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Synthesis and reactivity study of 4-aryliodonium substituted arylboronic acids as potential *para*-benzyne precursors

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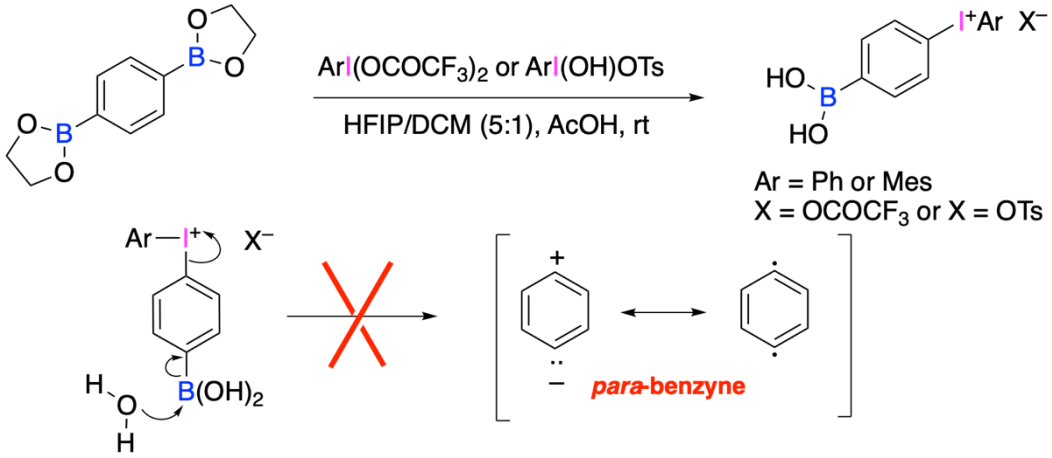
Abstract

General synthetic approach to novel 4-aryliodonium–substituted arylboronic acids as potential *para*-benzyne precursors is reported. 4-Phenyiodonium–substituted arylboronic acids were prepared by reacting ethylene glycol ester of *para*-phenylenediboronic acid with $PhI(OCOCF_3)_2$ or PhI(OH)OTs, which simultaneously effected *in situ* deprotection. The reactivity of these iodonium salts as *para*-benzyne precursors in reactions with Ph_2S under various conditions was evaluated; however, no reaction occurred, and the starting materials were recovered quantitatively. This result demonstrates that 4-iodonium-substituted arylboronic acids cannot serve as *para*-benzyne precursors under mild aqueous conditions, and neither the identity of the anion (TsO^- or $CF_3CO_2^-$) nor the aryl substituent (Ph or Mes) significantly influences their reactivity. Finally, the product distributions observed in the reactions of 4-aryliodonium–substituted arylboronic acids with sodium azide and potassium thiocyanate are in good agreement with previously reported nucleophilic aromatic substitution reactions of *para*-triisopropylsilyl-substituted diaryliodonium salts.



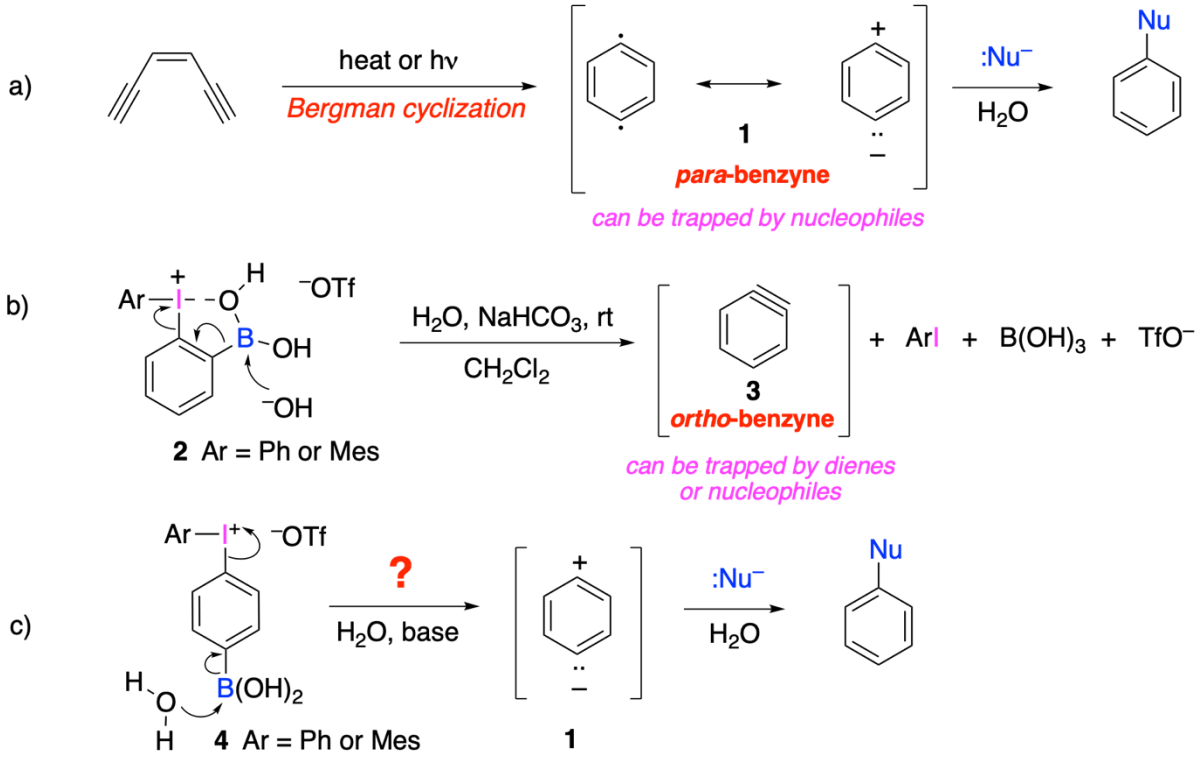
Keywords: Hypervalent iodine, iodonium salts, iodonium, *para*-benzyne

