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Preparation and structure of phenolic arylodonium salts†

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Phenol based arylodonium salts were prepared by the reaction of [hydroxy(tosyloxy)iodo]arenes with aryl silyl ethers in the presence of trifluoromethanesulfonic acid. Structures of several arylodonium salts with the hydroxy group in the *para*-position of the phenyl ring were established by single crystal X-ray crystallography. Under basic conditions, 4-hydroxyphenyl(phenyl)iodonium salts form a dimeric hypervalent iodine(III) complex, oxyphenyl(phenyl)iodonium ylidic salt, the solid structure of which was confirmed by X-ray crystallography. Phenolic iodonium salts are potentially useful phenol transfer reagents in reactions with various anionic nucleophiles.

In recent years, organohypervalent iodine compounds have found a broad range of applications in organic chemistry because of their environmentally benign nature, oxidative ability similar to heavy metal oxidants, and the reactivity pattern similar to transition metals.^{1–5} Diaryliodonium salts belong to a particularly important class of organohypervalent iodine(III) compounds, which have numerous synthetic applications under metal or metal-free conditions.^{6–8} Symmetrical or unsymmetrical diaryliodonium salts are effective electrophilic arylating reagents whose reactions with various organic nucleophilic substrates involve oxidative transfer of aryl groups resulting in the formation of new aryl–carbon atom bonds, aryl–heteroatom bonds, and aryl–radioactive isotope bonds. Diaryliodonium salts can also serve as efficient benzyne precursors under appropriate conditions.^{9–11} In particular,

reactions of diaryliodonium salts with various substrates under strongly basic conditions produce the corresponding benzyne adducts.^{12–14} Recently, diaryliodonium compounds with silyl or boron-containing substituents have been developed and used as efficient precursors to reactive species.^{15–17} For example, Kitamura and co-workers reported the preparation and reactivity of [2,5-bis(trimethylsilyl)-4-(triflyloxy)phenyl](phenyl)iodonium triflate, which could be used as the 1,4-benzdiyne equivalent in the presence of a fluoride source.¹⁵ Legault's group has reported zwitterionic iodonium trifluoroborates which react with phenols under basic conditions forming the corresponding arylation products containing a trifluoroborate group in the aryl group.¹⁶ Our group has reported the preparation and structural investigation of novel benzyne precursors, pseudocyclic arylbenziodoxaborole triflates, which could react with various substrates in the presence of water to give the respective benzyne adducts in moderate to good yields.¹⁷ Despite significant current interest in functionalized diaryliodonium compounds, only few examples of phenol-derived arylodonium salts have been reported.^{18–22} Moreover, most of these examples deal with the *ortho*-hydroxy substituted diaryliodonium salts, which are important precursors to phenolic iodonium ylides. To the best of our knowledge, only a single example of the *para*-hydroxy substituted diaryliodonium salt was reported in the literature,¹⁸ and general synthetic procedures for the preparation of phenolic iodonium salts have been not established.

Herein, we report a straightforward one-pot synthesis and structural investigation of *para*-hydroxy substituted diaryliodonium salts, which can be prepared starting from the corresponding hypervalent iodine(III) reagents and triisopropylsiloxybenzene in the presence of trifluoromethanesulfonic acid. The obtained *para*-hydroxyphenyl(phenyl)iodonium bromide under basic conditions can be converted into a novel dimeric hypervalent iodine(III) complex, oxyphenyl(phenyl)iodonium ylidic salt, the solid structure of which was confirmed by X-ray crystallography.

