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Reactions of [Fluoro(methylsulfonyloxy)iodo]benzene: II.* Reaction of [Fluoro(sulfonyloxy)iodo]benzene with Acyclic Olefins

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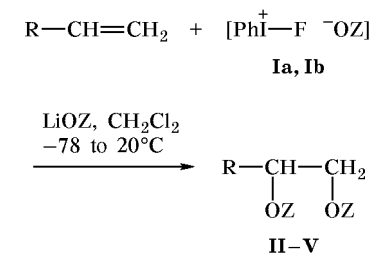
Abstract—Reactions of [fluoro(sulfonyloxy)iodo]benzene with 1-hexene and 1-heptene smoothly yield the corresponding 1,2-disulfonates. Reaction of [fluoro(sulfonyloxy)iodo]benzenes with methyl methacrylate results in formation of isomeric α-fluoro-β-sulfonyloxy products. A possible reaction mechanism is discussed.

Sulfonates derived from multivalent iodine compounds are widely used as reagents in fine organic synthesis [2]. Their accessibility, stability, and pronounced electrophilic properties make them indispensable for functionalization and transformation of various organic molecules [3, 4], including unsaturated ones [5–7]. Electrophilic addition to olefins was studied mainly with iodine(III) derivatives containing a tosyloxy group [8]. Chemical properties of trifluoromethylsulfonyloxy and methylsulfonyloxy derivatives of polyvalent iodine were studied in detail using [hydroxy(methylsulfonyloxy)iodo]benzene [7, 9] and Zefirov's reagent $(PhIOTf)_2O$ as examples [3, 9, 10].

In the present work we tried to extend the series of sulfonyloxy derivatives of tervalent iodine compounds. For this purpose we examined electrophilic properties of [fluoro(sulfonyloxy)iodo]benzenes **Ia** and **Ib** in reactions with acyclic olefins. Compounds **Ia** and **Ib** were synthesized by the procedure developed by us previously, by oxidation of iodobenzene with xenon(II) derivatives [11]. Preliminary experiments showed that [fluoro(sulfonyloxy)iodo]benzenes **Ia** and **Ib** vigorously react with various acyclic olefins in a nonpolar solvent (CH_2Cl_2) even at –78°C. As a result, complex mixtures were formed, from which we failed to isolate individual products. When the reaction of **Ia** and **Ib** with 1-hexene, 1-heptene, or methyl methacrylate was performed in the presence of a salt (lithium sulfonate), we obtained addition products with the anion. However, we did not succeed in isolating stable products in the reactions of **Ia** and **Ib** with trimethylethylene, styrene, and some other olefins even in the presence of a salt additive.

The reactions of **Ia** and **Ib** with 1-hexene and 1-heptene in methylene chloride in the presence of lithium trifluoromethanesulfonate or methanesulfonate in 5 h gave 1,2-bis(sulfonyloxy) derivatives **II**–**V** (Scheme 1) which were isolated by column chromatography on silica gel. The products are stable at room temperature. Their structure was proved by comparing with samples obtained previously [3, 10].

Scheme 1.



Ia, **II**, **IV**, Z = CF_3SO_2; **Ib**, **III**, **V**, Z = CH_3SO_2; **II**, **III**, R = C_4H_9; **IV**, **V**, R = C_5H_{11}.

* For communication I, see [1].

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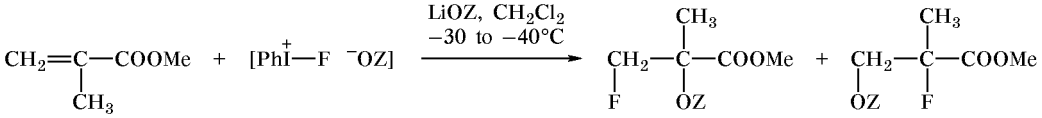
Scheme 2.



VI, Z = CF_3SO_2 (21%); **VII**, Z = CH_3SO_2 (23%); **VIII**, Z = CF_3SO_2 (14%); **IX**, Z = CH_3SO_2 (11%).

