Iodosyl Fluorosulfate – A New Efficient Reagent for the Direct Synthesis of Diaryliodonium Salts

Nikolai S. Zefirov,*[a] Tahir M. Kasumov,[a] Anatoly S. Koz'min,[a] Viktor D. Sorokin,[a] Peter J. Stang,[b] Viktor V. Zhdankin[b]

[a] Department of Chemistry, Moscow State University, Moscow 119899, Russia
[b] Chemistry Department, The University of Utah, Salt Lake City, Utah 84112, USA

Received 30 April 1993

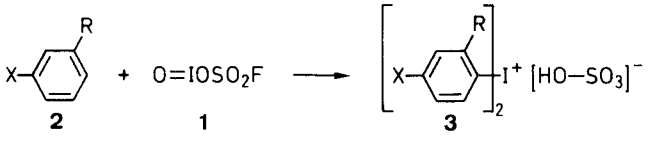
Iodosyl fluorosulfate **(1)** reacts with aromatic compounds **2** under mild conditions to give diaryliodonium hydrosulfates **3** in good yield.

Diaryliodonium salts, $Ar_2I^+X^-$, represent the most important class of polyvalent iodine compounds;[1-3] they are widely used in organic synthesis as efficient arylating reagents[1-3] and also have practical application due to their antimicrobial activity and photochemical properties.[1] Recently diaryliodonium salts with non-nucleophilic anions, such as tetrafluoroborate or trifluoromethanesulfonate (triflate), have been suggested as efficient catalysts for radiation-initiated polymerization.[4]

Several different methods for the preparation of diaryliodonium salts are known,[1-3,5-14] however, most of them lack generality and require a multistep reaction sequence, for example, ArI → $ArI(OAc)_2$ → ArIO → Ar_2I^+X. The only known direct syntheses of iodonium salts by the reaction of aromatic hydrocarbons with trichloroiodine,[10] tris(trifluoroacetoxy)iodine,[13] and iodosyl sulfate[9,14] are restricted by the very limited number of aromatic substrates and afford the desired products only in low yield.

In a search toward new, more efficient iodinating reagents we turned our attention recently to two highly electrophilic inorganic iodosyl derivatives, namely triflate and fluorosulfate which have been prepared more than 15 years ago,[15] however, to our knowledge none of their reactions with organic substrates have been reported. Recently, we found that the first of these reagents, iodosyl triflate, can be used for the synthesis of diaryliodonium triflates from trimethylsilylarenes.[16]

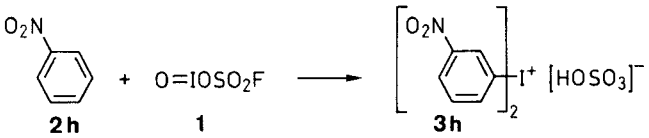
In the present communication we wish to report an efficient direct synthesis of diaryliodonium hydrosulfates **3** from iodosyl fluorosulfate **(1)** and aromatic compounds **2**. We have found that benzene and its derivatives **2b–g** with o,p-directing substituents react with reagent **1** under mild conditions to afford exclusively diaryliodonium hydrosulfates **3a–g** with the substituent X in the para-position to the iodonium moiety (Scheme 1). Reaction conditions and yields of products **3a–g** are shown in the Table.



	R	X		R	X
a	H	H	**e**	H	F
b	H	Me	**f**	H	Cl
c	H	*t*-Bu	**g**	H	Br
d	Me	Me			

Scheme 1

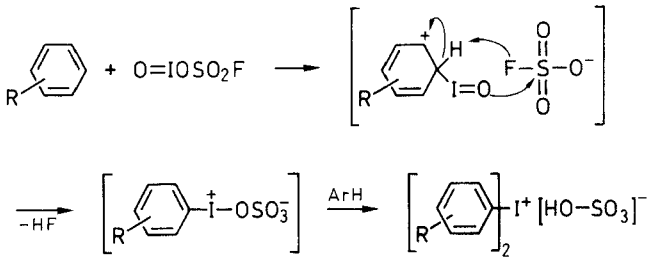
The regioselectivity of this reaction (Scheme 1) is consistent with the electrophilic character of reagent **1**. Moreover, reagent **1** is highly reactive towards deactivated substrates such as halogenated benzenes **2e–g** and even nitrobenzene (Scheme 2). The latter reaction proceeds at room temperature to afford *m*-nitroiodonium salt **3h** as a single product.



