A General Synthetic Approach to Aryl(perfluoroalkyl)iodonium Sulfonates by the Reaction of [Hydroxy(sulfonyloxy)iodo]perfluoroalkanes with Arylsilanes

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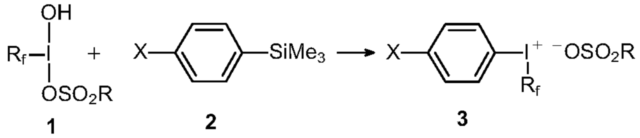
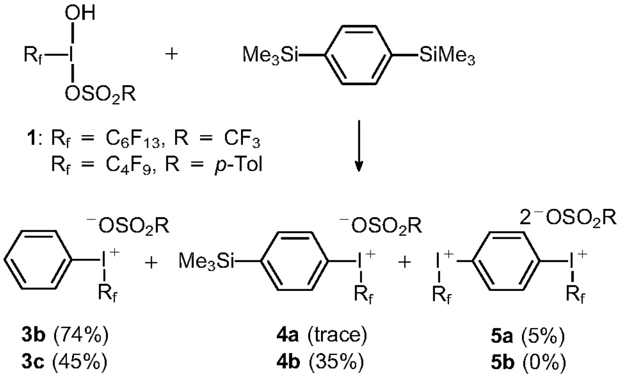
Various aryl(perfluoroalkyl)iodonium salts **3** can be conveniently prepared by the reaction of [hydroxy(sulfonyloxy)iodo]perfluoroalkanes $C_nF_{2n+1}I(OH){\cdot}OSO_2R$ **1** with trimethylsilyl-substituted arenes **2**.

There is considerable current interest and research activity in the development of new reagents and synthetic methods based on the organic chemistry of hypervalent iodine.[1] Especially interesting and promising are perfluoroalkyliodonium derivatives such as fluoroalkyl(phenyl)iodonium triflates (FITS reagents) developed by Umemoto and co-authors and widely applied as electrophilic fluoroalkylating reagents.[2,3] FITS reagents, $PhIC_nF_{2n+1}{\cdot}OTf$, are usually synthesized by the reaction of [bis(trifluoroacetoxy)iodo]perfluoroalkanes with benzene in the presence of triflic acid.[4] This method can only be used in the synthesis of the phenyl derivatives, but a general synthetic approach to substituted aryl sulfonates, $ArIC_nF_{2n+1}{\cdot}OSO_2R$, is still unknown. In the present communication we wish to report a synthetic procedure for the preparation of fluoroalkyl(aryl)iodonium sulfonates by the reaction of novel perfluoroalkyliodonium reagents **1**[5] with arylsilanes **2** (Scheme 1).



Scheme 1

The starting reagents **1** were prepared in high yield from the readily available [bis(trifluoroacetoxy)iodo]perfluoroalkanes[6] and *p*-toluenesulfonic acid or trimethylsilyl triflate.[5] Reactions of compounds **1** with arylsilanes **2** were carried out in CH_2Cl_2 in the presence of trifluoroacetic acid or trimethylsilyl triflate.† Triflates **1** are significantly more reactive than the analogous *p*-toluenesulfonates, and their reactions with activated arylsilanes (**2**, X = OMe, Me) proceed almost instantaneously even at subzero temperatures. Reactions of *p*-toluenesulfonates **1** are much slower and require 1–2 days for completion. The products **3** were in most cases isolated in good yield as white crystalline solids after filtration of the crude reaction mixture through a short silica gel column (Table 1). The structure of products **3** was confirmed by spectral data and elemental analysis.‡ Triflates **3a,b** have melting points and spectra similar to previously reported data.[4]



Scheme 2

Several different products were obtained in reactions of reagents **1** with 1,4-bis(trimethylsilyl)benzene (Scheme 2). Only reaction of *p*-toluenesulfonate **1** gave the expected trimethylsilyl-substituted iodonium salt **4** in moderate yield. The major products in these reactions (Scheme 2) were phenyl(fluoro-alkyl)iodonium salts **3b,c** resulting from the desilylation side reaction. In addition, bis(iodonium) salt **5a** was isolated in a low yield from the reaction of triflate

Table 1 Reactions of [hydroxy(sulfonyloxy)iodo]perfluoroalkanes **1** with arylsilanes **2**.