Methyl methacrylate in which the double bond is deactivated due to effect of the ester group reacted with compounds **Ia** and **Ib** in methylene chloride in the presence of lithium sulfonate at –30 to –40°C at a considerably lower rate. The products were mixtures of isomeric addition products **VI**/**VIII** (3 : 2) and **VII**/**IX** (2 : 1) (Scheme 2). The isomers were separated by chromatography on silica gel; compounds **VI** and **VII** readily crystallized on cooling. These are colorless low-melting substances (mp 18 and 13°C, respectively) which are stable in an inert medium and at low temperature. They readily decompose on exposure to air or at room temperature. The structure of products **VI**–**IX** was proved by the IR and ^1H, ^{13}C, and ^{19}F NMR spectra. The IR spectra of **VI**–**IX** contained absorption bands in the region 1430–940 cm^{-1}, which are typical of a sulfonate group. In the ^1H NMR spectra of **VI** and **VII** we observed only three signals: a two-proton singlet from the CH_2F group at δ 3.91–3.96 ppm, a three-proton singlet from the methoxy group at δ 3.69–3.88 ppm, and a three-proton singlet from the methyl group at δ 1.77–1.90 ppm. The considerable downfield shift of the latter can be explained by the effect of the neighboring tertiary carbon atom which is attached to strongly electron-acceptor sulfonate group. The effect of the sulfonate group is also reflected in the chemical shift of the tertiary carbon atom in the ^{13}C NMR spectra of **VI** and **VII**, which is equal to 92–94 ppm. The signal from the CF_3 carbon atom is a quadruplet at δ_C 118.2 ppm ($J_{C,F}$ = 319 Hz). The covalent character of the bond with the trifluorosulfonyloxy group in compounds **VI**–**IX** follows from the position of the fluorine signal in the ^{19}F NMR spectrum: δ_F –74.57 ppm. In addition, the ^{19}F NMR spectra of **VI** and **VII** contain a signal at δ_F –203 to –204 ppm, which belongs to the CH_2F atom. The proposed structures of **VI**–**IX** are also supported by the data of elemental analysis.

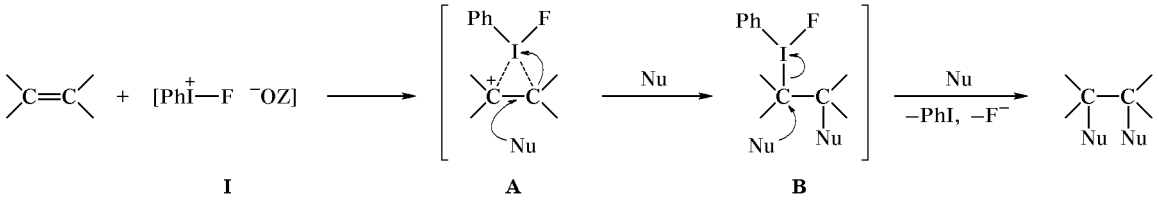
It should be noted that compounds **VI** and **VII** are unique examples of stable covalent tertiary sulfonates (one of such compounds was described in [12]). Presumably, their stability originates from the presence of two electron-acceptor groups, CH_2F and CO_2CH_3, at the tertiary carbon atom. Steric shielding of the latter by bulky substituents is likely to favor the stability of sulfonates **VI** and **VII**.

The data obtained for reactions of [fluoro(sulfonyloxy)iodo]benzenes **Ia** and **Ib** with various olefins suggest a commonly accepted mechanism for electrophilic addition of organic polyvalent iodine compounds at multiple bonds. In the first stage, electrophilic attack by the iodonium group on the double bond of the substrate yields cyclic cationoid intermediate **A**. Opening of the latter by the action of counterion OZ^- or F^- (which is a part of the initial reagent or external nucleophile) from the rear side leads to unstable tervalent iodine derivative **B** with *trans* configuration of the substituents. In the final stage, the iodonium fragment is replaced by the second nucleophile with inversion of configuration (Scheme 3).