Introduction

In contrast to well-known *ortho*-benzyne intermediates, the isomeric *para*-benzyne has been far less-investigated.[1-8] *para*-Benzyne **1** was proposed as the reactive intermediate in the classic Bergman cyclization of enediynes (Scheme 1a);[1,2] a process responsible for the anticancer activity of natural products such as calicheamicin.[2] *para*-Benzynes generated from enediynes are also known to react with nucleophiles (e.g., LiCl, LiBr, and LiI) in the presence of carboxylic acid to yield the respective products of electrophilic arylation.[3-6] *para*-Benzyne **1** can also be generated in the gas phase starting from *p*-dinitrobenzene derivatives.[7,8]

In principle, *para*-benzynes should also be accessible in solution using appropriate precursors, analogous to common *ortho*-benzyne intermediates. Recently, we reported very mild and highly efficient *ortho*-benzyne (**3**) precursors, *ortho*-aryliodonium-substituted arylboronic acids **2**, that can be triggered by water at room temperature (Scheme 1b).[9-11] Reagents **2** can be synthesized on a gram scale in a straightforward sequence starting from commercially available arylboronic acids.[9,10]

Herein, we report the preparation and reactivity of the analogous *para*-benzyne precursors, *para*-aryliodonium-substituted arylboronic acids **4** (Scheme 1c). We anticipated that *p*-benzyne species generated from precursors **4** would act as efficient electrophilic arylating reagents toward various nucleophiles, yielding the respective products of aromatic nucleophilic substitution (Scheme 1c), analogous to *p*-benzyne generated from enediynes.[3-6] Although several examples of pinacol esters of *para*-aryliodonium-substituted arylboronic acids **4** were previously reported by Kita's group, the unprotected boronic acids **4** remain unknown.[12]

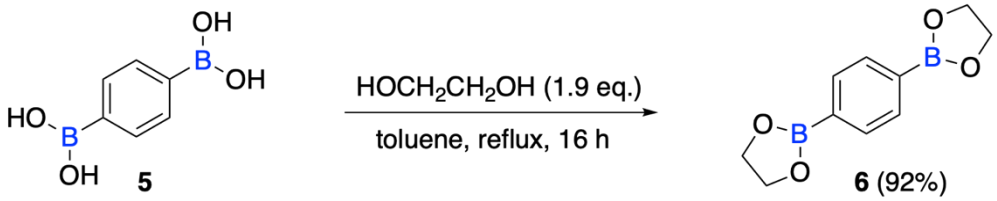


Scheme 1. (a) Generation of *para*-benzyne **1** from enediynes by Bergman cyclization, (b) our approach to *ortho*-benzyne **3** from precursor **2**, and (c) hypothetical generation of *para*-benzyne from *para*-aryliodonium-substituted arylboronic acids **4**

