Generation of benzyne from aryl benziodoxaborole triflate under aqueous conditions and its reactions with alkyl aryl sulfides

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Dedicated to Alan R. Katritzky and Charles W. Rees

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Abstract

Mesityl benziodoxaborole triflate is a unique benzyne precursor under aqueous conditions in the presence of NaHCO\textsubscript{3} at room temperature. Reactions of alkyl aryl sulfides with benzyne generated under these conditions selectively afford the corresponding sulfonium salts. In contrast, the previously reported reactions of alkyl aryl sulfides with common benzyne precursors under strongly basic anhydrous conditions lead to various products of cyclization, rearrangement, or elimination but not to sulfonium salts. This very mild procedure can be further extended to the preparation of sulfonium salts from diaryl sulfides, dialkyl sulfides, cyclic alkyl and arylsulfides, as well as a selenonium salt from diphenyl selenide.

Keywords: Hypervalent iodine, benziodoxaborole, benzyne, iodonium salts, sulfonium salts

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**Introduction**

In 1990, A. R. Katritzky and co-workers published a ground-breaking structural study on the cyclic structure of 2-iodosyl and 2-iodylbenzoic acids and their derivatives.\(^1\) Since then, various new hypervalent iodine-oxygen five-membered heterocycles (benziodoxoles) have been synthesized and their utility for organic synthesis has been demonstrated.\(^2\)–\(^5\) In modern organic synthesis, cyclic and pseudocyclic hypervalent iodine compounds are widely used as oxidants and the group-transfer reagents especially useful for arylation, alkynylation, and azidation of organic substrates.\(^5\)–\(^7\) Benziodoxoles in general have greater stability, higher solubility in non-polar solvents, and modified chemical reactivity in comparison with their non-cyclic analogs.\(^2\)–\(^5\) Structures of these compounds are characterized by the presence of a planar iodoxol ring with the I-O distance varying in a broad range: 2.18-2.55 Å for cyclic and 2.55-3.00 Å for pseudocyclic benziodoxoles.\(^5\)

In the course of our search for new five-membered hypervalent iodine heterocycles, in 2017 we reported the preparation of pseudocyclic arylbenziodoxaboroles \(3\) in two steps from commercial 2-iodoboronic acids \(1\) via acetoxybenziodoxaboroles \(2\) (Scheme 1). The pseudocyclic structure of arylbenziodoxaboroles with 2.69-2.71 Å I-O bond distance was confirmed by single crystal X-ray analysis.\(^8\) Furthermore, we have reported unique reactivity of arylbenziodoxaborole \(3b\) as a benzyne precursor that can be triggered under neutral or slightly acidic conditions in aqueous solutions at room temperature.\(^8\) It should be noted that the previously known, common benzyne precursors,\(^9\),\(^10\) such as: aryl halides,\(^11\)–\(^13\) arene-diazonium-2-carboxylates,\(^14\)–\(^16\) 1,2,3-benzothiadiazole 1,1-dioxides,\(^17\) 1-aminobenzotriazole,\(^18\),\(^19\) ortho-silylaryl triflates (Kobayashi’s reagent),\(^20\) diarylodonium salts,\(^21\) and ortho-silyl phenyl iodonium triflate (Kitamura’s reagent),\(^21\),\(^22\) require activation by applying heat, irradiation, strong base (NaNH\(_2\), BuLi, RMgBr, LiHMDS, etc.), or the anhydrous fluoride anion, which is also a strong base and requires special handling to avoid moisture. In contrast, compound \(3b\) can generate the corresponding aryne species by stirring its solution in a dichloromethane/water (9:1) mixture at room temperature.\(^8\),\(^23\) The generated aryne species in aqueous solution can be effectively trapped in the presence of dienes,\(^8\) azides,\(^8\) or organic sulfides.\(^23\) We have also confirmed the formation of aryne from precursor \(3b\) in these reactions by labelling and kinetics experiments.\(^23\) The non-fluorinated precursor \(3a\) has demonstrated lower reactivity compared to \(3b\) and required the presence of NaHCO\(_3\) to activate the reaction.\(^23\)

![Scheme 1. Preparation of pseudocyclic arylbenziodoxaboroles 3.](image-url)
In the present paper, we describe the reactions of benzyne precursor 3a with organic sulfides triggered by water in the presence of NaHCO$_3$ at room temperature and leading to selective formation of various sulfonium salts. This result is sharply different from the previously reported reactions of common benzyne precursors with organic sulfides under anhydrous basic conditions generally leading to various products of cyclization, rearrangement, or elimination but not to sulfonium salts.$^{24,25}$

