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Selective Aromatic Electrochemical Fluorination of Methyl Phenyl Sulfone*

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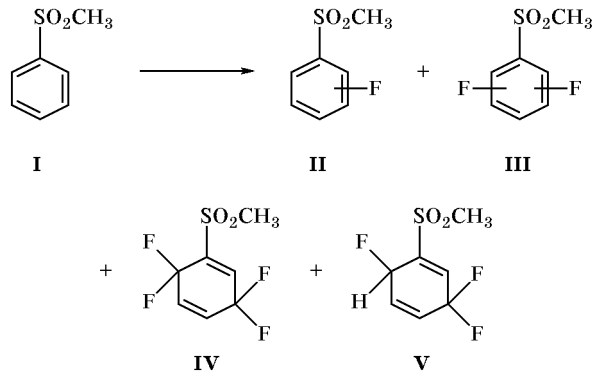
Abstract—Electrochemical fluorination of methyl phenyl sulfone occurs exclusively at the aromatic ring to give isomeric methyl mono- and difluorophenyl sulfones and methyl 3,3,6,6-tetrafluoro-1,4-cyclohexadienyl sulfone.

It is believed that electrochemical fluorination of sulfones RSO_2R' and sulfonyl chlorides RSO_2Cl does not involve the sulfonyl group and yields perfluorinated sulfones $R_FSO_2R'_F$ and sulfonyl fluorides R_FSO_2F [1]. However, this is the case only when radical R is the simplest alkyl group (e.g., Me or Et). The yield of sulfonyl fluorides R_FSO_2F in the electrochemical fluorination of sulfonyl chlorides RSO_2Cl sharply decreases as the length of the R radical increases [2]. Saturated and unsaturated sulfones behave strongly differently in electrochemical fluorination. The fluorination of phenyl vinyl sulfone is accompanied by complete desulfurization and saturation, leading to perfluorinated compounds of the cyclohexane series $C_6F_{11}C_nF_{2n+1}$ (n = 0–2) [3]. We presumed [3] that desulfurization of unsaturated sulfones is determined by more facile fluorination of the C=C bond as compared to C–H.

In the present work we studied electrochemical fluorination of methyl phenyl sulfone (**I**) with the goal of elucidating the possibility for concurrent fluorination at the aromatic ring and side chain. Momota *et al.* [4, 5] reported on the concurrent fluorination of fatty–aromatic compounds using toluene and isomeric fluorotoluenes as examples. The authors showed that the reaction occurs both at the side chain with formation of fluoromethylbenzenes and at the aromatic ring to give trifluoro(methyl)-1,4-cyclohexadienes.

^1H, ^{13}C, and ^{19}F NMR and GC–MS analysis of the liquid products obtained by electrochemical fluorination of methyl phenyl sulfone (**I**) showed that the reaction occurs exclusively at the aromatic ring, the methyl group remaining intact. Even traces of perfluoroalkylperfluorocyclohexanes (which are the main products of electrochemical fluorination of phenyl vinyl sulfone [3]) were not detected. The major products were two isomeric fluorophenyl methyl sulfones **II**, two isomers of difluorophenyl methyl sulfone **III**, and methyl 3,3,6,6-tetrafluoro-1,4-cyclohexadienyl sulfone (**IV**) (Scheme 1). In addition, the product mixture contained a small amount of trifluoro derivative **V** which is precursor of tetrafluoride **IV**.

Scheme 1.



