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Preparation, Structure, and Reactivity of Pseudocyclic Benziodoxole Tosylates: New Hypervalent Iodine Oxidants and Electrophiles

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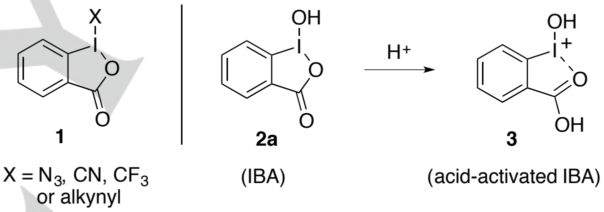
Dedication ((optional))

Abstract: New pseudocyclic benziodoxole tosylates were prepared by the treatment of 1-hydroxybenziodoxolones with p-toluenesulfonic acid or via ligand transfer reaction between PhI(OH)OTs (Koser's reagent) and substituted 2-iodobenzoic acids under mild condition. Single crystal X-ray crystallography of these compounds revealed a pseudocyclic structure with a short intramolecular interaction of 2.362 Å between oxygen and iodine in the iodoxole ring. Pseudocyclic benziodoxole tosylates readily react with various organic substrates as electrophiles or oxidants to afford the corresponding iodonium salts or the products of oxidation. Furthermore, these compounds can be used as efficient recyclable hypervalent iodine reagents. The reduced form of a pseudocyclic benziodoxole tosylate, 2-iodobenzoic acid, can be efficiently recovered from the reaction mixture by a simple acid-base liquid-liquid biphasic procedure.

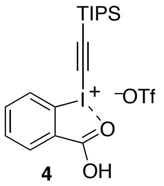
Introduction

Organohypervalent iodine compounds have found broad synthetic application as efficient oxidants and environmentally friendly reagents for various synthetically important chemical transformations.[1] Particularly useful are the recently developed benziodoxole-based cyclic atom-transfer reagents **1** (Scheme 1).[2] Reactions of these reagents with organic substrates result in a facile formation of the corresponding products of azidation,[3] cyanation,[4] trifluoromethylation,[5] or alkynylation.[6] The benziodoxole-based atom-transfer reagents **1** are commonly prepared from 2-iodosylbenzoic acid (IBA, **2a**) by ligand exchange reaction in the presence of a strong acid followed by treatment with a base. The initial reaction of IBA with a strong acid forms the highly electrophilic, acid-activated IBA species **3**. The structure of protonated species **3** is characterized by the presence of a strong secondary bonding between the positively charged iodine center and the carboxylic oxygen, and therefore these species are called pseudocyclic benziodoxoles. Because of the high electrophilic reactivity, the pseudocyclic benziodoxole species **3** represent potential interest as reagents; however, the structural features and the chemistry of these species have not been systematically investigated. In general, the pseudocyclic organohypervalent iodine reagents are characterized by higher thermal stability, better solubility, and improved reactivity pattern compared to the common iodine(III) and iodine(V) reagents.[7,8]



Scheme 1. Benziodoxole-based atom-transfer reagents **1** and IBA **2a**.

The known examples of pseudocyclic benziodoxole reagents are represented by structures **4**–**6** shown in Scheme 2.[9] In particular, Waser and co-workers have prepared triisopropylsilylethynyl benziodoxole triflate salt **4**, which is a potentially effective electrophilic alkynylating reagent.[9a] Very recently, Toste and co-workers have reported the acid-activated electrophilic trifluoromethylating reagent **5**, which was prepared by treatment of trifluoromethylbenziodoxole (Togni's reagent) with HCl gas.[9b] Our group has reported the synthesis and structural characterization of the new acid-activated hypervalent iodine reagent, benziodoxole triflate **6**, which was prepared from IBA **2** and trifluoromethanesulfonic acid. This highly electrophilic reagent readily reacts with various organic substrates to give the corresponding products of oxidation in good yields.[9c]



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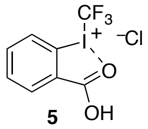

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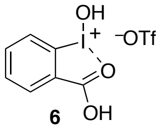

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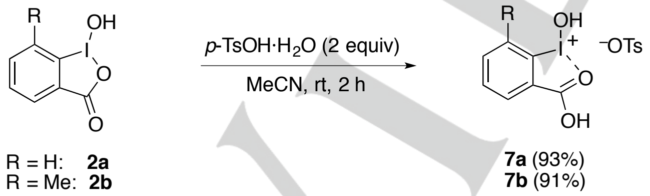
Scheme 2. Known pseudocyclic benziodoxole reagents.

