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[Hydroxy(sulfonyloxy)iodo]perfluoroalkanes - New Hypervalent Iodine Species and Promising Reagents for Organic Synthesis

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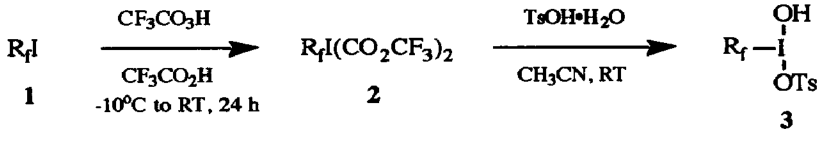
Abstract. [Hydroxy(sulfonyloxy)iodo]perfluoroalkanes ($C_nF_{2n+1}I^+OH\bullet^-OSO_2R$, n = 3, 4, 6; R = *p*-$CH_3C_6H_4$, CF_3) can be prepared in two steps from the corresponding perfluoroalkyliodides by oxidation with pertrifluoroacetic acid and subsequent reaction with TsOH or Me_3SiOTf. These compounds react with trimethylsilyl derivatives of aromatic compounds under mild conditions forming the corresponding perfluoroalkyl(aryl)iodonium salts in good yield.

In recent years, there has been considerable interest in (sulfonyloxy)iodoarenes as reagents for organic syntheses.[1,2] A number of these compounds, for example, Koser's reagent, PhI(OH)OTs, and Zefirov's reagent, $PhIO\bullet Tf_2O$ are widely used for various synthetic purposes, such as the preparation of sulfonate esters from alkenes and ketones, numerous oxidations, and the synthesis of some useful aryliodonium salts.[2]

In the present communication we wish to report the preparation and properties of a new structural type of iodine(III) sulfonate, namely, perfluoroalkyl derivatives **3**, **4**. These compounds can be conveniently prepared in two steps from the commercially available perfluoroalkyliodides **1**. In the first step, the starting iodides **1** are oxidized with peroxytrifluoroacetic acid to bis(trifluoroacetates) **2** in quantitative yield by the known procedure of Yagupolskii and coworkers.[3] The subsequent treatment of trifluoroacetates **2** with monohydrate of p-toluenesulfonic acid in acetonitrile at room temperature results in the formation of tosylates **3** in 85-95% yield.[4]



3a: $R_f = C_3F_7$ (83%), **3b**: $R_f = C_4F_9$ (91%), **3c** $R_f = C_6F_{13}$ (92%)

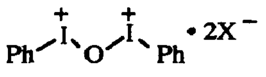
In contrast to starting trifluoroacetates **2**, tosylates **3** have a substantially higher thermal stability with a decomposition point at 150-160 °C. These compounds are not water sensitive, can be purified by crystallization from acetonitrile, and can be stored indefinitely at room temperature. The structure of compounds **3** was determined by IR, multinuclear NMR spectroscopy, and elemental analysis.[5]

The analogous triflates **4** can be prepared in quantitative yields by the reaction of trifluoroacetates **2** with trimethylsilyltriflate in trifluoroacetic acid and isolated as colorless hygroscopic solids.[6] Triflates **4** are less stable, than tosylates **3**, however, they can be stored under dry conditions for several weeks at room temperature without decomposition. When exposed to moist air these compounds form crystalline monohydrates, contact of **4** with liquid water results in slow decomposition.

$$\underset{\mathbf{2}}{R_fI(CO_2CF_3)_2} + Me_3SiOSO_2CF_3 \xrightarrow[\text{-15 to 20 °C}]{CF_3CO_2H} \underset{\mathbf{4}}{R_fI(OH)OSO_2CF_3}$$

4a: $R_f = C_3F_7$, **4b**: $R_f = C_4F_9$, **4c** $R_f = C_6F_{13}$

The structural assignment for compounds **4** was confirmed by spectral data and elemental analysis.[7] In contrast to the analogous, known adducts of iodosobenzene with strong acids **5**[8a] and iodosotriflate **6**,[8b] which all have bright yellow color due to the $^+$I-O-I$^+$ bridging fragment,[8] compounds **4** are completely colorless. The IR spectra and elemental analysis of **4** also indicate the presence of the hydroxy group in its structure instead of the $^+$I-O-I$^+$ moiety.