Our approach to the one-pot synthesis of hydroxyphenyl(aryl)-iodonium salts is based on the reaction of various hypervalent iodine(III) reagents with phenyl silyl ethers involving the initial

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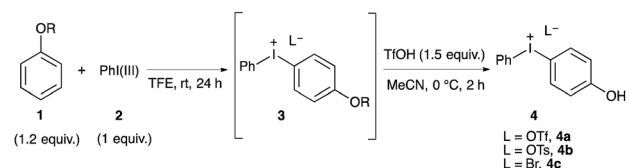
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Table 1 Optimization of preparation of 4-hydroxyphenyl(phenyl)iodonium salts **4a**^a


Entry	1/R	2/PhI(III)	4 ^b (%)
1	1a /TIPS	2a /PhI(OH)OTs	(3a 87%) ^c
2	1a	2a	4a 97%
3	1b /TBDMS	2a	4a 83%
4	1c /TBDPS	2a	4a 65%
5	1d /TMS	2a	— ^d
6	1e /H	2a	— ^d
7	1a	2b /PhI(OAc) ₂	4a 22%
8	1a	2c /PhI(OCOCF ₃) ₂	4a 96%
9	1a	2d /PhIO	4a 32%
10 ^e	1a	2a	4a 35%
11 ^f	1a	2a	4b 86%
12 ^g	1a	2a	4c 83%

^a All reactions were performed using substrate **1** (1.2 equiv.) and hypervalent iodine reagent **2** (1 equiv.) in 2,2,2-trifluoroethanol at room temperature for 24 hours. The reaction mixture was evaporated and then TfOH (1.5 equiv.) was added to the reaction mixture in acetonitrile solution and stirred at 0 °C for 2 hours. ^b Yields of isolated products. ^c No TfOH added in the reaction mixture and isolated as **3a** (R = TIPS; L = OTs). ^d Complex mixture. ^e TfOH (1.5 equiv.) was added from the beginning. ^f *p*-TsOH·H₂O (3.0 equiv.) was used instead of TfOH and stirred for 24 hours. ^g KBr (10.0 equiv.) was added to the reaction mixture and stirred for 2 hours.

formation of silyloxyphenyl(aryl)iodonium salts followed by desilylation of the intermediate product in the presence of trifluoromethanesulfonic acid (TfOH) to produce the desired hydroxyphenyl(aryl)iodonium salts. In our initial experiment, the reaction of Koser's reagent **2a** and triisopropylsiloxybenzene **1a** in 2,2,2-trifluoroethanol (TFE) gave the 4-triisopropylsiloxyphenyl(phenyl)iodonium tosylate **3a** (R = TIPS; L = OTs) in 87% yield (Table 1, entry 1). Without purification, the initial compound **3** was transformed to the desired 4-hydroxyphenyl(phenyl)iodonium triflate **4a** in 97% yield *via* treatment with TfOH in acetonitrile at 0 °C (entry 2). The structure of **4a** was confirmed by NMR, elemental analysis, and high-resolution ESI mass spectrometry. Reactions of other phenyl silyl ethers protected with a *tert*-butyldimethylsilyl (TBDMS) group **1b** or a *tert*-butyldiphenylsilyl (TBDPS) group **1c** under similar conditions gave the corresponding phenolic iodonium triflate **4a** in 65–83% yields (entries 3 and 4). However, the reaction of trimethylsiloxybenzene **1d** or phenol **1e** instead of **1a** using Koser's reagent **2a** did not afford the desired product (entries 5 and 6). Screening of other hypervalent iodine(III) reagents **2b–d** has indicated that the Koser's reagent **2a** and [bis(trifluoroacetoxy)iodo]benzene **2c** are the most effective reagents in this reaction (entries 2 and 7–9). Since [hydroxy(tosyloxy)iodo]arenes are readily available and stable compounds, we decided to use these reagents in our following studies. The reaction in the presence of TfOH added from the beginning gave product **4a** in only 35% yield (entry 10). The tosylate product **4b** was obtained in 86% yield when *p*-toluenesulfonic acid was used instead of TfOH (entry 11).