Benziodoxole triflate **6** represents the only known example of the stable, acid-activated IBA species **3**. The non-cyclic analog of compound **6** is [hydroxyl(tosyloxy)iodo]benzene (HTIB, Koser's reagent), which can be considered as the acid-activated iodosylbenzene, PhIO•TsOH. Koser's reagent is one of the most important common hypervalent iodine reagents.[10] Several other examples of acid-activated iodine(III) derivatives have been reported as unstable species that were difficult to isolate from reaction mixture because of low thermal stability and sensitivity to moisture.[11]

Herein, we report the preparation, structural investigation, and reactivity of new pseudocyclic benzoiodoxole tosylate derivatives, which are the analogs of benziodoxole triflate **6**. Pseudocyclic benziodoxole tosylates are efficient recyclable hypervalent iodine reagents that readily react as electrophiles or oxidants with various organic substrates.

Results and Discussion

In our initial experiments, we have found that the reaction of 2-iodosylbenzoic acid **2a** (1 equiv) with *p*-toluenesulfonic acid (2 equiv) in acetonitrile for 2 hours at room temperature yields the desired 2-[hydroxy(tosyloxy)]iodobenzoic acid **7a** in 93% yield. Decreasing amount of *p*-toluenesulfonic acid results in a lower yield of product **7a**. Tosylate **7a** is soluble in methanol, and moderately soluble in acetonitrile. In the solid state **7a** is relatively stable at room temperature and can be stored for several months in a refrigerator without any noticeable decomposition. The analogous reaction of 3-methyl-2-iodosylbenzoic acid **2b** under same condition affords the expected product **7b** in 91% (Scheme 3). Composition of tosylates **7a** and **7b** was confirmed by elemental analysis and ESI mass-spectrometry. In particular, their ESI mass spectra in positive mode demonstrated the presence of molecular ion [ArI(OH)]$^+$. The solid-state structure of tosylate **7b** was established by single crystal X-ray crystallography (Figure 1).



R = H: **2a**
R = Me: **2b**

7a (93%)
7b (91%)

Scheme 3. Preparation of benziodoxole-based pseudocyclic tosylates.

According to the X-ray crystallographic data, compound **7b** has a pseudocyclic structure with a close intramolecular interaction of 2.362(3) Å between the hypervalent iodine atom and the carboxylate oxygen atom O(2). Molecular structure of tosylate **7b** demonstrates the presence of a tetracoordinated iodine center with one short iodine-oxygen covalent bond [I(1)–O(1) = 1.926(4) Å], iodine-carbon covalent bond [I(1)–O(1) = 1.926(4) Å], and two iodine-oxygen secondary bonds to carboxylate and tosylate oxygen atoms. This molecular arrangement is similar to the previously reported structure of benziodoxole triflate **6**. The intramolecular geometry of the iodine(III) center in the cationic fragment of **7b** corresponds to a distorted T-sharped form characteristic of hypervalent iodine(III) compounds. The intermolecular distance between iodine and tosylate oxygen [I(1)–O(4) 2.947(3) Å] indicates the presence of a relatively weak non-covalent interaction. Taking into account primary and secondary bonding, the hypervalent iodine(III) center in **7b** has a pseudo square-planar coordination.

