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Preparation and Chemistry of 1-Organosulfonyloxy-1,2-benziodoxol-3-(1*H*)-ones: First Example of a Stable Adduct of 2-Iodosobenzoic Acid with Strong Acid

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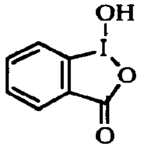
Abstract: 1-Organosulfonyloxy-1,2-benziodoxol-3-(1*H*)-ones (**3**,**4**,**5**) can be prepared in one step from 2-iodosobenzoic acid and the corresponding sulfonic acids or Me_3SiOTf. Reactions of these compounds with bis(trimethylsilyl)acetylene or cyanotrimethylsilane afford the respective alkynyl or cyano iodonium salts **6**, **7**, **8**.

2-Iodosobenzoic acid **1** and its derivatives have attracted considerable current research efforts due to an excellent catalytic activity in cleavage of toxic phosphates and reactive esters.[2] Cyclic iodosobenzoates **2** have been proposed as the reactive intermediates in the catalytic ester cleavage on the basis of spectral and kinetic mechanistic studies.[2b,c] However, with the exception of acetate[3] none of adducts **2** with acids were reported in the literature as individual compounds. Moreover, the possible existence of adducts of **1** with <u>strong acids</u>, such as organosulfonic, was never even considered in the literature despite acute interest in the chemistry of 2-iodosobenzoic acid and wide-spread application of other iodonium sulfonates in organic synthesis.[4]



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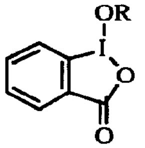
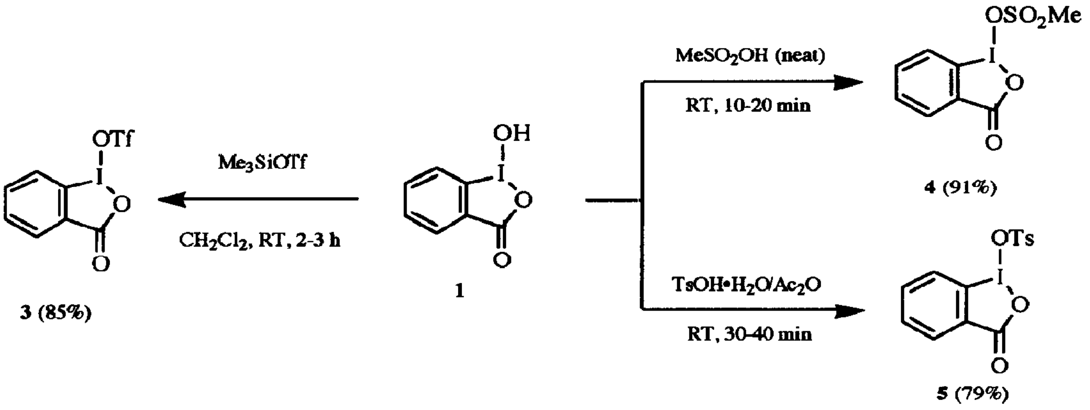


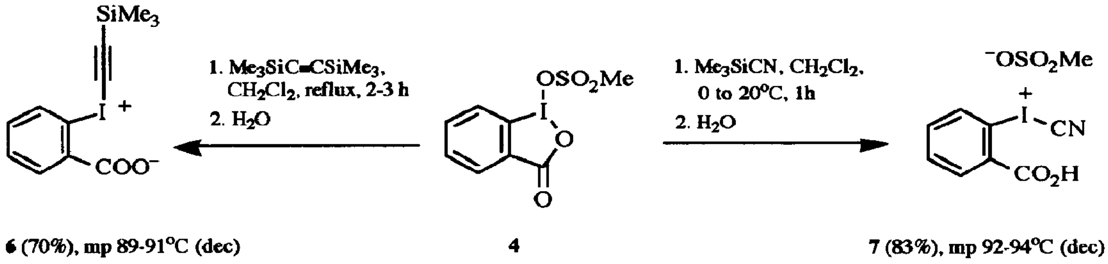
2: R = Ac, $\overset{O}{\overset{\|}{P}}(OR)_2$, etc