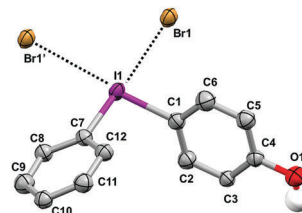
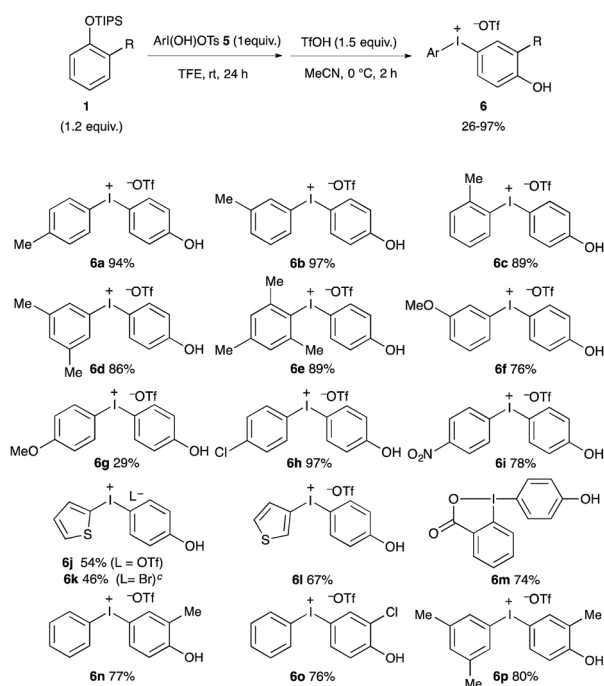


Fig. 1 X-ray crystal structure of compound **4c**. All non-oxygen hydrogen atoms are removed for clarity. Ellipsoids drawn to the 50% probability level. Selected bond lengths and angles: I(1)–C(1) 2.094(13); I(1)–C(7) 2.137(11); I(1)–Br(1) 3.277(2); O(1)–C(4) 1.379(15); I(1)–Br(1') 3.280(1); C(1)–I(1)–C(7) 92.7(4); C(1)–I(1)–Br(1) 86.8(3); Br(1)–I(1)–Br(1') 89.9(1); Br(1')–I(1)–C(7) 90.5(2). Br(1') is located in the neighboring asymmetric unit (Fig. S1, ESI†).

The triflate product **4a** could be further converted into 4-hydroxyphenyl(phenyl)iodonium bromide **4c** *via* treatment with aqueous potassium bromide solution at room temperature (entry 12). The bromide **4c** was recrystallized from methanol, and characterized by X-ray crystallography (Fig. 1).

According to the X-ray crystallography data, compound **4c** has a pseudo-square-planar coordination formed by two covalent iodine–carbon bonds and two close contact bromide anions, with one of the bromide anions in the neighboring asymmetric unit (Br1'). The I⋯Br non-covalent intermolecular interaction distances were 3.277(2) and 3.280(1) with angles nearly 90° between the iodine atom and the four contacts (Fig. S1, ESI†). Additionally, a least-squares plane fit through I1, C1, C7, Br1 and Br1' resulted in a root-mean square deviation of 0.029 Å. The bond angles and bond distances of C–I–C are similar to those of the previously reported structure of diaryliodonium salts.²³ The bond distance between oxygen and carbon atoms falls within the typical range for a phenolic C–O bond length.