Results and Discussion

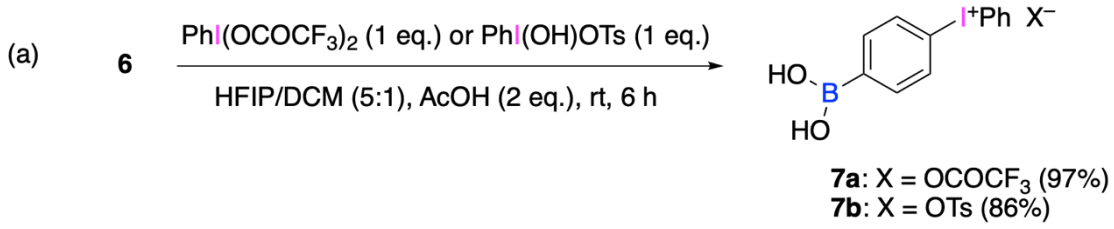
Synthesis of *para*-aryliodonium-substituted arylboronic acids **4** is a challenging goal because hypervalent iodine compounds are highly reactive with arylboronic acids; consequently, the unprotected -$B(OH)_2$ group is generally incompatible with an iodine(III) substituent. In our initial attempts, we evaluated the oxidation of *p*-iodobenzeneboronic acid, analogous to the synthesis of *ortho*-aryliodonium-substituted arylboronic acids **2**.[9,10] Unfortunately, attempts to oxidize *p*-iodobenzeneboronic acid or its pinacol ester using various oxidants (bleach, $NaIO_4$, mCPBA, peracetic acid, sodium perborate, or Oxone) resulted in partial or complete decomposition.

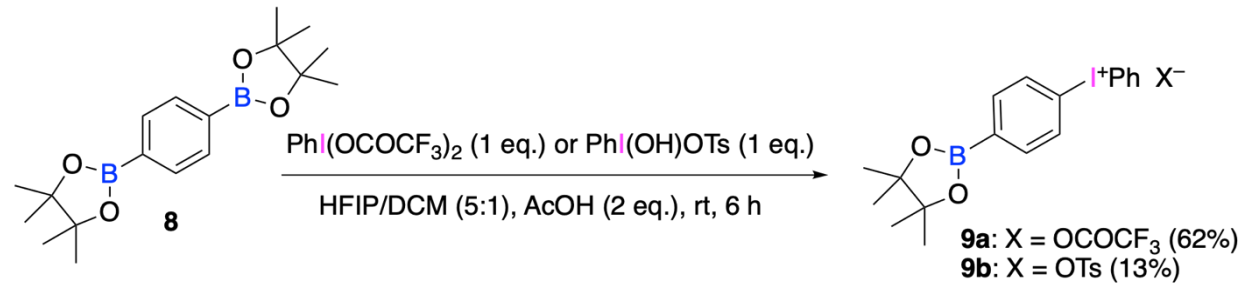
Next, we investigated an alternative approach to *para*-aryliodonium-substituted arylboronic acids **4** starting from the commercially available *para*-phenylenediboronic acid **5**. Direct reaction of diboronic acid **5** with hypervalent iodine reagents [bis(trifluoroacetoxy)iodo]benzene or [hydroxy(tosyloxy)iodo]benzene was unsuccessful, leading to decomposition of the reaction mixture. Therefore, we converted *p*-phenylenediboronic acid into the protected derivative **6** by treatment with ethylene glycol in boiling toluene (Scheme 2).



Scheme 2. Preparation of ethylene glycol ester of *p*-phenylenediboronic acid.

The ethylene glycol ester **6** was further reacted with the appropriate hypervalent iodine reagent directly yielding deprotected arylboronic acids as aryliodonium trifluroacetate **7a** or tosylate **7b** (Scheme 3a). Previously, Kita's group reported a similar reaction using the pinacol ester of *para*-phenylenediboronic acid **8** to yield the corresponding iodonium salts **9a,b** (Scheme 3b).[12] In contrast to Kita's findings, the reaction of ethylene glycol ester **6** with hypervalent iodine reagents was accompanied by *in situ* deprotection. Iodonium salts **7a,b** were isolated as stable, microcrystalline products and characterized by NMR spectroscopy and HRMS analysis.



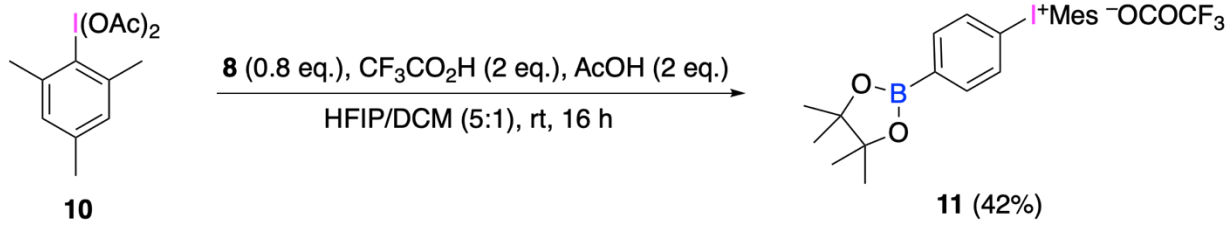


Scheme 3. (a) Our preparation of *para*-aryliodonium-substituted arylboronic acids **7a,b**; (b) Previously reported reaction of pinacol ester of *p*-phenylenediboronic acid **8** with hypervalent iodine reagents.[12]

Next, we investigated the reactivity of *para*-aryliodonium-substituted arylboronic acids **7a,b** as potential *para*-benzyne precursors analogous to reagent **2** as shown in Scheme 1c. Previously, we reported a very mild and selective reaction of benzyne precursor **2** with diarylsulfides Ar_2S, leadind to triarylsulfonium salts $Ar_3S^+ X^-$ in excellent yields.[10] We tested the reactions of compounds **7** with Ph_2S in the absence of a base and in the presence of $NaHCO_3$ or Na_2CO_3 in acetonitrile or dichloromethane, both at room temperature and under reflux. However, no reaction was observed under these conditions, and starting materials **7** were recovered unchanged from the reaction mixture.