Scheme 2

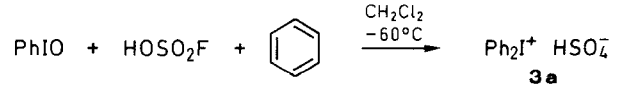
All of the iodonium salts **3** were isolated from the reaction mixtures as stable, crystalline solids and identified by ^1H, ^{13}C, ^{19}F NMR and microanalysis.

The result of the reaction of fluorosulfate **1** is different from the previously reported reaction of iodosyl triflate, O=IOTf.[16] Instead of the expected fluorosulfate iodonium salts, hydrosulfates **3a–h** are isolated. This result can be explained by the elimination of hydrogen fluoride[17] in the course of the reaction by the following mechanism (Scheme 3).



Scheme 3

For additional experimental support of this mechanism (Scheme 3) we carried out the reaction of iodosobenzene, fluorosulfonic acid and benzene (Scheme 4). This reaction



Scheme 4

Table. Compounds **3** Prepared

Product	Reaction Conditions		Yield[a] (%)	mp (°C)[b]	Lit. mp (°C)	^{1}H NMR (200 MHz, CD_3OD/TMS) δ, J (Hz)
	Temp. (°C)	Time (h)				
3a	−60	0.5	53	167–168	167–169	7.45–8.18 (m, C_6H_5)
	−30 to 0	0.5				
3b	−30 to 0	1	95	178–180	–[c]	2.2 (s, 3H, CH_3), 7.25–8.45 (dd, $4H_{arom}$, J = 8.5)
	20	0.5				
3c	−50 to 0	0.5	67	173–175	–[c]	2.0 (s, 9H, t-C_4H_9), 7.9–8.6 (dd, $4H_{arom}$, J = 8.5)
3d	−50 to 0	1	71	140–141	–[c]	2.15 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 6.9 (d, $1H_{arom}$, J = 7.8), 7.14 (s, $1H_{arom}$), 7.9 (d, $1H_{arom}$, J = 7.8)
	20	0.5				
3e	−30	1	83	204–205	–[c]	6.5–7.5 (dd, C_6H_4, J = 7.5)[d]
	20	0.5				
3f	−20	1	87	190–192	190	7.45–8.14 (dd, C_6H_4, J = 8.54)
	20	1				
3g	−20	0.5	78	200–202	203	7.55–8.1 (dd, C_6H_4, J = 8.5)[e]
3h	20	3	60	166–167	165–167	8.55 (t, $1H_{arom}$, J = 8.5), 9.35 (d, $1H_{arom}$, J = 8.54), 9.9 (s, $1H_{arom}$)

[a] Yield of isolated analytically pure product, based on **1**.
[b] Crystallized from $MeOH/Et_2O$.
[c] For new compounds, satisfactory microanalyses obtained: C ± 0.36, H ± 0.25.
[d] ^{19}F NMR ($CD_3OD/CFCl_3$): δ = −106.45 (s, Ar–F).
[e] ^{13}C NMR (CD_3OD): δ = 137.95, 135.62, 127.54, 115.50 (all s, C_{arom}).

models the second step of the sequence of Scheme 3 and, indeed, affords diphenyliodonium hydrosulfate **(3a)** in high yield and under mild conditions.

The reaction of iodosyl sulfate with aromatic compounds also affords iodonium hydrosulfates.[9,14] However, this reaction requires sulfuric acid as a solvent and gives only moderate yields of iodonium salts.[9,14] In contrast, iodosyl fluorosulfate **(1)** reacts in dichloromethane under mild conditions even with deactivated aromatic substrates, such as nitrobenzene and fluorobenzene, to give iodonium salts in significantly better yields.