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(X = CF_3SO_3, ONO_2, $OClO_3$, OSO_2OH, etc.)

$(CF_3SO_2OIO)_n$

6

Similarly to their aryl substituted analogs, compounds **3**, **4** are highly reactive towards unsaturated organic compounds and other carbon nucleophiles. To demonstrate the synthetic usefulness of the triflates **4**, we have studied their reaction with trimethylsilylbenzene **7**. The reaction proceeds in methylene chloride under very mild conditions to give the known perfluoroalkyl(aryl)iodonium triflates **8** (FITS-reagents[9]) which are important electrophilic perfluoroalkylating reagents.[10]

$$\underset{\mathbf{7}}{PhSiMe_3} + \underset{\mathbf{4}}{R_fI(OH)OSO_2CF_3} \xrightarrow[\text{-78 to 0 °C}]{CH_2Cl_2} \underset{\mathbf{8}}{Ph\text{-}\overset{+}{I}\text{-}R_f\ \overset{-}{O}SO_2CF_3}$$

8a: $R_f = C_4F_9$ (85%), **8b**: Ar = C_6F_{13} (89%)

In conclusion, we have prepared a new structural type of iodine(III) sulfonate, namely, perfluoroalkyl derivatives **3**,**4**. These compounds are potentially useful reagents for the preparation of perfluoroalkyl iodonium salts by the reaction with the corresponding silylated organic substrates.

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3. Yagupolskii, L.M.; Maletina, I.I.; Kondratenko, N.V.; Orda, V.V. *Synthesis* **1978**, 835.
4. Typical procedure for the preparation of **3**: To a stirred solution of TsOH•H_2O (0.95 g, 5 mmol) in acetonitrile (20-30 ml) the appropriate trifluoroacetate **2** (4 mmol) was added at 0°C. The mixture was warmed to room temperature and stirred until the formation of a white crystalline precipitate of **3**. The product was filtered, washed with dry CH_2Cl_2 (30 ml) and dried in vacuo. Analytically pure materials were obtained by recrystallization from acetonitrile.
5. Identification data: **3a**: white needles, mp 131-132 °C (from MeCN); IR (CCl_4): 3400 (OH), 3035 (Ar), 2925 (Me), 1595, 1549, 1349, 1242, 1211, 1141, 1003 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6, 20:1): δ 10.3 (br. s, 1H, OH), 7.65 (dd, 2H, J = 8 Hz, C_6H_4), 7.15 (dd, 2H, J = 8 Hz, C_6H_4), 2.3 (s, 3H, Me); ^{19}F NMR ($CDCl_3$/DMSO-d_6, 1:20): δ -67.3, -84.9, -124.1 (C_3F_7); ^{13}C NMR ($CDCl_3$/DMSO-d_6, 1:20): δ 142.8, 139.3, 129.2, 126.0 (Ar), 118 to 110 (m, C_3F_7), 21.3 (Me). Anal: Calc. for $C_{10}H_8IF_7O_4S$: C, 24.81; H, 1.67. Found: C, 24.57; H, 1.75. **3b**, white needles, mp 137-139 °C (from MeCN); IR (CCl_4): 3400 (OH), 3035 (Ar), 2925 (Me), 1595, 1549, 1349, 1242, 1211, 1141, 1003 cm^{-1}; ^1H NMR (CD_3CN): δ 7.55 (dd, 2H, J = 8 Hz, C_6H_4), 7.15 (dd, 2H, J = 7.8 Hz, C_6H_4), 3.9 (br. s, 1H, OH), 2.3 (s, 3H, Me); ^{19}F NMR (CD_3CN): δ -80.7, -85.6, -116.9, -125.6 (C_4F_9); ^{13}C NMR (CD_3CN): δ 142.7, 139.2, 129.3, 126.4 (Ar), 118 to 110 (m, C_4F_9), 21.3 (Me). Anal: Calc. for $C_{11}H_8IF_9O_4S$: C, 24.74; H, 1.51; I, 23.76. Found: C, 24.83; H, 1.54; I, 23.69. **3c**, white crystals, mp 142-144 °C (from MeCN); IR (CCl_4): 3400 (OH), 3035 (Ar), 2925 (Me), 1595, 1549, 1349, 1242, 1211, 1141, 1003 cm^{-1}; ^1H NMR (CD_3CN/DMSO-d_6, 20:1): δ 7.55 (dd, 2H, J = 8 Hz, C_6H_4), 7.15 (dd, 2H, J = 8 Hz, C_6H_4), 5.9 (br. s, 1H, OH), 2.3 (s, 3H, Me); ^{19}F NMR