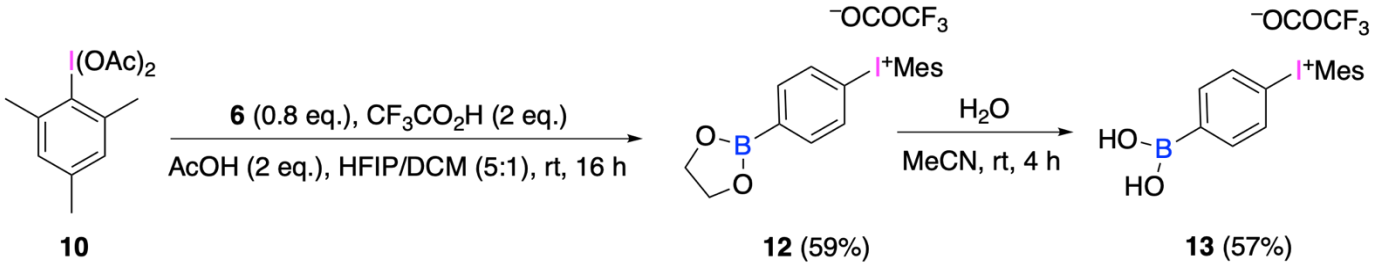
In our previous work, we found that mesityl-substituted triflate salts **2** (Ar = Mes) were the most reactive benzyne precursors.[10] We attempted to convert the trifluoroacetate and tosylate salts into the corresponding triflate by treatment with triflic acid or triflate salts, but these attempts were unsuccessful. Consequently, we sought to prepare mesityl-substituted aryliodonium salts.

To synthesize mesityl-substituted aryliodonium salts, we adapted the procedure reported by Kita and co-workers as shown in Scheme 3b.[12] Mesityl(iodo)diacetate **10** was prepared according to a known literature procedure[13] and subsequently reacted with commercially available *para*-phenylenediboronic acid pinacol ester **8** to give mesityl-substituted iodonium salt **11** (Scheme 4). We tested the reactivity of iodonium salt **11** as potential *para*-benzyne precursor in the reaction with Ph_2S under different conditions; however, no reaction was observed, and starting materials were recovered unchanged from the reaction mixture. Our attempts to remove the pinacol ester protection from iodonium salt **11** by treatment with water under acidic conditions were also unsuccessful.



Scheme 4. Preparation of mesityl-substituted trifluoroacetate iodonium salt **11**.

Following the successful synthesis of mesityl-substituted iodonium salt **11**, the preparation of deprotected *para*-aryliodonium-substituted arylboronic acid **13** (Scheme 5) was pursued. Synthesis of this salt followed the same general route as that for the 4-phenyliodonium-substituted arylboronic acids outlined in Scheme 3a, with the appropriate adjustments to incorporate the mesitylene moiety. Unexpectedly, when synthesizing salt **12** bearing a mesitylene dummy group rather than a phenyl ring, the ethylene glycol boronic ester remained intact throughout the reaction and standard workup, affording salt **12** in 59% yield. Subsequent treatment of iodonium salt **12** with an acetonitrile/water mixture yielded the deprotected salt **13** in 57% yield. The lower reactivity of the mesityliodonium salt toward hydrolysis compared to the phenyliodonium analogue is likely attributable to the electron-donating effect of the three methyl groups in **12**.