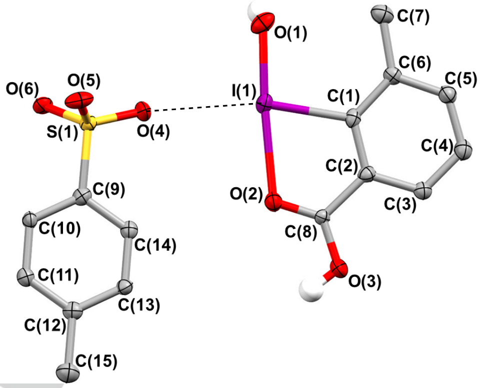
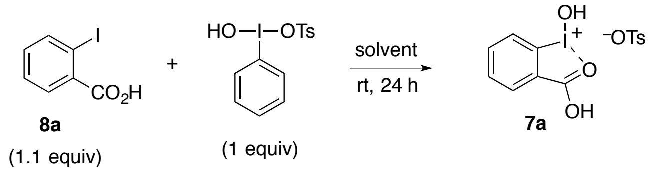


Figure 1. X-ray crystal structure of compound **7b**. Thermal ellipsoid plot of **7b** drawn to the 50% probability level. Hydrogen atoms bound to carbon atoms were removed for clarity. Selected bond lengths (Å) and angles (°): I(1)–O(1) 1.926(4) ; I(1)–O(2) 2.362(3); I(1)–C(1) 2.156(4); I(1)–O(4) 2.947(3); C(8)–O(2) 1.232(5); C(8)–O(3) 1.286(5); O(1)–O(5) 2.634(4); O(3)–O(6) 2.516(4); O(1)–I(1)–O(2) 174.58(12); C(1)–I(1)–O(1) 100.45(16); C(1)–I(1)–O(2) 75.72(15).

The experimental procedure shown in Scheme 3 involves the use of benziodoxoles **2** as starting materials and is limited to the readily available precursors **2a** and **2b**. In a search for a more general procedure utilizing the commercially available substituted *ortho*-iodobenzoic acids, we have investigated the preparation of tosylate **7a** directly from 2-iodobenzoic acid **8a** via ligand transfer reaction with a commercially available [hydroxy(tosyloxy)iodo]benzene (Koser's reagent). In order to optimize reaction conditions, we have studied the reaction of 2-iodobenzoic acid **8a** (1.1 equiv) with Koser's reagent (1 equiv) in various solvents at room temperature (Table 1). The screening of solvents has demonstrated that dichloromethane is the best solvent in this ligand transfer reaction (entries 1-7). The shortening of the reaction time and refluxing reaction mixture did not improve the product yield (entries 8-10). Compared to our initial preparation of **7a** from IBA **2a** and *p*-toluenesulfonic acid (Scheme 3), the ligand transfer reaction under optimized conditions affords product **7a** in better yield (entry 1). Previously, Koser and co-workers reported the reaction of 2-iodobenzoic acid **8a** with Koser's reagent under similar conditions; however, they were not able to prepare product **7a** and isolated only 2-iodosylbenzoic acid **2a** in 76%.[12]

Table 1. Optimization of ligand transfer reaction between 2-iodobenzoic acid **8a** and Koser's reagent.[a]

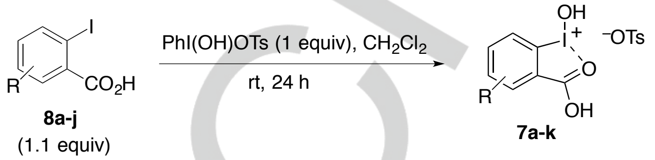


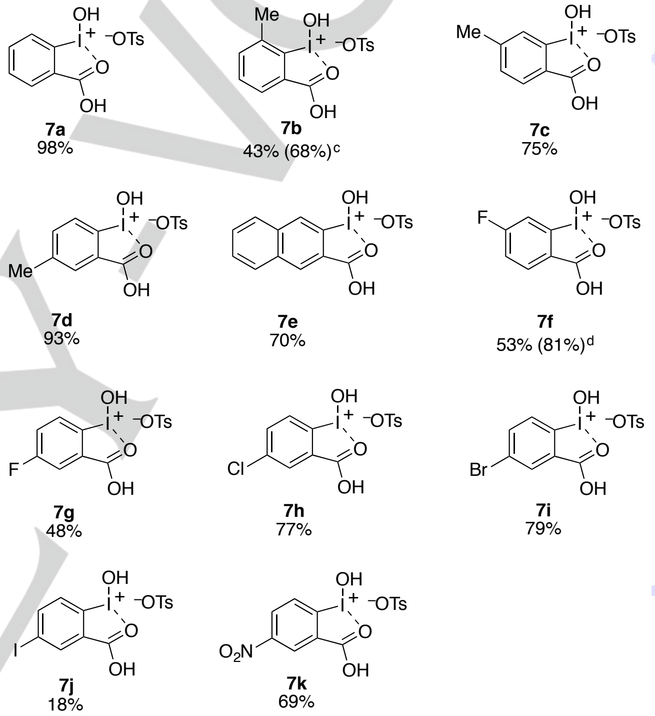
Entry	Solvent]	Time (h)	Yield of **7a** (%)[b]
1	CH_2Cl_2	24	98
2	MeCN	24	44
3	Hexane	24	70
4	AcOEt	24	90
5	THF	24	trace
6	Benzene	24	79
7	Et_2O	24	0
8	CH_2Cl_2	2	74
9	CH_2Cl_2	4	94
10[c]	CH_2Cl_2	1	91