In the present communication we wish to report the preparation and properties of sulfonate derivatives of **1**, namely triflate **3**, mesylate **4**, and tosylate **5**. These compounds can be conveniently prepared in one step from the commercially available 2-iodosobenzoic acid **1** and the corresponding sulfonic acids or trimethylsilyltriflate.[5,6,7] All three adducts were isolated as hygroscopic but thermally stable crystalline solids. The most stable to moisture is tosylate **5**, which is obtained in the form of microcrystalline precipitate in an exothermic reaction of **1** with $TsOH{\bullet}H_2O$ in acetic anhydride.[7] Precipitate of **5** can be filtered and treated in open air, and only extended contact with moist air results in the formation of a microcrystalline dihydrate, $\mathbf{5}{\bullet}2H_2O$. Mesylate **4** slowly crystallizes from the solution of **1** in neat methanesulfonic acid in the form of colorless crystals, which turn into white powder of pentahydrate after contact with moist air.[6] Triflate **3** precipitates as yellow microcrystalline solid from the solution of **1** and trimethylsilyltriflate in methylene chloride.[5] It is extremely hygroscopic and forms colorless microcrystalline dihydrate after 10-13 min of contact with moist air; however, for further reactions triflate **3** can be conveniently used in situ.

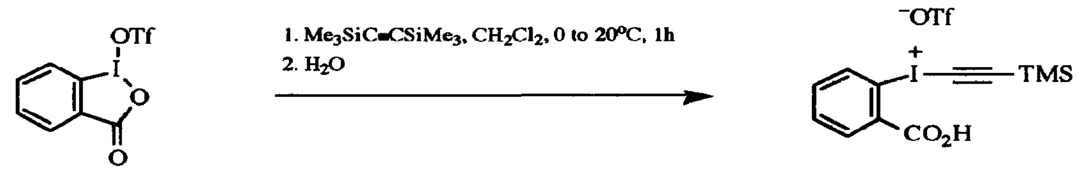


All three adducts (**3**-**5**) were identified by spectral data and elemental analyses.[5,6,7] Particularly characteristic are ^{1}H NMR spectra, in which signals of *o*-protons to iodine ($\delta \approx 8.3$ ppm) appear in slightly lower field, than the analogous proton in **1** ($\delta = 8.25$ ppm in the same solvent).

Similarly to the known aryliodososulfonates,[4] compounds **3**, **4** and **5** can react with unsaturated organic substrates and other carbon nucleophiles. As a representative example mesylate **4** reacts with bis(trimethylsilyl)acetylene or cyanotrimethylsilane with the formation of alkynyliodonium derivative **6** and cyanoiodonium salt **7**, respectively.



It is noteworthy that the analogous reaction of triflate **3** with bis(trimethylsilyl)acetylene affords alkynyliodonium triflate salt **8**, but not product **6**. Considering useful properties of alkynyliodonium salts,[8a] products **6** and **8** represent particular interest.



3

8 (75%), mp 121-123°C (dec)

Products **6**, **7** and **8** were identified by elemental analysis, IR and NMR spectra. Specifically, IR spectrum of compound **7** displays characteristic stretch of the cyano group at 2157 cm^{-1}, while triple bonds in **6** and **8** show up at 2028 and 2107 cm^{-1}, respectively. In ^{13}C NMR of **6** and **8**, the acetylenic signals have chemical shifts 46-47 (C≡$\underline{C}$-I) and 115-116 ($\underline{C}$≡C-I) ppm, which are typical of alkynyliodonium salts.[8b-d] Analogous to product **6** 1-alkynyl-1,2-benziodoxol-3-(1*H*)-ones were recently reported in the literature.[8d] Previously these compounds were prepared by a single step reaction of **1** with alkynyltrimethylsilanes and BF_3•Et_2O in a 22-35% yield.[8d]

In conclusion, we have prepared and isolated as individual, stable compounds adducts of 2-iodosobenzoic acid with sulfonic acids. These compounds are potentially useful reagents for the preparation of iodonium salts by the reaction with the corresponding silylated organic substrates.

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5. Preparation of **3**: To a stirred mixture of 2-iodosobenzoic acid (0.526 g, 2 mmol) in dry CH_2Cl_2 (20 ml), trimethylsilyltriflate (0.43 ml, 2.2 mmol) was added under nitrogen at room temperature. The resulting mixture turned into a clear solution after 10-20 min stirring and then yellow precipitate of **3** formed. The precipitate was filtered under nitrogen and dried in vacuum; yield 0.67 g (85%), mp 166-168°C (dec.); IR (CCl_4): 3071 (Ar), 1614 (C=O), 1271, 1233, 1166, 1024 (OTf) cm^{-1};