($CD_3CN/DMSO$-d_6, 20:1): δ -62.6, -77.9, -110.6, -118.0, -119.6, -123.0 (C_6F_{13}); ^{13}C NMR ($CD_3CN/DMSO$-d_6, 20:1): δ 142.8, 139.3, 129.3, 126.4 (Ar), 118 to 110 (m, C_6F_{13}), 21.3 (Me). Anal: Calc. for $C_{13}H_8IF_{13}O_4S$: C, 24.64; H, 1.27. Found: C, 24.65; H, 1.23.

6. General procedure for the preparation of **4**: To a stirred mixture of the appropriate trifluoroacetate **2** (1 mmol) with 2 ml of trifluoroacetic acid 0.3 ml (1.5 mmol) of trimethylsilyltriflate was added at -15°C. The resulting mixture was stirred for 10 min at -5 to 0°C to give a colorless solution. Removal of the solvent and drying of the solid residue in high vacuum gives **4** in quantitative yield.
7. For **4a**: white waxy solid, dec. at 78-80 °C, IR (CCl_4): 3300 (OH), 1360, 1250, 1220, 1150, 1000 cm^{-1}; ^{19}F NMR (CD_3CN): δ -75.5 (m), -77.9 (s, CF_3SO_3), -83.9 (m), -123.6 (m). **4b**: white hygroscopic solid, mp 75-80 °C; IR (CCl_4): 3300 (OH), 1365, 1250, 1220, 1150, 1005 cm^{-1}; ^{19}F NMR (CD_3CN): δ -75.8 (m), -78.0 (s, CF_3SO_3), -80.2 (m), -115.5 (m), -124.9 (m). Calc. for $C_5H_7IF_{12}O_7S$ (**4b**•$3H_2O$): C, 10.61; H, 1.25. Found: C, 10.42; H, 1.32. **4c**: white hygroscopic solid, mp 75-80 °C; IR (CCl_4): 3300 (OH), 1360, 1250, 1220, 1150, 1000 cm^{-1}; ^{19}F NMR (CD_3CN): δ -76.0 (m), -78.0 (s, CF_3SO_3), -80.9, -110.6, -118.0, -119.6, -123.0 (C_6F_{13}). Anal: Calc. for $C_7H_3IF_{16}O_5S$ (**4c**•H_2O): C, 13.34; H, 0.48. Found: C, 13.28; H, 0.51.
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9. (a) Umemoto, T.; Kuriu, Y.; Shuyama, H.; Miyano, O.; Nakayama, S. *J. Fluorine Chem.* **1982**, *20*, 695. (b) In the work of Umemoto[9a] fluoroalkyl(phenyl)iodonium triflates (**8**) were prepared by the reaction of trifluoroacetates **2** with benzene in the presence of triflic acid. Most likely, the actual electrophilic iodonium transfer reagents in this reaction[9a] are triflates **4** formed in situ from trifluoroacetates **2** and triflic acid.
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