The structure of isomeric sulfones **II** was determined on the basis of the ^{13}C NMR spectrum of the product mixture. Apart from signals belonging to

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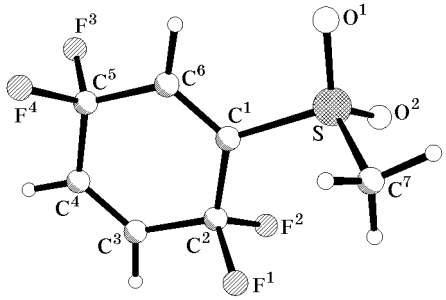
initial sulfone **I**, the spectrum contained two sets of doublet signals which were split due to coupling with fluorine. The corresponding chemical shifts and coupling constants $J_{C,F}$ coincide with those calculated for *ortho*- and *meta*-substituted sulfones **IIa** and **IIb** using ACDLabs program (the mean-square deviations are 0.34 and 0.78 ppm, respectively). According to the ^{19}F NMR data, the isomer ratio **IIa**:**IIb** is 1:2.6. An additional proof for the above assignment of isomers **IIa** and **IIb** is the presence of a weak coupling, $^4J_{CH_3,F}$ = 2.6 Hz, in the ^{13}C NMR spectrum of minor isomer **IIa** (such coupling is absent in the spectrum of **IIb**).

Detailed analysis of the ^{13}C and ^{19}F NMR spectra allowed us to assign with certainty the structure of 2,5-difluorophenyl methyl sulfone to one of isomers **III**. The observed ^{19}F NMR signals (δ_F –112.67 and –113.37 ppm) are very similar to the corresponding signals of 2,5-difluorobenzenesulfonyl fluoride, δ_F –113.01 (*o*-F) and –114.68 (*m*-F)] [6]. Hydrofluorination of 2,5-difluorophenyl methyl sulfone at positions *2,5*, followed by electrochemical fluorination, is likely to give fluorinated cyclohexadiene derivatives **IV** and **V**. Most probably, the second isomer of **III** is 2,6-difluorophenyl methyl sulfone. However, we failed to determine its structure without ambiguity because of its low concentration in the product mixture. Methyl tetrafluorocyclohexadienyl sulfone **IV** was isolated in the pure state, and its structure was proved by the X-ray diffraction data (see figure). Its geometric parameters are given in table.

Compounds **I**–**III** are characterized by similar fragmentation patterns in the electron impact mass spectra. Their decomposition follows two main pathways: expulsion of the $CH_2{=}S{=}O$ molecule to form radical cations $[C_6H_{4-n}F_n(OH)]^{+\cdot}$ and demethylation with subsequent desulfonylation to give cations $[C_6H_{5-n}F_n]^+$; the latter are the most abundant in the mass spectra.

The fragmentation of compound **IV** follows a more complicated pattern. Its molecular ion is extremely unstable, and it decomposes mainly at the $C_{sp^2}{-}S$ bond with charge localization both at the sulfonyl group and at the cyclohexadiene fragment; elimination of the $CH_2{=}S{=}O$ molecule contributes little to the total ion current. The subsequent defluorination processes are likely to be accompanied by rearrangements leading to 1,4-pentadiyne cation whose peak has the maximal intensity in the spectrum.

Thus, unlike phenyl vinyl sulfone, electrochemical fluorination of methyl phenyl sulfone yields no perfluoroalkylperfluorocyclohexanes, in agreement with our previous conclusions on the reasons for ready desulfurization of unsaturated sulfones [3]. The process occurs regioselectively at the aromatic ring, and the methyl group remains unchanged.



Structure of the molecule of methyl 3,3,6,6-tetrafluoro-1,4-cyclohexadienyl sulfone (**IV**).

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400, 100, and 376 MHz, respectively; $CDCl_3$ was used as solvent, and HMDS, as internal reference. The chemical shifts are given relative to TMS (^1H, ^{13}C) and CCl_3F (^{19}F). Gas chromatographic–mass spectrometric analysis was performed on a Hewlett–Packard HP 5971A mass-selective detector (70 eV) which was coupled with an HP 5890 gas chromatograph; Ultra-2 column (5% of phenylmethylsilicone), injector temperature 250°C, oven temperature programming from 70 to 280°C at 20°C/min. GLC analysis was performed using an LKhM-80 chromatograph; 1000 × 3-mm column packed with 5% of SE-30 on Chromaton N-AW-DMCS, thermal conductivity detector, carrier gas helium.

