

# Preparation, X-ray Crystal Structure, and Chemistry of ((Arylsulfonyl)methyl)(phenyl)iodonium Triflates. Stable Alkylidonium Salts

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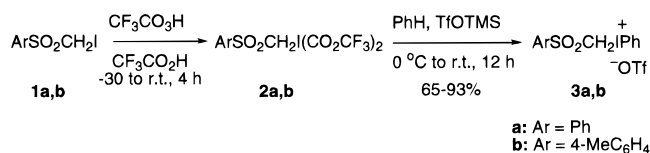
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Derivatives of polyvalent iodine with an alkyl substituent at iodine generally are highly unstable and can exist only as short-lived reactive intermediates in the oxidation of alkyl iodides and some other reactions.<sup>1</sup> For example, the low-temperature reaction of iodomethane with chlorine results in the formation of a yellow precipitate of (dichloroiodo)methane which rapidly decomposes above  $-28\text{ }^{\circ}\text{C}$ .<sup>1b</sup> The introduction of an electron-withdrawing substituent into the alkyl moiety may lead to stabilization of the molecule; for example, (dichloroiodo)methyl sulfones,  $\text{ArSO}_2\text{CH}_2\text{ICl}_2$ ,<sup>2</sup> 1-(dichloroiodo)-1*H*,1*H*-perfluoroalkanes,  $\text{R}_f\text{CH}_2\text{ICl}_2$ ,<sup>3</sup> and tosylates,  $\text{R}_f\text{CH}_2\text{I}(\text{OH})\text{OTs}$ ,<sup>4</sup> are known, relatively stable compounds. Several examples of iodonium salts,  $\text{R}_2\text{I}^+\text{X}^-$ , with one or two aliphatic alkyl groups were generated and investigated by NMR spectroscopy at low temperatures, and some of them even were isolated in the form of highly unstable crystalline products.<sup>5</sup> The only known example of stable derivatives of this type are polyfluoroalkyl(aryl)iodonium salts. These salts as chlorides were first prepared in the 1970s by Yagupolskii and co-workers<sup>6</sup> and later widely applied as electrophilic polyfluoroalkylating reagents by Umemoto and co-workers.<sup>7</sup>

In this paper, we report the preparation, X-ray crystal structure, and chemical reactivity of ((arylsulfonyl)methyl)iodonium triflates **3**, stable alkylidonium salts of a new structural type.

((Arylsulfonyl)methyl)iodonium salts **3** can be conveniently prepared in two steps starting from the readily available<sup>2</sup> iodomethyl sulfones **1**. In the first step, starting iodides **1** are oxidized with peroxytrifluoroacetic acid to trifluoroacetates **2** in almost quantitative yield. The subsequent treatment of trifluoroacetates **2** with benzene and trimethylsilyltriflate in dichloromethane affords products **3** in a good yield.<sup>8</sup> Both iodonium salts **3a** and **3b** are not moisture sensitive, can be purified by crystallization from acetonitrile, and can be stored for several months in a refrigerator.



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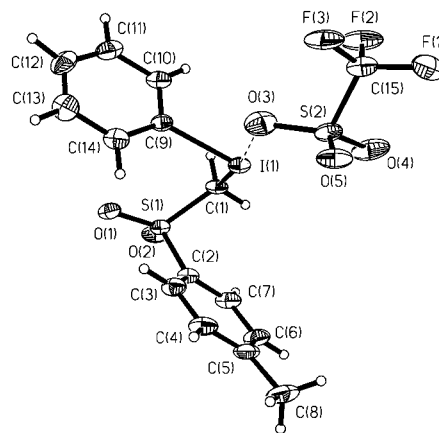
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**Figure 1.** X-ray structure of ((*p*-tolylsulfonyl)methyl)(phenyl)iodonium triflate **3b**. Selected bond lengths (Å): I(1)–C(1) 2.131(3), I(1)–C(9) 2.209(3), I(1)–O(3) 2.797, I(1)–O(5) 2.999, C(1)–S(1) 1.839(3), S(1)–C(2) 1.691(3). Selected bond angles (deg): C(1)–I(1)–C(9) 91.53(11), S(1)–C(1)–I(1) 113.84(14).