EXPERIMENTAL

The IR spectra were recorded from solutions in methylene chloride on a UR-10 spectrometer. The ^1H, ^{13}C, and ^{19}F NMR spectra were obtained on Varian-S60T (60 MHz) and Varian-400 spectrometers at 400, 100, and 187 MHz, respectively. The ^1H and ^{13}C

Scheme 3.



chemical shifts were measured relative to the solvent signal or tetramethylsilane as internal reference; trichlorofluoromethane was used as standard for ^{19}F. Methylene chloride was dried and purified by the procedure described in [13].

Reactions of 1-hexene and 1-heptene with [fluoro(sulfonyloxy)iodo]benzenes I in the presence of lithium sulfonate. To a suspension of 2.36 mmol of compound **I** in 15 ml of methylene chloride at –78°C under argon we added 8 mmol of lithium sulfonate and a solution of 3.5 mmol of olefin in 5 ml of methylene chloride. The mixture was stirred for 1 h at –78°C and for 1 h at –30°C. It was then allowed to warm up to room temperature over a period of 2.5 h and was stirred for 0.5 h at that temperature. The mixture was filtered through a thin layer of silica gel and washed with a 10% solution of sodium thiosulfate, the aqueous layer was extracted with chloroform, and the combined organic phases were dried over magnesium sulfate and evaporated. The products were isolated by chromatography on silica gel using ethyl acetate–hexane as eluent.

1,2-Bis(trifluoromethylsulfonyloxy)hexane (II). R_f 0.7 (ethyl acetate–hexane, 1:6). Decomposition point 131–132°C (130–133°C [10]). IR spectrum (CCl_4), ν, cm^{-1}: 1430, 1260, 1230, 1160, 990, 930 (OSO_2CF_3). ^1H NMR spectrum (60 MHz, CCl_4), δ, ppm: 0.9–1.9 m (9H, C_4H_9), 4.6 m (2H, CH_2OSO_2), 5.1 m (1H, $CHOSO_2$).

1,2-Bis(methylsulfonyloxy)hexane (III). R_f 0.25 (ethyl acetate–hexane, 1:2). mp 34–36°C (34–36°C [10]). IR spectrum (CCl_4), ν, cm^{-1}: 1350, 1180, 920 (S=O). ^1H NMR spectrum (60 MHz, $CDCl_3$), δ, ppm: 0.9–1.9 m (9H, C_4H_9), 3.0 s (6H, $2CH_3$), 4.3 m (2H, C**H**$_2$OSO$_2$CH$_3$), 4.8 m (1H, C**H**OSO$_2$CH$_3$).

1,2-Bis(trifluoromethylsulfonyloxy)heptane (IV). R_f 0.61 (ethyl acetate–hexane, 1:6). Decomposition point 125–129°C. IR spectrum (CCl_4), ν, cm^{-1}: 1427, 1271, 1232, 1160, 990, 927 (OSO_2CF_3). ^1H NMR spectrum (60 MHz, CCl_4), δ, ppm: 1.0–2.0 m (11H, C_5H_{11}), 4.5 m (2H, $CH_2OSO_2CF_3$), 5.1 m (1H, $CHOSO_2CF_3$). Found, %: C 27.39; H 3.61. $C_9H_{14}F_6O_6S_2$. Calculated, %: C 27.27; H 3.54.

1,2-Bis(methylsulfonyloxy)heptane (V). R_f 0.4 (ethyl acetate–hexane, 1:2). mp 41–44°C. IR spectrum (CCl_4), ν, cm^{-1}: 1358, 1183, 921 (S=O). ^1H NMR spectrum (60 MHz, $CDCl_3$), δ, ppm: 1.0–2.0 m (11H, C_5H_{11}), 3.1 s (6H, $2CH_3$), 4.4 m (2H, C**H**$_2$OSO$_2$CH$_3$), 4.9 m (1H, C**H**OSO$_2$CH$_3$). Found, %: C 37.65; H 6.87. $C_9H_{20}O_6S_2$. Calculated, %: C 37.50; H 6.94.