**Results and Discussion**

Reagent 3a was prepared in gram-scale by a modified, combined procedure based on our previous works.$^{8,26}$ Acetoxybenziodoxaborole 2a was prepared by the hypochlorite oxidation in acetic acid (Scheme 1) and used without purification for conversion to mesityl benziodoxaborole triflate 3a by treatment with mesitylene in the presence of triflic acid (Scheme 1). Compound 3a was isolated in 80% overall yield after 2 steps as a stable colourless solid that can be stored for long time in a refrigerator in the absence of moisture.

We have investigated reactions of various alkyl aryl sulfides 4a-f with reagent 3a in a dichloromethane/water (9:1) mixture in the presence of NaHCO$_3$ at room temperature. All reactions were complete in 3 hours and after simple work-up afforded analytically pure alkyl aryl sulfonium salts 5a-f in excellent yields (Scheme 2). The procedure worked well for the preparation of alkyl sulfonium salts from alkyl phenyl sulfides 4a-d with methyl, ethyl, isopropyl, and cyclopropyl groups, as well as from dibutyl sulfide 4e and tetrahydrothiophene 4f. Noteworthy, the reaction of ethyl phenyl sulfide 4b with aryne generated from reagent 3a in aqueous solution produced sulfonium salt 5b in 84% yield. For comparison, the previously reported similar reaction of ethyl phenyl sulfide with benzyne generated from benzenediazonium-2-carboxylate under anhydrous conditions proceeded with elimination of ethylene leading to the corresponding diphenyl sulfide (Ph$_2$S) in 92% yield.$^{27}$

![Scheme 2. Reactions of reagent 3a with organic sulfides.](image-url)
It is important to note that the reactions of diphenyl sulfide 4g and dibenzothiophene 4h with reagent 3a at room temperature in aqueous solution afforded the corresponding triaryl sulfonium salts 5g and 5h. For comparison, the most common existing approach to triaryl sulfonium salts is based on aryl transfer from diaryliodonium salts to diaryl sulfides at 120-230 °C and usually in the presence of copper catalysts.\textsuperscript{28-31} Preparation of triaryl sulfonium salts in moderate yields using the Kobayashi aryne precursor in acetonitrile (25 °C, 36 h) in the presence of CsF under dry conditions has recently been reported.\textsuperscript{32} Based on the labeling experiments, the authors assumed that the molecule of acetonitrile acted as the source of protons in this reaction.\textsuperscript{32}

The reactions of reagent 3a can be further extended to organic selenides. Reagent 3a reacts with diphenyl selenide 6 in CH\textsubscript{2}Cl\textsubscript{2}-H\textsubscript{2}O (9:1) in the presence of NaHCO\textsubscript{3} to give the corresponding triphenyl selenonium salt 7 in good yield (Scheme 3). Previously reported synthesis of selenonium salt 7 required heating of diphenyl selenide with diphenyliodonium triflate in a chloroform solution in a thick-walled glass tube sealed with a Teflon screwcap maintained at 120 °C for 24 h.\textsuperscript{30}

\begin{align*}
\text{Ph}^\text{Se}^-\text{Ph} &\xrightarrow{\text{reagent 3a (1.2 eq.)}} \text{Ph}^\text{Se}^+\text{OTf}^- \\
6 &\xrightarrow{\text{CH}_2\text{Cl}_2/\text{sat. aq. NaHCO}_3 (9:1), 3 h, rt}} \text{Ph}^\text{Se}^+\text{Ph} \\
&\xrightarrow{7 (70\%)}
\end{align*}

**Scheme 3.** Reaction of reagent 3a with diphenyl selenide.

Based on our previously published studies,\textsuperscript{8,23} we propose a two-step mechanism for the reactions of reagent 3a with organic sulfides and selenide (Scheme 4). At the first step, benzyne is generated by nucleophilic addition of a hydroxide anion (present in the aqueous solution of NaHCO\textsubscript{3}) to the boron atom of reagent 3a, followed by immediate elimination of boronic acid and mesityl iodide. Mesityl iodide (MesI), formed as a by-product in this step, was detected by NMR in the reaction mixture. This step is facilitated by the oxophilic character of the -B(OH)\textsubscript{2} group and by the hypernucleofugic properties of the MesI\textsuperscript{+} moiety in the iodonium salt 3a. At the second step, the addition of sulfide to the benzyne followed by protonation by water molecule gives the final product 5 or 7.