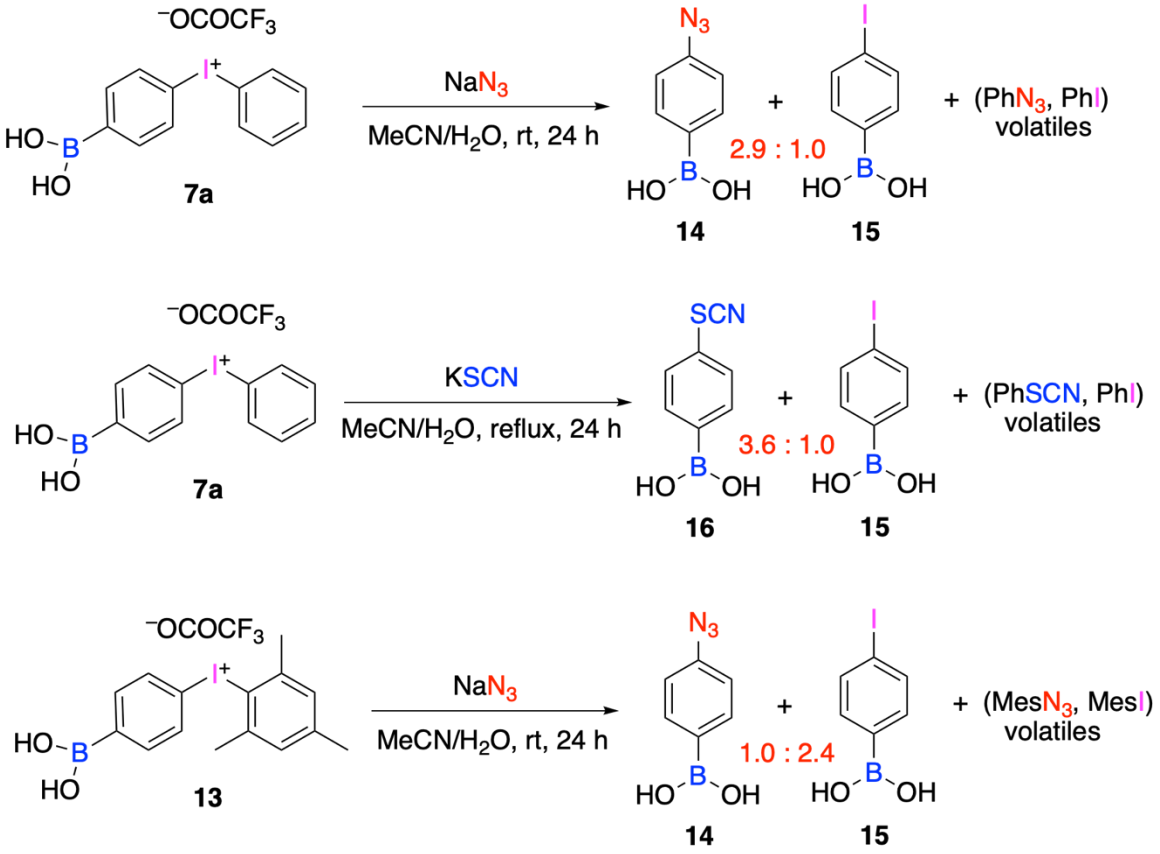
Scheme 5. Preparation of deprotected *para*-aryliodonium-substituted arylboronic acid **13**.

Similar to the other proposed *para*-benzyne precursors, the reaction between iodonium salt **13** and diphenyl sulfide did not proceed to give the desired triphenylsulfonium salt. Although discouraging, this result demonstrates that neither the identity of the anion (TsO^- or $CF_3CO_2^-$) nor the aryl sybstituent (Ph or Mes) significantly influences the ability of 4-iodonium–substituted arylboronic acids to form *para*-benzyne under these conditions. Consequently, stronger nucleophiles (e.g., azide and thiocyanate ions) were investigated in arylation reactions using these potential *para*-benzyne precursors.

Previously, the nucleophilic aromatic substitution reactions of *para*-triisopropylsilyl–substituted diaryliodonium salts with azide and thiocyanate ions as nucleophiles were investigated.[14] In particular, it was found that diaryliodonium triflate, 4-TIPS-C_6H_4IPhOTf, reacts with NaN_3 in boiling acetonitrile to yield 4-TIPS-$C_6H_4N_3$ and 4-TIPS-C_6H_4I in a 2.6 : 1.0 ratio (determined by ^{1}H NMR), along with volatile PhN_3 and PhI. A similar reaction of 4-TIPS-C_6H_4IPhOTf with KSCN afforded 4-TIPS-C_6H_4SCN and 4-TIPS-C_6H_4I in a 2.8 : 1.0 ratio.

We have found that the reaction of phenyliodonium salt **7a** with sodium azide proceeds in aqueous acetonitrile at room temperature, yielding a mixture of 4-azidoboronic acid **14** and 4-iodoboronic acid **15** in a 2.9: 1.0 ratio based on ^{1}H NMR analysis, alongside with volatile PhN_3 and PhI (Scheme 6). Under identical conditions, the reaction of mesityliodonium salt **13** with sodium azide gives a mixture of 4-azidophenylboronic acid **14** and 4-iodophenylboronic acid **15** in a 1.0 : 2.4 ratio. Similarly, the reaction of phenyliodonium salt **7a** with KSCN in aqueous acetonitrile under reflux yields 4-thiocyanatophenylboronic acid **16** and 4-

iodophenylboronic acid **15** in a 3.6 : 1.0 ratio based on ^{1}H NMR analysis, along with volatile PhSCN and PhI. (Scheme 6).