In conclusion, we have demonstrated, that iodosyl fluorosulfate **(1)** is a powerful electrophilic reagent which can be used for an efficient direct preparation of iodonium hydrosulfate salts from aromatic compounds under mild conditions.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AC 200 MHz spectrometer at 200 MHz (^{1}H NMR), 50.323 (^{13}C NMR) and 188.313 MHz (^{19}F NMR), respectively. Chemical shifts for ^{1}H and ^{13}C NMR are reported in ppm (δ) relative to internal TMS or the proton resonance due to the residual protons in the deuterated NMR solvent (CD_3OD); fluorine chemical shifts are given relative to external $CFCl_3$. Microanalyses were performed on a Carlo Erba instrument. Iodosyl fluorosulfate **(1)** was prepared from I_2, I_2O_5 and FSO_3H by a known procedure.[15]

Diaryliodonium Hydrosulfates 3a–h; General Procedure:
The appropriate aromatic compound (10.74 mmol) was added to a cooled suspension of iodosyl fluorosulfate (**1**; 1.30 g, 5.37 mmol) in anhydr. CH_2Cl_2 (20 mL) under stirring. The mixture was stirred at the appropriate temperature (see Table) until the reagent completely dissolved. The resulting solution was concentrated in vacuo to give a yellow oil. Crystallization from MeOH afforded analytically pure products **3** as white crystalline solids; the yields, melting points and spectral data are given in the Table.

Diphenyliodonium hydrosulfate (3a) from Iodosobenzene and Fluorosulfonic Acid:
Fluorosulfonic acid (1.1 m, 19.1 mmol) was added dropwise to a suspension of iodosobenzene (4.2 g, 19 mmol) and benzene (1.8 mL, 20.2 mmol) in anhydr. CH_2Cl_2 (35 mL) at −60 °C under Ar. The mixture was stirred for 30 min at −60 °C and then for 30 min at −30 to −0 °C. Concentration of the solution and crystallization from MeOH afforded analytically pure **3a** as a white crystalline solid; yield: 5.9 g (82%); mp 167–168 °C.

(1) Koser, G.F.; In *The Chemistry of Functional Groups, Suppl. D*, Patai, S.; Rappoport, Z., Eds.; Wiley Interscience: New York, 1983; Chapters 18 and 25, pp 721–811 and 1265–1851.
(2) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: New York, 1992.
(3) Grushin, V.V. *Acc. Chem. Res.* **1992**, *25*, 529.
(4) Crivello, J.V. *Adv. Polym. Sci.* **1984**, *62*, 1.
(5) Sandin, R.B. *Chem. Rev.* **1943**, *32*, 249.
(6) Banks, D.F. *Chem. Rev.* **1966**, *66*, 243.
(7) Lukas, H.J.; Kennedy, E.R. *Org. Synth. Coll. Vol. III*, **1955**, 185.
(8) Beringer, F.M.; Drexler, M.; Gindler, E.M.; Yumpkin, C.C. *J. Am. Chem. Soc.* **1953**, *75*, 2705.
(9) Beringer, F.M.; Falk, R.A.; Karniol, M.; Yiellen, I.; Masullo, G.; Mauser, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, *81*, 342.
(10) Beringer, F.M.; Dehn, J.W.; Winkov, M. *J. Am. Chem. Soc.* **1960**, *82*, 2948.
(11) Koser, G.F.; Wettach, R.H.; Smith, C.S. *J. Org. Chem.* **1980**, *45*, 1543.
(12) Sandin, R.B.; Hay, A.S. *J. Am. Chem. Soc.* **1952**, *74*, 274.
(13) Beringer, F.M.; Bachafer, H.E.; Falk, R.A.; Leff, M. *J. Am. Chem. Soc.* **1958**, *80*, 4279.
(14) Masson, I.; Hanby, W.E. *J. Chem. Soc.* **1938**, 1699.
(15) Dalziel, J.R.; Carter, H.A.; Aubke, F. *Inorg. Chem.* **1976**, *15*, 1247.
(16) Stang, P.J.; Zhdankin, V.V.; Tykwinski, R.; Zefirov, N.S. *Tetrahedron Lett.* **1991**, *32*, 7497.
(17) For another example of the cleavage of fluorosulfate anion see: Jache, A.W. *Advan. Inorg. Chem. Radiochem.* **1974**, *16*, 177.