which was purified by recrystallization from petroleum ether. Yield, 0.81 g (83%); m.p. 36 °C. Analysis: $C_{18}H_{13}F_{13}O_4S$ (572.34) requires: C, 37.77; H, 2.28; F, 43.15; S, 5.60%. Found: C, 38.56; H, 2.18; F, 43.85; S, 5.42%. ^{1}H NMR ($CDCl_3$/TMS) δ: 2.09; 2.13, 2.18, 2.22 (s, 12H, $2CH_3$ for each diastereoisomer **7b** and **7'b**); 5.90 (m, 1H, C_2H); 6.51 (d, 1H, C_1H for diastereoisomer **7b**, J=4.0 Hz); 6.46 (d, 1H, C_1H for the other diastereoisomer **7'b**, J=5.5 Hz); 7.32–7.79 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.4 (3F, CF_3); −117.0 to −120.9 (2F, 1-CF_aF_b, J_{ab}=290 Hz for diastereoisomer **7b**); −117.7 to −122.0 (2F, 1-$CF_{a'}F_{b'}$, $J_{a'b'}$=289 Hz for the other diastereoisomer **7'b**); −122.7 (4F, 2,3-CF_2); −123.3 (2F, 4-CF_2); −126.6 (2F, 5-CF_2) ppm. IR (KBr) ν (cm^{-1}): 1771 (C=O); 1477 (C=C); 1250–1100 (C−F). MS (70 eV) *m/z* (%): 572 (M^+, 0.1); 110 (8); 69 (0.22); 43 (100).

3.11. Preparation of 2-F-octyl-1,2-diacetoxyethylphenyl sulfide (7c)

Sulfoxide **3c** (1 g, 1.7 mmol) treated as above led to the formation of compound **7c**. Yield, 0.96 g (84%); m.p. 68 °C. Analysis: $C_{20}H_{13}F_{17}O_4S$ (672.35) requires: C, 35.72; H, 1.94; F, 48.03; S, 4.76%. Found: C, 36.20; H, 1.27; F, 48.59; S, 4.58%. ^{1}H NMR ($CDCl_3$/TMS) δ: 2.10, 2.15, 2.18, 2.30 (s, 12H, $2CH_3$ for each diastereoisomer **7c** and **7'c**); 5.94 (m, 1H, C_2H); 6.48 (d, 1H, C_1H for diastereoisomer **7c**, J=7.0 Hz); 6.54 (d, 1H, C_1H for the other diastereoisomer **7'c**, J=4.8 Hz); 7.33–7.76 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.4 (3F, CF_3); −117.0 to −121.2 (2F, 1-CF_aF_b, J_{ab}=290 Hz for diastereoisomer **7c**); −117.8 to −122.3 (2F, 1-$CF_{a'}F_{b'}$, $J_{a'b'}$=291 Hz for the other diastereoisomer **7'c**); −122.5 (8F, 2,3,4,5-CF_2); −123.4 (2F, 6-CF_2); −126.8 (2F, 7-CF_2) ppm. IR (KBr) ν (cm^{-1}): 1772 (C=O); 1757 (C=O); 1377 (C=C); 1250–1100 (C−F). MS (70 eV) *m/z* (%): 672 (M^+, 0.07); 563 (0.06); 152 (2); 119 (0.11); 110 (18); 109 (2); 77 (0.32); 69 (0.49); 43 (100).

3.12. Preparation of 2-F-butyl-1-acetoxy-2-methoxyethylphenyl sulfide (8a)

A mixture of sulfoxide **4a** (0.67 g, 1.66 mmol), sodium acetate (1 g, 1.2 mmol) and acetic anhydride (7 ml) was heated at 140 °C for 4 h. After evaporation of acetic anhydride and excess acetic acid, the residue obtained was chromatographed on a silica gel column using a mixture of PhH/AcOEt (90:10) as eluent. The solvents were removed under reduced pressure and compound **8a** obtained as a crude oil was purified by distillation under vacuum. Yield, 0.66 g (89%); b.p. 68 °C/0.25 Torr.

Analysis: $C_{15}H_{13}F_9O_3S$ (444.31) requires: C, 40.54; H, 2.94; F, 38.48; S, 7.21%. Found: C, 40.32; H, 2.75; F, 37.88; S, 7.08%; ^{1}H NMR ($CDCl_3$/TMS) δ: 2.06 (s, 3H, CH_3CO_2 for diastereoisomer **8a**); 2.09 (s, 3H, CH_3CO_2 for the other diastereoisomer **8'a**); 3.68 (s, 3H, CH_3O for diastereoisomer **8a**); 3.71 (s, 3H, CH_3O for the other diastereoisomer **8'a**); 4.04 (m, 1H, C_2H); 6.49 (d, 1H, C_1H for diastereoisomer **8a**, J=5.6 Hz); 6.56 (d, 1H, C_1H for the other diastereoisomer **8'a**, J=4.0 Hz); 7.26–7.70 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.5 (3F, CF_3); −116.6 to −123.2 (2F, 1-CF_aF_b, J_{ab}=289 Hz for diastereoisomer **8a**); −117.6 to −124.0 (2F, 1-$CF_{a'}F_{b'}$, $J_{a'b'}$=286 Hz for the other diastereoisomer **8'a**); −123.4 (2F, 2-CF_2); −126.8 (2F, 3-CF_2) ppm. IR (film) ν (cm^{-1}): 1756 (C=O); 1483 (C=C); 1250–1100 (C−F). MS (70 eV) *m/z* (%): 444 (M^+, 0.8); 110 (32); 110 (32); 109 (8); 77 (2); 69 (2); 43 (100).