^{1}H NMR ($CDCl_3/CF_3COOH$, 20:1): δ 8.32 (d, 1H, J = 8 Hz), 8.11 (t, 1H, J = 8 Hz), 7.98 (d, 1H, J = 8 Hz), 7.80 (t, 1H, J = 8 Hz); ^{13}C NMR (DMSO-d_6): δ 167.9 (C=O), 134.6, 131.4, 131.1, 130.4, 126.3, 120.5 (Ar), 121.82 (q, J = 320 Hz, $CF_3SO_3^-$); ^{19}F NMR (CD_3CN): δ -78.61 (s, $CF_3SO_3^-$). Compound **3** is highly hygroscopic. After brief exposure to air the original yellow color of **3** disappears and a white, microcrystalline crystallohydrate **3**•$2H_2O$ forms. For **3**•$2H_2O$: ^{1}H NMR (CD_3CN): δ 8.27 (d, 1H), 8.06 (t, 1H), 7.94 (d, 1H), 7.77 (t, 1H), 7.45 (br. s, 4H, $2H_2O$). Anal: Calc. for $C_8H_8IF_3O_7S$: C, 22.24; H, 1.87. Found: C, 22.25; H, 1.80.

6. Preparation of **4**: 2-Iodosobenzoic acid (4.22 g, 16 mmol) was dissolved in 5-7 ml of neat methanesulfonic acid at room temperature under stirring. Then dry acetonitrile (10 ml) and anhydrous ether (20 ml) were added and the resulting solution was left for several hours at 0°C for crystallization of the product. Colorless crystals of **4** were filtered under nitrogen, washed with anhydrous ether and dried in vacuum; yield 4.98 g (91%), mp 174-176°C (dec.). Compound **4** is hygroscopic. After exposure to air the original colorless crystals turn into white, microcrystalline crystallohydrate **4**•$5H_2O$, mp 140-145°C (dec.). For **4**•$5H_2O$: IR (CCl_4): 3383 (br., OH), 3074 (Ar), 2927 (Me), 1615 (C=O), 1337, 1206, 1149, 1039 (OSO_2Me) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOH$, 20:1): δ 8.31 (d, 1H, J = 8 Hz), 8.09 (t, 1H, J = 8 Hz), 8.00 (d, 1H, J = 8 Hz), 7.82 (t, 1H, J = 8 Hz), 2.99 (s, 3H, Me); ^{13}C NMR ($CDCl_3/CF_3COOH$, 20:1): δ 174.6 (C=O), 138.4, 128.7, 126.8, 126.4, 124.9, 120.6 (Ar), 39.2 (Me). Anal: Calc. for $C_8H_{17}ISO_{10}$ (**4**•$5H_2O$): C, 22.23; H, 3.96; I, 29.36. Found: C, 22.23; H, 3.80; I, 29.57.
7. Preparation of **5**: To a stirred mixture of 2-iodosobenzoic acid (3.17 g, 12 mmol) in acetic anhydride (6 ml), TsOH•H_2O (4.56 g, 24 mmol) was added at room temperature. After 5 min stirring a slightly exothermic reaction began and the mixture turned into a clear solution. The solution was additionally stirred for 30 min until a white microcrystalline precipitate formed. Then the reaction mixture was diluted with dry ether (20 ml), the precipitate was filtered, washed with anhydrous ether (3x20 ml) and dried in vacuo to afford analytically pure product **5**; yield 3.9 g (79%), mp 178-180°C (dec.); IR (CCl_4): 3062 (Ar), 2921 (Me), 1610 (C=O), 1341, 1250, 1120, 1027 (OSO_2Tol) cm^{-1}; ^{1}H NMR ($CDCl_3/CF_3COOH$, 20:1): δ 8.30 (d, 1H, J = 8 Hz), 8.09 (t, 1H, J = 8 Hz), 7.94 (d, 1H, J = 8 Hz), 7.80 (t, 1H, J = 8 Hz), 7.71 (d, 2H, J = 8 Hz, *p*-Tol), 7.29 (d, 2H, J = 8 Hz, *p*-Tol), 2.40 (s, 3H, Me); ^{13}C NMR ($CDCl_3/CF_3COOH$, 20:1): δ 174.6 (C=O), 144.0, 138.7, 138.6, 136.2, 129.6, 128.7, 126.3, 126.0, 124.5, 120.6 (Ar), 21.2 (Me). Anal: Calc. for $C_{14}H_{11}ISO_5$: C, 40.21; H, 2.65; I, 30.35. Found: C, 39.95; H, 2.77; I, 30.20. Compound **5** is slightly hygroscopic: its extended exposure to moist air affords white, microcrystalline crystallohydrate **5**•$2H_2O$, mp 169-174°C (dec.).
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