Reactions of [fluoro(sulfonyloxy)iodo]benzenes Ia and Ib with methyl methacrylate in the presence of lithium sulfonate. The reactions were performed as described above using 2.36 mmol of compound **I**, 10 mmol of lithium sulfonate, and 2.5 mmol of methyl methacrylate. The solvent was distilled off from the reaction mixture, and the residue was extracted with several portions of chloroform. The solvent was removed from the extract, and the residue was subjected to chromatography on silica gel using ethyl acetate–hexane (1:8) as eluent.

Methyl 2-methyl-3-fluoro-2-trifluoromethylsulfonyloxypropionate (VI). R_f 0.8. IR spectrum (CCl_4), ν, cm^{-1}: 1770 (C=O), 1425, 1210, 1140, 940 (OSO_2CF_3). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.9 s (3H, CH_3), 3.88 s (3H, OCH_3), 3.91 s (2H, CH_2F). ^{19}F NMR spectrum (187 MHz, $CDCl_3$), δ_F, ppm: –74.56 s (3F, CF_3), –204.1 s (1F, CH_2F). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ_C, ppm: 21.17 (CH_3), 47.76 (OCH_3), 54.02 (CH_2), 92.6 (C–O), 118.2 q (CF_3, $J_{C,F}$ = 319 Hz), 167.52 (C=O). Found, %: C 26.74; H 2.83. $C_6H_8F_4O_5S$. Calculated, %: C 26.87; H 2.99.

Methyl 2-fluoro-2-methyl-3-trifluoromethylsulfonyloxypropionate (VIII). R_f 0.25. IR spectrum (CCl_4), ν, cm^{-1}: 1772 (C=O), 1422, 1219, 1135, 940 (OSO_2CF_3). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.86 s (3H, CH_3), 3.82 s (3H, OCH_3), 4.55 and 4.80 d.d (2H, *AB* system, CH_2O, J = 10 Hz). ^{19}F NMR spectrum (187 MHz, $CDCl_3$), δ_F, ppm: –74.64 s (3F, CF_3), –204.23 s (1F, CH_2F). Found, %: C 26.95; H 2.76. $C_6H_8F_4O_5S$. Calculated, %: C 26.87; H 2.99.

Methyl 3-fluoro-2-methyl-2-methylsulfonyloxypropionate (VII). R_f 0.69. IR spectrum (CCl_4), ν, cm^{-1}: 1768 (C=O), 1320, 1138, 952 (OSO_2). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.77 s (3H, CH_3), 3.69 s (3H, OMe), 3.76 s (3H, OSO_2CH_3), 3.96 s (2H, CH_2F). ^{19}F NMR spectrum (187 MHz, $CDCl_3$), δ_F, ppm: –203.8 s (1F, CH_2F). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ_C, ppm: 20.87 (CH_3), 39.65 (OSO_2CH_3), 46.55 (OCH_3), 53.76 (CH_2), 93.2 (C–O), 167.52 (C=O). Found, %: C 33.71; H 5.44. $C_6H_{11}FO_5S$. Calculated, %: C 33.64; H 5.14.

Methyl 2-fluoro-2-methyl-3-methylsulfonyloxypropionate (IX). R_f 0.28. IR spectrum (CCl_4), ν, cm^{-1}: 1765 (C=O), 1325, 1143, 948 (OSO_2). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.82 s (3H, CH_3), 3.73 s (3H, OCH_3), 3.88 s (3H, OSO_2CH_3), 4.01 s (2H, CH_2F). ^{19}F NMR spectrum (187 MHz, $CDCl_3$), δ_F, ppm: –202.6 s (1F, CH_2F). Found, %: C 33.71; H 5.44. $C_6H_{11}FO_5S$. Calculated, %: C 33.64; H 5.14.

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