In the next step, we investigated the preparation of various substituted 4-hydroxyphenyl(aryl)iodonium triflates **6** from the corresponding [hydroxy(tosyloxy)iodo]arenes **5** under optimized conditions. In general, the reaction of reagents **5** bearing electron-withdrawing or electron-donating substituents in the *para*-position with phenyl silyl ether **1a** gave the corresponding 4-hydroxyphenyl(aryl)iodonium triflates **6a–i** in moderate to good yields. In the reaction of sterically hindered *ortho*-substituted [hydroxy(tosyloxy)iodo]arenes **5c,e** with **1a**, the desired products **6c,e** were also obtained in good yields. However, the reaction of the *para*-methoxy substituted reagent **5g** afforded the product **6g** only in 29% yield probably because this reagent was a relatively unstable compound that decomposed during the reaction.²⁴ In the reaction of 2-thienyl (**5j**) or 3-thienyl (**5k**), Koser's type reagents, with **1a**, the respective phenolic (thienyl)iodonium triflates **6j,k** were obtained in moderate yields. The bromide salt of **6k** was also prepared in 46% yield. The structures of phenolic (thienyl)iodonium salts **6j–l** were established by X-ray crystallography (see the ESI†). Molecular arrangements in these structures are similar to the previously reported aryl(thienyl)iodonium salts.^{25,26} The reaction of pseudocyclic Koser's reagent, 2-[hydroxy(tosyloxy)]iodobenzoic acid **5l**, with **1a** under the same conditions gave the corresponding 1-(4-hydroxyphenyl)benziodoxole **6m** in 74% yield. Compound **6m** was recrystallized

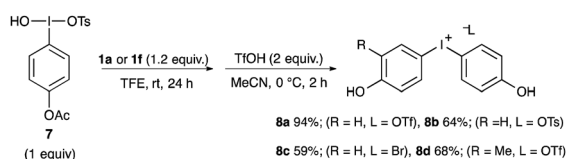
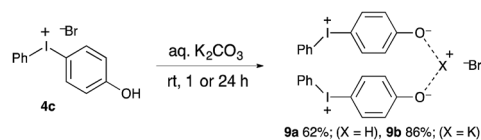
Table 2 Preparation of 4-hydroxyphenyl(aryl)iodonium salts **6a–o**^{a,b}

^a All reactions were performed using substrate **1** (1.2 equiv.) and hyper-valent iodine reagent **3** (1 equiv.) in 2,2,2-trifluoroethanol at room temperature for 24 hours. The reaction mixture was evaporated and then TfOH (1.5 equiv.) was added to the reaction mixture in acetonitrile solution and stirred at 0 °C for 2 hours. ^b Yields of isolated products. ^c KBr (10.0 equiv.) was added to the reaction mixture and stirred for 2 hours.

from methanol and characterized by X-ray crystallography (see the ESI†). The reaction of substituted aryl silyl ether **1f** or **1g** with **2a** or **3e** gave the corresponding phenolic iodonium triflates **6n–p** in good yields (Table 2).

Furthermore, we investigated the preparation of symmetrical diphenolic iodonium salts, from the reaction of 4-acetoxy[hydroxy-(tosyloxy)iido]benzene **7** with triisopropylsiloxybenzene **1a** (Scheme 1). The reaction of reagent **7** with **1a** under similar conditions afforded 4,4'-di(hydroxyphenyl)iodonium triflate **8a** in 94% yield. Other diphenolic iodonium derivatives, tosylate **8b** or bromide **8c**, could be produced in moderate yields *via* a ligand exchange reaction. Under the same conditions, asymmetrical compound **8d** was prepared in 68% yield from the reaction of **7** with **1f**.

Phenolic (aryl)iodonium salts have the acidic hydroxyl group on the aromatic ring. Previously, several research groups reported that *ortho*-phenolic iodonium salts could be converted into the corresponding arylidonium ylides under basic conditions.^{19,21}

Scheme 1 Preparation of 4,4'-di(hydroxyphenyl)iodonium salts **8a–d**.Scheme 2 Preparation of dimeric oxyphenyl(phenyl)iodonium ylides **9a,b**.

Thus, we investigated the preparation of the arylidonium ylide from phenolic salt **4c** under basic conditions. The reaction of 4-hydroxyphenyl(phenyl)iodonium bromide **4c** with aqueous potassium carbonate at room temperature for 1 hour afforded the dimeric oxyphenyl(phenyl)iodonium ylide–HBr complex **9a** in 62% yield (Scheme 2). The reaction mixture was stirred for 24 hours to give the respective potassium bromide complex **9b** in 86% yield. However, the reaction of triflate **4a**, tosylate **4b**, or symmetrical diphenolic iodonium salts **7** under similar conditions did not produce the respective product. The composition of compounds **9** was confirmed by elemental analysis. The solid structure of **9a** was established by X-ray crystallography (Fig. 2).