Scheme 6. Reactions of iodonium salts **7a,b** and **13** with nucleophiles.

These results indicate that the boronic acid moiety remains unchanged in the product, thereby ruling out the *para*-benzyne mechanism shown in Scheme 1c. The product distribution observed in the reactions of phenyliodonium salt **7a** with sodium azide and potassium thiocyanate is in good agreement with previously reported nucleophilic aromatic substitution reactions of *para*-triisopropylsilyl-substituted diaryliodonium salts with azide and thiocyanate ions.[14] The change in product ratio for the reaction of mesityliodonium salt **13** with sodium azide can be attributed to the effect of the bulkiness of mesityl group on the transition state in the nucleophilic aromatic substitution mechanism (the so-called ortho-effect[15]). According to literature data, in non-symmetrical diaryliodonium salts, the anion preferentially attacks the aryl ring in which the ortho methyl group is present giving product compositions opposite of those expected from nucleophilic aromatic substitution.[15,16]

Conclusions

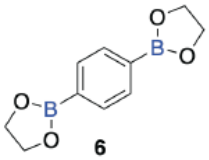
In summary, we have developed a general synthetic approach to novel 4-aryliodonium–substituted arylboronic acids as potential *para*-benzyne precursors. The deprotected arylboronic acids in the form of aryliodonium salts **7a,b** and **13** were prepared by reacting ethylene glycol ester **6** with the appropriate hypervalent iodine reagents, which simultaneously effected deprotection. We evaluated the reactivity of these iodonium salts as *para*-benzyne precursors in reactions with Ph_2S under various conditions; however, no

reaction occurred, and the starting materials were recovered quantitatively. This result demonstrates that 4-iodonium-substituted arylboronic acids cannot serve as *para*-benzyne precursors under mild aqueous conditions, and neither the identity of the anion (TsO^- or $CF_3CO_2^-$) nor the aryl substituent (Ph or Mes) significantly influences their reactivity. Finally, the product distributions observed in the reactions of phenyliodonium salt **7a** with sodium azide and potassium thiocyanate are in good agreement with previously reported nucleophilic aromatic substitution reactions of *para*-triisopropylsilyl-substituted diaryliodonium salts.

Experimental Section

General. The reactions requiring an inert atmosphere were conducted under argon atmosphere using standard Schlenk line techniques and oven-dried glassware. The chemicals and solvents utilized in this study were purchased from Sigma-Aldrich, Fisher, Alfa-Asear, or AmBeed and were used as received. Anhydrous solvents were obtained by distillation over calcium hydride before use unless otherwise stated. Chromatographic materials were purchased from SiliCycle or Sigma-Aldrich. NMR spectra were recorded using a Bruker 400 MHz NMR spectrophotometer (^{1}H NMR and ^{13}C NMR). Chemical shifts are reported in parts per million (ppm). Coupling constants were quoted in Hz (*J*). ^{1}H NMR spectroscopy splitting patterns were designated as singlet (s), doublet (d), or triplet (t). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m). ESI mass spectra were recorded on a Bruker MicroTOF-III mass spectrometer using anhydrous acetonitrile. Meting points were determined in an open capillary tube with a Mel-temp II melting point apparatus.

2,2'-(1,4-Phenylene)bis(1,3,2-dioxaborolane) 6[17]



6

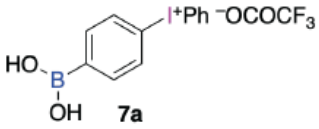
Ethylene glycol (0.950 mL, 17 mmol, 1.9 eq.) was added to a solution of 1,4-phenylenediboronic acid (1.49 g, 9 mmol) in 40 mL toluene. The reaction was refluxed with a Dean-Stark apparatus for 16 hours. Upon completion, the mixture is cooled to room temperature and toluene was removed using a rotary evaporator, and the remaining solid was washed with 50 mL dichloromethane and filtered to leave behind unreacted boronic acid. The filtrate is separated and solvent is removed under vacuum, leaving analytically pure product **6** as a white solid, yield 1.81 g (92%); mp: 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 4H), 4.38 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 66.2, B-*C* not observed due to quadrupolar relaxation effect. ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.75 ppm. GC-MS (EI): calcd for $C_{10}H_{12}B_2O_4$ $[M]^+$: 217.81, found 217.84

General procedure for synthesis of (4-phenylboronic acid)phenyliodonium salts 7a,b

2,2'-(1,4-phenylene)bis(1,3,2-dioxaborolane) **6** (326 mg, 1.5 mmol) was added to a mixture of 7.5 mL hexafluoroisopropanol and 1.5 mL dichloromethane. Upon complete dissolution, acetic acid (0.170 mL, 2 eq.) and hypervalent iodine reagent (1.5 mmol, 1 eq.) were added sequentially. The mixture was allowed to stir at

room temperature for 6 hours. After which, methanol (2-3 mL) was added to the mixture. Solvent was removed under reduced pressure, leaving behind a yellow-orange oily substance. Diethyl ether (5 mL) was added to induce precipitation. The mixture is filtered and washed with additional diethyl ether to yield salts **7a,b**. In some cases, the mixture must be triturated with diethyl ether for up to several hours to induce precipitation.