X-Ray diffraction data were obtained on an Enraf–Nonius CAD-4 diffractometer (MoK_α irradiation, β-filter, θ/2θ scanning). Arrays of experimental reflections were treated with account taken of the Lorentz factors and polarization with no regard to X-ray absorption by the sample. The structure was solved by the direct method and was refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms (which were localized experimentally from the Fourier difference syntheses). Compound **IV**: $C_7H_6F_4O_2S$, colorless prism, 0.65 × 0.38 × 0.24 mm. Monoclinic crystals with the following unit cell parameters: a = 5.060(1), b = 11.208(2), c = 15.736(3) Å; β = 96.57(3)°; V = 886.6(3) Å^3; Z = 4, d_{calc} = 1.724 g/cm^3; space group $P2_1/c$. The final divergence factors were R = 0.029, R_w = 0.082 [from 1178 reflections with $I > 2\sigma(I)$].

Bond lengths (*d*) and bond angles (ω) in the molecule of methyl 3,3,6,6-tetrafluoro-1,4-cyclohexadienyl sulfone (**IV**)

Bond	*d*, Å	Bond	*d*, Å
$S-O^1$	1.428 (2)	F^4-C^5	1.368 (3)
$S-O^2$	1.422 (2)	C^1-C^6	1.320 (3)
$S-C^1$	1.789 (2)	C^1-C^2	1.498 (3)
$S-C^7$	1.750 (2)	C^2-C^3	1.483 (3)
F^1-C^2	1.364 (2)	C^3-C^4	1.306 (3)
F^2-C^2	1.360 (2)	C^4-C^5	1.472 (3)
F^3-C^5	1.371 (3)	C^5-C^6	1.490 (3)
Angle	**ω, deg**	**Angle**	**ω, deg**
$O^2S^1O^1$	117.7 (1)	$F^2C^2C^1$	110.5 (2)
O^2SC^7	109.7 (1)	$F^1C^2C^1$	109.2 (2)
O^1SC^7	109.1 (1)	$C^3C^2C^1$	115.1 (2)
O^2SC^1	107.2 (1)	$C^4C^3C^2$	122.8 (2)
O^1SC^1	106.5 (1)	$C^3C^4C^5$	122.3 (2)
C^7SC^1	105.9 (1)	$F^4C^5F^3$	104.1 (2)
$C^6C^1C^2$	121.9 (2)	$F^4C^5C^4$	110.1 (2)
C^6C^1S	117.6 (1)	$F^3C^5C^4$	109.0 (2)
C^2C^1S	120.4 (1)	$F^4C^5C^6$	108.8 (2)
$F^2C^2F^1$	104.2 (2)	$F^3C^5C^6$	108.1 (2)
$F^2C^2C^3$	108.8 (2)	$C^4C^5C^6$	116.1 (2)
$F^1C^2C^3$	108.5 (2)	$C^1C^6C^5$	121.7 (2)

Electrochemical fluorination of methyl phenyl sulfone (I). The reaction was carried out in a steel (St-3) 130-cm^3 electrolyzer equipped with nickel anodes (overall area 63 cm^2), tubes with stop-cocks for supplying HF and discharging fluorination products, and reflux condenser filled with a 1:1 mixture of acetone and diethyl ether (which was cooled to –20°C with liquid nitrogen). The electrolytic cell was cooled and charged with 120 g of anhydrous HF, and 2 g of KF and 10 g of methyl phenyl sulfone (**I**) were added. The time of electrolysis was 14 h (13.8 A h), anode current density 1.6 A/dm^2, cell voltage 5.8–6.4 V, temperature ~5°C. The reaction mixture was poured into an ice–water mixture, NaF was added to adsorb HF, the mixture was extracted with diethyl ether, and the extract was dried over $CaCl_2$ and kept over NaF. The solvent was removed, and the residue was distilled under reduced pressure, bp 80–90°C (1 mm). The distillate and the still residue were passed through a column packed with 25 g of silica gel (Merck 60s). The column was eluted in succession with hexane–chloroform (1:1), chloroform, and hexane–acetone (1:1) to isolate pure sulfone **IV** and a mixture of unreacted sulfone **I** with fluorinated products **II** and **III**.