Entry	Product	R_f	R	X	Reaction conditions[a]	Yield (%)	M.p./°C
1	**3a**	C_4F_9	CF_3	H	A	75	124–126
2	**3b**	C_6F_{13}	CF_3	H	A	79	120–123
3	**3c**	C_4F_9	*p*-Tol	H	B	71	117–118
4	**3d**	C_4F_9	*p*-Tol	Me	B	67	99–101
5	**3e**	C_6F_{13}	*p*-Tol	Me	B	70	111–113
6	**3f**	C_4F_9	*p*-Tol	OMe	B	62	69–70
7	**3g**	C_4F_9	CF_3	OMe	A	65	[b]
8	**3h**	C_6F_{13}	CF_3	Cl	A	75	oil

[a] Method A: Me_3SiOTf (1 equiv.), CH_2Cl_2, –78 to 20 °C; Method B: CF_3CO_2H (3–4 equiv.), CH_2Cl_2, room temp., 1–2 days. [b] White crystals, decompose at room temp.

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† *Typical experimental procedure.* To a mixture of [hydroxy(tosyloxy)-iodo]perfluoroalkane **1**[5] (1 mmol) and the corresponding arylsilane **2** (1.5 mmol) in methylene dichloride (20 ml), trifluoroacetic acid (0.3–0.5 ml) was added dropwise at room temperature until the formation of a clear solution. The reaction mixture was stirred for 1–2 days at room temperature, then solvent was removed *in vacuo* to give a yellow residue of crude product **3**. The pure products **3** were obtained by filtration through a short column sealed with silica gel, applying methylene dichloride elution first to remove non-polar by-products and then acetonitrile to elute the product **3**. Additional crystallization from ether–hexane afforded analytically pure samples of *p*-toluenesulfonates **3**.

‡ All stable new compounds were identified by IR, ^1H and ^{19}F NMR data and elemental analyses consistent with the assigned structures. As a typical example, **3c** has the following data: IR (in CCl_4) ν/cm^{-1} 3058, 3035, 2958, 2923, 1557, 1340, 1241, 1209, 1140, 1097, 1004; ^1H NMR (200 MHz, $CDCl_3$) δ 8.21 (d, 2H, Ph), 7.78 (dd, 1H, Ph), 7.57 (dd, 2H, Ph), 7.45 (d, 2H, C_6H_4), 7.14 (d, 2H, C_6H_4), 2.45 (s, 3H, Me); ^{19}F NMR (300 MHz, $CDCl_3$) δ – 68.0, –80.2, –114.9, –125.6 (C_4F_9). Calc. for $C_{17}H_{12}IF_9O_3S$: C, 34.36; H, 2.04; I, 21.36%. Found: C, 34.23; H, 2.07; I, 21.48%.

reagent **1**. Triflate **5a** is similar to previously reported aryl-substituted analogues[7] and may be particularly interesting because the analogous *p*-phenylene bis(aryliodonium) salts have promising activity as highly effective PQQ inhibitors in the PQQ-catalysed redox cycling.[8]

Preliminary studies show that the stability and chemical properties of aryl(perfluoroalkyl)iodonium salts **3–5** depend sharply on the nature of the substituent in the aromatic ring. In particular, compounds **3f** and **3g** bearing an electron-donating methoxy group are significantly less stable in comparison with non-substituted derivatives **3a–c**.

In summary, the readily available and stable [hydroxy(sulfonyloxy)iodo]perfluoroalkanes $C_nF_{2n+1}I(OH){\cdot}OSO_2R$ can be used as reagents for the preparation of important aryl(perfluoroalkyl)iodonium salts (FITS reagents).

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