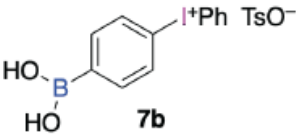
(4-Phenylboronic acid)phenyliodonium trifluoroacetate 7a



7a

General procedure was followed with [bis(trifluoroacetoxy)iodo]benzene (645 mg, 1 eq.) as the hypervalent iodine reagent to yield 637 mg (97%) of **7a** as a white solid; mp: 132-135 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (s, 2H), 8.24-8.19 (m, 4H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H) 7.53 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.9, 135.1, 134.0, 132.0, 131.7, 118.5, 116.5, *C*-B and F_3CCOO^- not observed. ^{19}F NMR (386 MHz, DMSO-d_6): δ -73.44. HRMS (ESI): calcd for $C_{12}H_{11}BIO_2^+$ [M-$OCOCF_3$]$^+$: 324.9296, found 325.0078.

(4-Phenylboronic acid)phenyliodonium tosylate 7b



7b

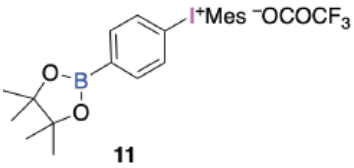
General procedure was followed with hydroxy(tosyloxy)iodobenzene (588 mg, 1 eq.) as the hypervalent iodine reagent to yield 640 mg (86%) of **7b** as a white solid ; mp: 145-149 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.39 (s, 2H), 8.27-8.17 (m, 4H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.7, 136.9, 135.2, 134.1, 133.0, 132.0, 131.7, 128.1, 125.5, 118.5, 116.4, 20.8, B-*C* not observed, remaining not observed or hidden. HRMS (ESI): calcd for $C_{12}H_{11}BIO_2^+$ [M-OTs]$^+$: 324.9296, found 325.0022.

General procedure for synthesis of mesityl iodonium salts 11 and 12

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (247 mg, 0.75 mmol) (synthesis of **11)** or 2,2'-(1,4-phenylene)bis(1,3,2-dioxaborolane) (163 mg, 0.75 mmol) (synthesis of **12**) was added to a mixture of hexafluoroisopropanol (5 mL) and dichloromethane (1 mL). Upon complete dissolution, glacial acetic acid (0.085 mL, 1.5 mmol, 2 eq.), trifluoroacetic acid (0.105 mL, 1.5 mmol, 2 eq.), and 2-(diacetoxyiodo)mesitylene (364 mg, 1 mmol, 1.33 eq.) were added sequentially. The reaction mixture rapidly changes color from bright teal to a pale golden color over the course of a few minutes and is allowed to stir for 16 hours at room temperature. Upon completion, methanol (1 mL) was added, and the volatiles were removed under reduced

pressure to yield an orange oily substance. Diethyl ether was added to induce precipitation; the residue was triturated for several minutes to several hours before filtering and washing with diethyl ether and drying in vacuo for several hours.

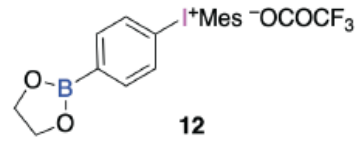
Mesityl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)iodonium trifluoroacetate 11



11

General procedure was followed with 1,4-bis(4,4,5,5-tetramethyl-1,3,22-dioxaborolan-2-yl)benzene (247 mg, 0.75 mmol) to yield 177 mg (42%) of compound **11** as a white solid. mp: 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.07 (s, 2H), 2.61 (s, 6H), 2.33 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 141.9, 137.9, 131.5, 130.2, 84.5, 27.0, 24.8, 21.0. *C*-B not observed due to quadrupolar relaxation effect, others hidden/not observed. ^{19}F NMR (386 MHz, $CDCl_3$): δ -75.8. HRMS (ESI): calcd for $C_{21}H_{27}BIO_2^+$ $[M\text{-}OCOCF_3]^+$: 449.1493, found 449.1153.