2-Fluorophenyl methyl sulfone (IIa). ^{13}C NMR spectrum, δ_C, ppm: 43.68 d (CH_3, $^4J_{C,F}$ = 2.6 Hz), 117.02 d (C^3, $^2J_{C,F}$ = 21.1 Hz), 124.71 d (C^5, $^4J_{C,F}$ = 3.9 Hz), 128.84 d (C^1, $^2J_{C,F}$ = 29.2 Hz), 130.10 d (C^6, $^3J_{C,F}$ = 9.9 Hz), 136.12 d (C^4, $^3J_{C,F}$ = 8.2 Hz), 159.25 d (C^2, $^1J_{C,F}$ = 254.8 Hz). ^{19}F NMR spectrum: δ_F –107.60 ppm, m. Mass spectrum, *m*/*z* (I_{rel}, %): 174 (31) $[M]^{+\cdot}$, 159 (20) $[M-CH_3]^+$, 112 (39) $[M-CH_2=S=O]^{+\cdot}$, 95 (100) $[C_6H_4F]^{+\cdot}$.

3-Fluorophenyl methylsulfone (IIb). ^{13}C NMR spectrum, δ_C, ppm: 44.06 s (CH_3), 114.50 d (C^2, $^2J_{C,F}$ = 24.6 Hz), 120.80 d (C^4, $^2J_{C,F}$ = 21.1 Hz), 123.04 d (C^6, $^4J_{C,F}$ = 3.4 Hz), 131.28 d (C^5, $^3J_{C,F}$ = 7.8 Hz), 142.42 d (C^1, $^3J_{C,F}$ = 6.5 Hz), 162.25 d (C^3, $^1J_{C,F}$ = 252.2 Hz). ^{19}F NMR spectrum: δ_F –106.82 ppm, m. Mass spectrum, *m*/*z* (I_{rel}, %): 174 (38) $[M]^{+\cdot}$, 159 (41) $[M-CH_3]^+$, 112 (62) $[M-CH_2=S=O]^{+\cdot}$, 95 (100) $[C_6H_4F]^{+\cdot}$.

Methyl 3,3,6,6-tetrafluoro-1,4-cyclohexadienyl sulfone (IV). mp 81–82°C. ^1H NMR spectrum, δ, ppm: 3.11 s (3H, CH_3), 6.34 m (2H, 4-H, 5-H), 7.23 m (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 43.96 (CH_3), 109.19 t (C^3, $^1J_{C,F}$ = 232.6 Hz), 109.35 t (C^6, $^1J_{C,F}$ = 231.9 Hz), 128.51 t.t (C^5, $^2J_{C,F}$ = 29.3, $^3J_{C,F}$ = 9.1 Hz), 129.50 t.t (C^4, $^2J_{C,F}$ = 30.0, $^3J_{C,F}$ = 9.1 Hz), 136.68 t.t (C^2, $^2J_{C,F}$ = 32.8, $^3J_{C,F}$ = 5.6 Hz), 141.67 t.t (C^1, $^2J_{C,F}$ = 28.8, $^3J_{C,F}$ = 8.9 Hz). ^{19}F NMR spectrum, δ, ppm: –93.49 m (3-F), –93.11 m (5-F). Found, %: C 36.51; H 2.90; F 32.78; S 14.04. $C_7H_6F_4O_2S$. Calculated, %: C 36.53; H 2.63; F 33.01; S 13.93.

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