\begin{align*}
\text{MesI}^+ &\xrightarrow{\text{H}_2\text{O, NaHCO}_3, \text{rt}} \text{benzyne} \\
&\xrightarrow{\text{CH}_2\text{Cl}_2} \text{MesI}^- + \text{B(OH)}_3^- + \text{TiO}^- \\
&\xrightarrow{5 \text{ or } 7} \text{X}^+\text{R}^2^-\text{OTf}^- + \text{OH}^{-}
\end{align*}

**Scheme 4.** Mechanism of reactions of reagent 3a with organic sulfides and selenide.
Conclusions

In summary, we have demonstrated that mesityl benziodoxaborole triflate 3a is a unique benzyne precursor under aqueous conditions in the presence of NaHCO₃ at room temperature. Reactions of alkyl aryl sulfides with benzyne generated under these conditions selectively afford the corresponding sulfonium salts, which is in contrast with the previously reported non-selective reactions of sulfides with common benzyne precursors under strongly basic anhydrous conditions. This very mild procedure works well for the preparation of sulfonium salts from alkyl aryl sulfides, diaryl sulfides, cyclopropyl phenyl sulfide, dialkyl sulfides, cyclic alkyl and arylsulfides, as well as selenonium salt from diphenyl selenide.

Experimental Section

General. All reactions were performed under dry argon atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane and acetonitrile were distilled from CaH₂ immediately prior to use. Diethyl ether was distilled from Na/benzophenone. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer. ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra were recorded on a Bruker 400 MHz or JEOL JNM-AL300 NMR spectrometers. Chemical shifts are reported in parts per million (ppm). ¹H and ¹³C chemical shifts are referenced relative to tetramethylsilane.

Preparation of mesityl-1-phenyboronic acid-2-iodonium triflate (3a) from 2-iodophenylboronic acid

A solution of commercial 2-iodophenylboronic acid 1a (620 mg, 2.5 mmol) in acetic acid (6 mL) was cooled to 15 °C, and the commercial bleach solution (6.5 mL of ~5% aqueous NaOCl) was added by small portions (about 0.1 mL each) under stirring. The stirring was continued at rt for overnight. After reaction, the colourless precipitate was filtered, washed with water, hexane, and ether, then dried in vacuum to afford 677.2 mg (89%) of 1-acetoxy-benziodoxaborole 2a, which was used in the next step without purification. The colourless solid was dissolved in dichloromethane (2.2 mL), cooled to 0 °C and TfOH (300.2 mg, 4.43 mmol) was added under stirring. The reaction mixture was stirred at 0 °C for 2 hours, then mesitylene (3.32 mL) was added to the reaction mixture, and stirring was continued overnight at room temperature. After reaction, the solvent was removed under reduced pressure to give an oily product, which was washed with diethyl ether several times then dried in vacuum to give mesityl-1-phenyboronic acid-2-iodonium triflate 3a, 1.037 g (80% yield; 2 steps), as a colourless solid (mp 160.8-164.3 °C). ¹H NMR (CD₂CN): δ 8.09 (d, J 7.6 Hz, 1H), 7.66-7.59 (m, 1H), 7.53-7.42 (m, 2H), 7.36 (s, 2H), 6.83 (d, J 8.4 Hz, 1H), 2.53 (s, 6H), 2.46 (s, 3H).
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate with sulfides or selenide

Sulfide 4 or diphenylselenide 6 (0.1 mmol) was added to a solution of mesityl-1-phenyboronic acid-2-iodonium triflate 3a (0.12 mmol) in a mixture of dichloromethane (0.9 mL) and sat. NaHCO₃ (0.1 mL). The reaction was stirred at room temperature for 3 hours. After reaction, water (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude mixture was washed with diethyl ether several times and then dried in vacuum to give the analytically pure sulfonium triflate 5 or selenonium triflate 7.