According to the X-ray crystallography data, compound **9a** has a pseudo-square-planar coordination formed by two covalent I–C bonds and two non-covalent intermolecular interactions: an I···Br interaction at 3.3076(3) Å and an I···O interaction from a neighboring asymmetric unit at 2.760(2) Å (Fig. S6, ESI†). The C–I–C bond angle is close to the expected T-shaped geometry of diaryliodonium salts or iodonium zwitterion compounds.

Finally, we investigated the reactivity of a phenolic iodonium salt as a phenol transfer reagent. Previously, Olofsson and co-workers reported that the reaction of sodium nitrite with diaryliodonium salts under weakly basic conditions afforded the respective nitro-arenes in good yields.²⁷ Thus, we tested the reactivity of the phenolic (aryl)iodonium salt as a phenol transfer reagent (Scheme 3). The reaction of sodium nitrite with **8a** in the presence of NaOTf gave *para*-nitrophenol **10** in 46% yield. Reactions of other anionic nucleophiles with **8a** under similar conditions gave the respective compounds **11–14** in low to good yields. The obtained azide **11** is potentially useful as a click chemistry synthon.^{28,29}

In summary, we have reported a practical one-pot synthetic procedure for the preparation of 4-hydroxyphenyl(aryl)iodonium salts from triisopropylsiloxybenzene using hydroxy(tosyloxy)iido-arenes in the presence of TfOH. Several solid-state structures of

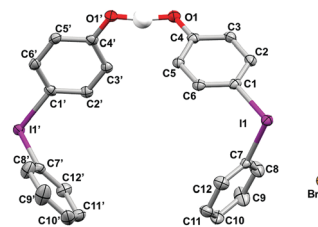
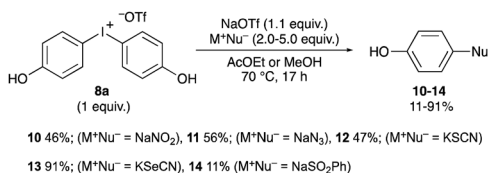


Fig. 2 X-ray crystal structure of compound **9a**. Non-oxygen hydrogen atoms are removed for clarity. Ellipsoids drawn to the 50% probability level. Selected bond lengths and angles: I(1)–C(1) 2.108(2); I(1)–C(7) 2.106(2); I(1)–Br(1) 3.3076(3); O(1')–I(1) 2.760(2); C(1)–I(1)–C(7) 93.33(8); C(1)–I(1)–O(1') 85.93(6); C(7)–I(1)–Br(1) 81.84(6); O(1')–I(1)–Br(1) 98.71(3). O(1') is located in the neighboring asymmetric unit (Fig. S6, ESI†).



Scheme 3 Phenolation reactions of various nucleophiles using **8a**.