**Table 1.** Reactions of ((Arylsulfonyl)methyl)(phenyl)iodonium Triflates (**3a,b**) with Organic Substrates

entry	substrate	reaction conditions <sup>a</sup>	product	yield (%)
1	PhSLi	<b>3a</b> , 3 hrs	PhSO <sub>2</sub> CH <sub>2</sub> SPh	90% <sup>b</sup>
2	PhSLi	<b>3b</b> , 3 hrs	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> SPh	80% <sup>b</sup>
3	PhNMe <sub>2</sub>	<b>3a</b> , 30 min	PhSO <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> (Me) <sub>2</sub> Ph OTf <sup>-</sup>	61% <sup>b</sup>
4	PhNMe <sub>2</sub>	<b>3b</b> , 20 min	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> (Me) <sub>2</sub> Ph OTf <sup>-</sup>	95% <sup>b</sup>
5		<b>3a</b> , 10 min	PhSO <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> (TfO) <sup>-</sup> pyridine	78% <sup>c</sup>
6		<b>3b</b> , 10 min	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> (TfO) <sup>-</sup> pyridine	85% <sup>c</sup>
7	Ph <sub>3</sub> P	<b>3a</b> , 2 hrs	PhSO <sub>2</sub> CH <sub>2</sub> PPh <sub>3</sub> <sup>+</sup> OTf <sup>-</sup>	82% <sup>b</sup>
8	Ph <sub>3</sub> P	<b>3b</b> , 2 hrs	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> PPh <sub>3</sub> <sup>+</sup> OTf <sup>-</sup>	85% <sup>b</sup>
9		<b>3b</b> , KF, 3 days		95% <sup>b</sup>

<sup>a</sup> All reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub>, under N<sub>2</sub>, at room temperature. <sup>b</sup> Yields determined by <sup>1</sup>H NMR. <sup>c</sup> Isolated yields.

Products **3a,b** were identified by spectral data and elemental analyses.<sup>8</sup> In particular, the <sup>1</sup>H NMR displayed the characteristic signals of methylene protons at  $\delta = 5.52$  ppm, shifted about 1 ppm downfield compared to the starting iodomethyl sulfones **1**. The structure of iodonium triflate **3b** was unambiguously established by a single-crystal X-ray analysis (Figure 1). The structural data revealed the expected geometry for iodonium salts with the C1–I–C9 bond angle of 91.53(11)°. The I–C bond distances of 2.131 and 2.209 Å are longer than a typical bond length in diaryliodonium salts (2.0 to 2.1 Å<sup>1a</sup>). The distance between the iodine atom and the nearest oxygen of the triflate anion, I···O3, is 2.797 Å. A weaker secondary bonding between the iodine atom and the triflate anion (I···O5 = 2.999 Å) is also present. To our knowledge, no X-ray crystal structural data on polyvalent iodine species with an I–C<sub>sp<sup>3</sup></sub> bond were previously reported in the literature.

Similarly to the known polyfluoroalkyl(aryl)iodonium salts,<sup>7</sup> ((arylsulfonyl)methyl)iodonium triflates **3** can be used as efficient electrophilic alkylating reagents. We investigated

reactions of compounds **3** with various organic nucleophiles, such as thiophenolate anion, dimethylaniline, pyridine, triphenylphosphine, and silyl enol ether of acetophenone. All of