**Methyl-diphenylsulfonylum triflate (5a)**

\[
\begin{align*}
\text{Ph} & + \text{S} \quad \text{Me} \quad -\text{OTf}
\end{align*}
\]

Reaction of thioanisole 4a (12.4 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 29.7 mg (85%) of product 5a, isolated as a colourless solid: mp 95.1-96.8 °C (lit. mp 95-96.5 °C); IR (KBr) cm⁻¹ 3098, 3077, 3024, 2938, 1587, 1484, 1255, 1222, 1158, 1029, 635; ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, J 7.2 Hz, 4H), 7.77-7.60 (m, 6H), 3.73 (s, 3H); ¹³C NMR (100 MHz, CD₃CN): δ 134.9, 131.8, 130.5, 126.8, 121.7 (q, ¹J_CF = 318.8 Hz), 28.1; ¹⁹F NMR (376 MHz, CD₃CN): δ -79.3; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₄S ([M-OTf]⁺): 201.0732, found: 207.0731.

**Ethyl-diphenylsulfonylum triflate (5b)**

\[
\begin{align*}
\text{Ph} & + \text{S} \quad \text{Et} \quad -\text{OTf}
\end{align*}
\]

Reaction of ethyl phenyl sulfide 4b (13.8 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 30.7 mg (84%) of product 5b, isolated as a colourless oil; IR (neat) cm⁻¹ 3092, 3065, 2984, 2944, 1582, 1481, 1261, 1225, 1157, 1030, 638; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, J 8.4 Hz, 4H), 7.77-7.62 (m, 6H), 4.28 (q, J 7.2 Hz, 2H), 1.47 (t, J 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 134.7, 131.6, 130.7, 124.1, 120.9 (q, ¹J_CF = 318.5 Hz), 40.3, 9.7; ¹⁹F NMR (376 MHz, CDCl₃): δ -78.2.; HRMS (ESI-TOF-positive mode): calcd for C₁₄H₁₅S ([M-OTf]⁺): 215.0889, found: 215.0891.

**Isopropyl-diphenylsulfonylum triflate (5c)**

\[
\begin{align*}
\text{Ph} & + \text{S} \quad \text{Me} \quad +\text{Me} \quad -\text{OTf}
\end{align*}
\]
Reaction of isopropyl phenyl sulfide 4c (15.2 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 31.4 mg (83%) of product 5c, isolated as a colourless oil; IR (neat) cm⁻¹ 3100, 3066, 2988, 1582, 1260, 1225, 1158, 1030, 637; ¹H NMR (400 MHz, CDCl₃): δ 8.15 (dd, J 8.0 Hz, 1.6 Hz, 4H), 7.79-7.68 (m, 6H), 5.42 (sept, J 6.4 Hz, 1H), 1.52 (d, J 6.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 135.5, 132.1, 131.9, 124.1, 121.8 (q, J_CF = 318.9 Hz), 51.5, 18..; ¹⁹F NMR (376 MHz, CDCl₃): δ -79.2.; HRMS (ESI-TOF-positive mode): calcd for C₁₅H₁₇S ([M-OTf])+: 229.1045, found: 229.1055.

Cyclopropyl-diphenylsulfonium triflate (5d)

Reaction of cyclopropyl phenyl sulfide 4d (15 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 30.7 mg (82%) of product 5d, isolated as a light yellow oil; IR (neat) cm⁻¹ 3145, 3050, 1581, 1480, 1265, 1224, 1157, 1030, 637; ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, J 6.8 Hz, 4H), 7.76-7.62 (m, 6H), 4.03-3.94 (m, 1H), 1.72-1.63 (m, 2H), 1.49-1.41 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 134.4, 131.4, 130.2, 126.5, 120.9 (q, J_CF = 318.7 Hz), 22.5, 8.1; ¹⁹F NMR (376 MHz, CDCl₃): δ -78.2; HRMS (ESI-TOF-positive mode): calcd for C₁₅H₁₅S ([M-OTf])+: 227.0889, found: 227.0882.

Dibutyl-phenylsulfonium triflate (5e)

Reaction of dibutyl sulfide 4e (14.6 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 37.1 mg (100%) of product 5e, isolated as a light yellow oil; IR (neat) cm⁻¹ 3065, 2988, 2878, 1468, 1260, 1225, 1157, 1030, 638; ¹H NMR (400 MHz, CDCl₃): δ 7.94-7.85 (m, 3H), 7.77 (t, J 7.6 Hz, 2H), 3.65-3.49 (m, 4H), 1.67-1.56 (m, 4H), 1.51-1.41 (m, 4H), 0.92 (t, J 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 135.6, 131.8, 121.8 (q, J_CF = 318.9 Hz), 121.7, 44.2, 26.6, 21.5, 13.1. ¹⁹F NMR (376 MHz, CDCl₃): δ -79.3; HRMS (ESI-TOF-positive mode): calcd for C₁₄H₂₃S ([M-OTf])+: 223.1515, found: 223.1519.