these products were established by X-ray crystallography. These phenolic diaryliodonium salts are potentially important precursors of novel hypervalent iodine(III) ylidic compounds. In particular, the treatment of 4-hydroxyphenyl(phenyl)iodonium salts under basic conditions converts them to dimeric oxyphenyl-(phenyl)iodonium ylidic salts. We have also demonstrated that the symmetrical bis(phenolic)iodonium salt is a potentially useful electrophilic phenol transfer reagent.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 *Top. Curr. Chem.*, ed. T. Wirth, 2016, vol. 373, pp. 1–310.
- 2 V. V. Zhdankin, *Hypervalent Iodine Chemistry: Preparation, Structure and Synthetic Application of Polyvalent Iodine Compounds*, John Wiley & Sons Ltd, 2014.
- 3 *Iodine Chemistry and Applications*, ed. T. Kaiho, John Wiley & Sons, Inc., 2015.
- 4 T. Dohi and Y. Kita, *Curr. Org. Chem.*, 2016, **20**, 580–615.
- 5 A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328–3435.
- 6 V. W. Pike, *J. Labelled Compd. Radiopharm.*, 2018, **61**, 196–227.
- 7 M. Fananas-Mastral, *Synthesis*, 2017, 1905–1930.
- 8 E. A. Merritt and B. Olofsson, *Angew. Chem., Int. Ed.*, 2009, **48**, 9052–9070.
- 9 A. Yoshimura, A. Saito and V. Zhdankin, *Chem. – Eur. J.*, 2018, DOI: 10.1002/chem.201802111.
- 10 D. R. Stuart, *Synlett*, 2017, 275–279.
- 11 T. Kitamura, *Aust. J. Chem.*, 2010, **63**, 987–1001.
- 12 S. K. Sundalam, A. Nilova, T. L. Seidl and D. R. Stuart, *Angew. Chem., Int. Ed.*, 2016, **55**, 8431–8434.
- 13 M. Wang and Z. Huang, *Org. Biomol. Chem.*, 2016, **14**, 10185–10188.
- 14 H. Chen, J. Han, L. Wang and J. Han, *Beilstein J. Org. Chem.*, 2018, **14**, 354–363.
- 15 T. Kitamura, K. Gondo and J. Oyamada, *J. Am. Chem. Soc.*, 2017, **139**, 8416–8419.
- 16 R. Robidas, V. Guerin, L. Provencal, M. Echeverria and C. Y. Legault, *Org. Lett.*, 2017, **19**, 6420–6423.
- 17 A. Yoshimura, J. M. Fuchs, K. R. Middleton, A. V. Maskaev, G. T. Rohde, A. Saito, P. S. Postnikov, M. S. Yusubov, V. N. Nemykin and V. V. Zhdankin, *Chem. – Eur. J.*, 2017, **23**, 16738–16742.
- 18 F. M. Beringer and I. Lillien, *J. Am. Chem. Soc.*, 1960, **82**, 725–731.
- 19 S. W. Page, E. P. Mazzola, A. D. Mighell, V. L. Himes and C. R. Hubbard, *J. Am. Chem. Soc.*, 1979, **101**, 5858–5860.
- 20 P. B. Kokil and P. M. Nair, *Tetrahedron Lett.*, 1977, 4113–4116.
- 21 O. Prakash, M. Kumar and R. Kumar, *Tetrahedron*, 2010, **66**, 5827–5832.
- 22 E. Malamidou-Xenikaki and S. Spyroudis, *Synlett*, 2008, 2725–2740.
- 23 M. S. Yusubov, D. Y. Svitich, A. Yoshimura, B. J. Kastern, V. N. Nemykin and V. V. Zhdankin, *Eur. J. Org. Chem.*, 2015, 4831–4834.
- 24 I. Papoutsis, S. Spyroudis, A. Varvoglis and C. P. Raptopoulou, *Tetrahedron*, 1997, **53**, 6097–6112.
- 25 D. Bykowski, R. McDonald, R. J. Hinkle and R. R. Tykwinski, *J. Org. Chem.*, 2002, **67**, 2798–2804.
- 26 R. R. Tykwinski, K. Kamada, D. Bykowski, K. Ohta and R. McDonald, *Adv. Mater.*, 2000, **12**, 133–137.
- 27 G. L. Tolnai, U. J. Nilsson and B. Olofsson, *Angew. Chem., Int. Ed.*, 2016, **55**, 11226–11230.
- 28 A. Baschieri, S. Muzzioli, V. Fiorini, E. Matteucci, M. Massi, L. Sambri and S. Stagni, *Organometallics*, 2014, **33**, 6154–6164.
- 29 V. E. Romanov and E. E. Shul'ts, *Chem. Nat. Compd.*, 2015, **51**, 1142–1146.