(8) Preparation of **3a**: Trifluoroacetic anhydride (12.1 mL, 85.6 mmol) and 80% hydrogen peroxide (1.80 mL, 55.9 mmol) were mixed at  $-30\text{ }^{\circ}\text{C}$ , and the resulting solution was slowly warmed to  $25\text{ }^{\circ}\text{C}$ . After an additional 10 min of stirring, the mixture was cooled back to  $-30\text{ }^{\circ}\text{C}$ , and a solution of (phenylsulfonyl)methyl iodide **1a** (2.2 g, 7.5 mmol) in dichloromethane (10 mL) was slowly added. The reaction mixture was slowly warmed to  $25\text{ }^{\circ}\text{C}$  and stirred for 4 h. Evaporation of solvent at  $0\text{ }^{\circ}\text{C}$  in vacuum afforded trifluoroacetate **2a** as a white solid in almost quantitative yield. [CAUTION: Trifluoroacetates **2a** and **2b** are unstable at room temperature and should be handled with care!] Product **2a** (3.81 g, 7.49 mmol) was mixed with trifluoroacetic acid (10 mL), benzene (1.4 mL, 15.8 mmol), and trimethylsilyl triflate (1.6 mL, 8.3 mmol) in dichloromethane (15 mL) at  $0\text{ }^{\circ}\text{C}$  under stirring. The resulting solution was allowed to warm to room temperature and was additionally stirred for 12 h at room temperature. The reaction mixture was evaporated to dryness, the residual solid was recrystallized from acetonitrile/ether. The resulting crystals were washed on filter with ether (30 mL) and dried under vacuum to give 3.53 g (93%) of ((phenylsulfonyl)methyl)(phenyl)iodonium triflate (**3a**): mp  $114\text{--}115\text{ }^{\circ}\text{C}$  (from  $\text{CH}_3\text{CN}$ ); IR (KBr) 3086, 3063 (Ar), 2997, 2914 ( $\text{CH}_2$ ), 1447 ( $\text{S}=\text{O}$ ), 1297, 1167, 1136 ( $\text{OTf}$ )  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  7.78 (m, 10H, 2Ph), 5.54 (s, 2H,  $\text{CH}_2$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{F}_3\text{IO}_5\text{S}_2$ : C, 33.08; H, 2.38; I, 24.83; S, 12.62. Found: C, 33.24; H, 2.40; I, 24.83; S, 12.59. Compound **3b** was prepared similarly in 65% yield: mp  $122\text{--}124\text{ }^{\circ}\text{C}$  (from  $\text{CH}_3\text{CN}$ ); IR (KBr) 3088, 3060 (Ar), 2999, 2947, 2915 ( $\text{CH}_2$  and  $\text{CH}_3$ ), 1596 ( $\text{S}=\text{O}$ ), 1297, 1167, 1136 ( $\text{OTf}$ )  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ )  $\delta$  7.78 (m, 9 H, Ph and  $\text{C}_6\text{H}_4$ ), 5.52 (s, 2H,  $\text{CH}_2$ ), 2.47 (s, Me). Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{F}_3\text{IO}_5\text{S}_2$ : C, 34.50; H, 2.70; I, 24.30; S, 12.28. Found: C, 34.62; H, 2.72; I, 24.41; S, 12.24. X-ray quality single crystals were obtained by slowly cooling a solution of **3b** in  $\text{CH}_3\text{CN}$  in a refrigerator.

these reactions proceeded under mild conditions and selectively afforded the appropriate product of alkylation (Table 1) along with iodobenzene as the byproduct. These reactions are similar to the previously reported reactions of polyfluoroalkyliodonium triflates and probably have the analogous mechanism.<sup>7</sup>

In summary, we have prepared stable alkylidonium salts of a new structural type. A first X-ray crystal structure of an alkylidonium salt has been reported. These novel ((arylsulfonyl)methyl)iodonium salts **3** can be used as efficient electrophilic alkylating reagents toward various organic substrates.

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**Supporting Information Available:** Selected experimental and characterization data and X-ray crystallographic report for compound **3b** (15 pages). See any current masthead page for ordering and Internet access instructions.

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