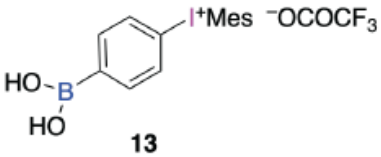
(4-Phenylboronic acid)(mesityl)iodonium trifluoroacetate 12



12

General procedure was followed with 1,4-bis(1,3,2-dioxaborolane)benzene (163 mg, 0.75 mmol) to yield 223 mg (59%) of compound **12** as a white solid, mp: 106-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.05 (s, 2H), 4.35 (s, 4H), 2.60 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.1, 137.8, 131.9, 130.1, 122.6, 118.2, 66.3, 27.0, 21.0. ^{19}F NMR (386 MHz, $CDCl_3$): δ -75.7. HRMS (ESI): calcd for $C_{17}H_{19}BIO_2^+$ $[M\text{-}OCOCF_3]^+$: 393.0448, found: 393.0485

(4-(1,3,2-Dioxaborolan-2-yl)phenyl)(mesityl)iodonium trifluoroacetate 13



13

General procedure was followed with 1,4-bis(1,3,2-dioxaborolane)benzene (163 mg, 0.75 mmol). After filtration, the white solid was collected and dissolved in 5 mL of acetonitrile and 1 mL distilled H_2O and stirred at room temp for 4 hours. The solvent was removed under reduced pressure, and the residue was triturated in diethyl ether for 3 hours, filtered, washed with diethyl ether, and dried in vacuo overnight to yield 205 mg

(57%) of compound **13** as a white solid, mp: 96-98 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.44 (s, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 2.59 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.0, 141.5, 137.0, 133.4, 129.7, 122.5, 116.7, 26.3, 20.5. ^{19}F NMR (386 MHz, DMSO-d_6): δ -73.5. HRMS (ESI): calcd for $C_{15}H_{17}BIO_2^+$ [M-OCOCF$_3$]$^+$: 367.0078, found: 367.0299.

Reaction of (4-phenylboronic acid)phenyliodonium trifluoroacetate 7a with NaN_3

Compound **7a** (36 mg, 0.082 mmol) and sodium azide (40 mg, 0.615 mmol) were added to a mixture of acetonitrile (5 mL) and water (0.5 mL) and stirred for 24 hours at room temperature. After completion, the reaction mixture was partitioned between ethyl acetate (7 mL) and water (3 mL). The organic layer was separated, washed with brine (3 mL), dried with Na_2SO_4, and solvent was removed under reduced pressure to yield 13 mg of inseparable mixture $(HO)_2B$-C_6H_4-N_3 **14** and $(HO)_2B$-C_6H_4-I **15** as a light brown oil in 2.9:1 ratio. According to ^{1}H NMR, the yield of **14** is 64%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.07 (s, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.0, 135.9, 118.1, *C*-B not observed. GC-MS (EI): calcd for $C_6H_6BN_3O_2$ [M]$^+$: 163.06, found 163.07.

Reaction of (4-phenylboronic acid)phenyliodonium trifluoroacetate 7a with KSCN

Compound **7a** (34 mg, 0.077 mmol) and potassium thiocyanate (41 mg, 0.421 mmol) were added to a mixture of acetonitrile (5 mL) and water (0.5 mL) and refluxed for 24 hours. After completion, the reaction mixture was partitioned between ethyl acetate (7 mL) and water (3 mL). The organic layer was separated, washed with brine (3 mL), dried with Na_2SO_4, and volatiles were removed under reduced pressure, leaving behind 11 mg of mixture $(HO)_2B$-C_6H_4-SCN **16** and $(HO)_2B$-C_6H_4-I **15** in a 3.6:1 ratio. These two were separated from each other by PTLC (petroleum ether:ethyl acetate:acetonitrile = 47.5:47.5:5) on silica gel to afford 8 mg (55%) of pure **16** as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 (s, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): 135.8, 128.6, 126.3, 111.2, 62.7. GC-MS (EI): calcd for $C_7H_6BNO_2S$ [M]$^+$: 179.02, found 179.02.

Reaction of (4-phenylboronic acid)(mesityl)iodonium trifluoroacetate 13 with NaN_3

Compound **13** (22 mg, 0.046 mmol) and sodium azide (30 mg, 0.461 mmol) were added to a mixture of acetonitrile (5 mL) and water (0.5 mL) in a round bottomed flask and stirred for 24 hours at room temperature. After completion, the reaction mixture was partitioned between ethyl acetate (7 mL) and water (3 mL). The organic layer was separated, washed with brine (3 mL), dried with Na_2SO_4, and volatiles were removed under reduced pressure, and the residue was washed twice with a 1-2 mL of cold CH_2Cl_2 to yield 9 mg of inseparable mixture $(HO)_2B$-C_6H_4-N_3 **14** and $(HO)_2B$-C_6H_4-I **15** as a light brown oily substance. According to ^{1}H NMR the ratio is 1.0 : 2.4, and the yield of **14** is 26%. The spectral data agrees with the data provided above.

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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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