1-Phenyltetrahydro-1H-1-thiophenium triflate (5f)

Reaction of tetrahydrothiophene 4f (8.8 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 27.5 mg (88%) of product 5f, isolated as a colourless oil; IR (neat) cm⁻¹ 3061, 2919, 2863, 1448, 1266, 1159, 1026, 637; ¹H NMR (300 MHz, CDCl₃): δ 7.84-7.76 (m, 2H), 7.76-7.63 (m, 3H), 4.34-4.19 (m, 2H), 3.76-3.61 (m, 2H), 2.64-2.52 (s, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 134.5, 131.6, 129.9, 126.4, 120.9 (q, J_CF
= 318.5 Hz), 48.8, 29.3; $^{19}$F NMR (376 MHz, CD$_3$CN): $\delta$ -79.3; HRMS (ESI-TOF-positive mode): calcd for C$_{10}$H$_{13}$S ([M-OTf])$^+$: 165.0732, found: 165.0725.

**Triphenylsulfonium triflate (5g)$^{30}$**

\[ \begin{array}{c}
\text{Ph}^{-} \quad \text{S}^{-} \quad \text{OTf}^+
\end{array} \]

Reaction of diphenyl sulfide 4g (18.6 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 39.1 mg (95%) of product 5g, isolated as a colourless solid: mp 132.1-133.6 °C (lit. mp 133-136 °C); $^{30}$ IR (KBr) cm$^{-1}$ 3090, 3063, 1581, 1477, 1275, 1225, 1155, 1030, 636; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80-7.65 (m, 15H); $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ 135.3, 132.1, 131.7, 125.1, 121.8 (q, $^1$J$_{CF}$ = 319.1 Hz); $^{19}$F NMR (376 MHz, CD$_3$CN): $\delta$ -79.2; HRMS (ESI-TOF-positive mode): calcd for C$_{18}$H$_{15}$S ([M-OTf])$^+$: 263.0889, found: 263.0882.

**5-Phenyl-5H-dibenzo[b,d]thiophen-5-ium triflate (5h)$^{39}$**

\[ \begin{array}{c}
\text{Ph}^{-} \quad \text{S}^{-} \quad \text{OTf}^+
\end{array} \]

Reaction of dibenzothiophene 4h (18.4 mg, 0.1 mmol) and 3a (61.9 mg, 0.2 mmol) according to the general procedure afforded 16.7 mg (41%) of product 5h, isolated as a colourless solid: mp 187.0-188.1 °C (lit. mp 187-188 °C); $^{39}$ IR (KBr) cm$^{-1}$ 3027, 2921, 2851, 1636, 1574, 1463, 1269, 1154, 1030, 636; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (d, $^1$J = 8.0 Hz, 2H), 8.15 (d, $^1$J = 7.6 Hz, 2H), 7.91-7.83 (m, 2H), 7.76-7.62 (m, 5H), 7.59-7.50 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.0, 134.9, 134.3, 132.1, 131.8, 131.6, 130.8, 128.9, 126.6, 123.9, 120.8 ($^1$J$_{CF}$ = 318.9 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -78.2; HRMS (ESI-TOF-positive mode): calcd for C$_{18}$H$_{13}$S ([M-OTf])$^+$: 261.0732, found: 261.0728.

**Triphenylselenonium triflate (7)$^{30}$**

\[ \begin{array}{c}
\text{Ph}^{-} \quad \text{Se}^{-} \quad \text{OTf}^+
\end{array} \]

Reaction of diphenyl selenide 6 (23.3 mg, 0.1 mmol) and 3a (61.9 mg, 0.12 mmol) according to the general procedure afforded 32.3 mg (70%) of product 7, isolated as a light yellow oil; IR (neat) cm$^{-1}$ 3088, 3062, 2950, 2875, 1573, 1479, 1261, 1224, 1029, 636; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74-7.69 (m, 3H), 7.67-7.59 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 133.8, 131.7, 131.2, 126.3, 120.8 ($^1$J$_{CF}$ = 318.7 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -78.2; HRMS (ESI-TOF-positive mode): calcd for C$_{18}$H$_{13}$S ([M-OTf])$^+$: 311.0333, found: 311.0327.
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Supplementary Material

NMR spectra of compounds are provided in the supplementary material file associated with this manuscript.

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