3.13. Preparation of 2-F-hexyl-1-acetoxy-2-methoxyethylphenyl sulfide (8b)

Sulfoxide **4b** (0.83 g, 1.66 mmol) was converted according to the previous typical procedure into compound **8b**. Yield, 0.82 g (91%); b.p. 118 °C/0.6 Torr. Analysis: $C_{17}H_{13}F_{13}O_3S$ (544.33) requires: C, 37.51; H, 2.40; F, 45.37; S, 5.89%. Found: C, 37.44; H, 2.22; F, 44.47; S, 5.37%. ^{1}H NMR ($CDCl_3$/TMS) δ: 2.06 (s, 3H, CH_3CO_2 for diastereoisomer **8b**); 2.09 (s, 3H, CH_3CO_2 for the other diastereoisomer **8'b**); 3.68 (s, 3H, CH_3O for diastereoisomer **8b**); 3.73 (s, 3H, CH_3O for the diastereoisomer **8'b**); 4.08 (m, 1H, C_2H); 6.50 (d, 1H, C_1H for diastereoisomer **8b**, J=5.6 Hz); 6.56 (d, 1H, C_1H for the other diastereoisomer **8'b**, J=4.8 Hz); 7.72–7.78 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ: −81.4 (3F, CF_3); −115.9 to −123.1 (2F, 1-CF_aF_b, J_{ab}=290 Hz for diastereoisomer **8b**); −116.8 to −124.4 (2F, 1-$CF_{a'}F_{b'}$, $J_{a'b'}$=287 Hz for the other diastereoisomer **8'b**); −122.5 (4F, 2,3-CF_2); −123.3 (2F, 4-CF_2); −126.7 (2F, 5-CF_2) ppm. IR (film) ν (cm^{-1}): 1761 (C=O); 1477 (C=C); 1250–1100 (C−F). MS (70 eV) *m/z* (%): 544 (M^+, 1); 543 (2); 152 (12); 110 (27); 77 (3); 69 (4); 43 (100).

3.14. Preparation of 2-F-octyl-1-acetoxy-2-methoxyethylphenyl sulfide (8c)

Sulfoxide **4c** (1 g, 1.66 mmol) treated as above led to the formation of compound **8c**. Yield, 1 g (94%); b.p. 125 °C/0.4 Torr. Analysis: $C_{19}H_{13}F_{17}O_3S$ (644.34) requires: C, 35.41; H, 2.03; F, 50.12; S, 4.97%. Found: C, 34.98; H, 1.88; F, 49.45; S, 4.55%. ^{1}H NMR ($CDCl_3$/TMS) δ: 2.10 (s, 3H, CH_3CO_2 for diastereoisomer **8c**);

2.13 (s, 3H, CH_3CO_2 for the other diastereoisomer **8'c**); 3.70 (s, 3H, CH_3O for diastereoisomer **8c**); 3.75 (s, 3H, CH_3O for the other diastereoisomer **8'c**); 4.09 (m, 1H, C_2H); 6.49 (d, 1H, C_1H for diastereoisomer **8c**, $J=6.4$ Hz); 6.54 (d, 1H, C_1H for the other diastereoisomer **8'c**, $J=4.8$ Hz); 7.29–7.78 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3/CFCl_3$) δ: −81.5 (3F, CF_3); −116.8 to 122.8 (2F, 1-CF_aF_b, $J_{ab}=289$ Hz for diastereoisomer **8c**); −117.9 to −123.8 (2F, 1-$CF_{a'}F_{b'}$, $J_{a'b'}=287$ Hz for the other diastereoisomer **8'c**); −122.6 (8F, 2,3,4,5-CF_2); −123.5 (2F, 6-CF_2); −126.9 (2F, 7-CF_2) ppm. IR (film) ν (cm^{-1}): 1759 (C=O); 1477 (C=C); 1250–1100 (C−F). MS (70 eV) *m/z* (%): 644 (M^+, 0.68); 553 (0.14); 152 (4); 119 (0.24); 110 (25); 109 (5); 77 (0.8); 69 (2); 43 (100).

3.15. Preparation of 2-F-octyl-2-acetoxyethylphenyl sulfoxide (9c)

A solution of sulfoxide **3c** (1 g, 1.7 mmol) in AcOH (8 ml) was heated at 140 °C for 5 h. After evaporation of excess acetic acid, the residue obtained was chromatographed on a silica gel column using a mixture of PhH/AcOEt (70:30) as eluent. The solvents were removed under reduced pressure and compound **9c** obtained was purified by recrystallization from petroleum ether. Yield, 0.67 g (63%); m.p. 71 °C.

Analysis: $C_{18}H_{11}F_{17}O_3S$ (630.32) requires: C, 34.29; H, 1.75; F, 51.23; S, 5.08%. Found: C, 34.89; H, 1.71; F, 50.42; S, 4.62%. ^1H NMR ($CDCl_3$/TMS) δ: 1.98 (s, 3H, CH_3); 3.30 (m, 2H, CH_2); 6.07 (m, 1H, CH); 7.76 (m, 5H, Ph) ppm. ^{19}F NMR ($CDCl_3/CFCl_3$) δ: −81.3 (3F, CF_3); −117.0 to −122.8 (2F, 1-CF_aF_b, $J_{ab}=289$ Hz); −121.8 (8F, 2,3,4,5-CF_2); −122.9 (2F, 6-CF_2); −126.5 (2F, 7-CF_2) ppm. IR ($CHCl_3$) ν (cm^{-1}): 1750 (C=O); 1450 (C=C); 1250–1100 (C−F); 1030 (S=O). MS (70 eV) *m/z* (%): 630 (M^+, 1); 615 (2); 125 (89); 109 (18); 77 (44); 69 (11); 43 (100).

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