[a] Reaction conditions: 2-iodobenzoic acid **8a** (1.1 equiv) and Koser's reagent (1 equiv) in a solvent at room temperature was stirred for 4 to 24 hours. [b] Isolated yields. [c] Under reflux conditions for 1 hour.

At the next step, we investigated the conversion of various substituted *ortho*-iodobenzoic acids **8** to the respective hydroxy(tosyloxy)]iodonium derivatives **7** under optimized reaction conditions (Table 2). In general, the reaction of *ortho*-iodobenzoic acids with either electron-donating or electron-withdrawing substituents **8a-i,k** gave the corresponding 2-[hydroxy(tosyloxy)]iodonium derivatives **7a-i,k** in moderate to good yields. The reaction of 4-fluoro- **8f** and 5-fluoro-2-iodobenzoic acid **8g** gave the respective products in lower yields. When the reaction of 4-fluoro-2-iodobenzoic acid **8f** was performed at reflux conditions in 1,2-dichloroethane, the yield of product **7f** improved up to 81%. In the reaction of a sterically hindered 3-methyl-2-iodobenozoic acid **8b**, product **7b** was obtained in a relatively low 43% yield. Addition of increased amounts of *p*-toluenesulfonic acid resulted in the improvement of the yield to 68%. The reaction of 2,5-diiodobenzoic acid **8j** afforded the corresponding product **7j** in 18%, and this yield could not improved by using 2 equivalents of *p*-toluenesulfonic acid or performing reaction at reflux conditions. Most of products **7** are stable compounds with clean NMR spectra. However, ^1H NMR of products **7e** and **7g** indicate some decomposition during measurement of the spectra. However, the ESI-Mass spectra (positive mode) of both compounds clearly demonstrate the corresponding molecular ion peaks $[ArI(OH)]^+$.

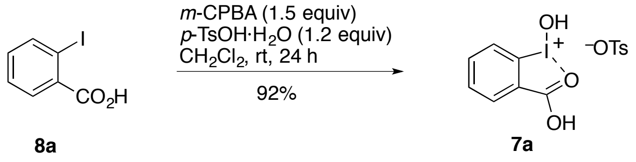
Table 2. Optimization of ligand transfer reaction between substituted 2-iodobenzoic acids **8** and Koser's reagent.[a,b]





[a] Reaction conditions: 2-iodobenzoic acid **6** (1.1 equiv) and Koser's reagent (1 equiv) in dichloromethane at room temperature for 24 hours. [b] Isolated yields. [c] *p*-TsOH·H₂O (2 equiv) was added. [d] At reflux condition for 24 hour using 1,2-dichloroethane.

Furthermore, we have found that 2-[hydroxy(tosyloxy)]iodobenzoic acid **7a** can also be prepared from 2-iodobenzoic acid **8a** in a one-pot procedure by using *m*-chloroperoxybenzoic acid (*m*-CPBA) as an oxidant in the presence of *p*-toluenesulfonic acid in dichloromethane at room temperature. Under these conditions, product **7a** is isolated in 92% yield (Scheme 4), which is slightly lower compared to the ligand transfer with Koser's reagent and similar to the reaction of IBA **2a** with *p*-toluenesulfonic acid in acetonitrile (Scheme 3). Olofsson and co-worker have also reported the in-situ generation of **7a** using similar conditions.[13]

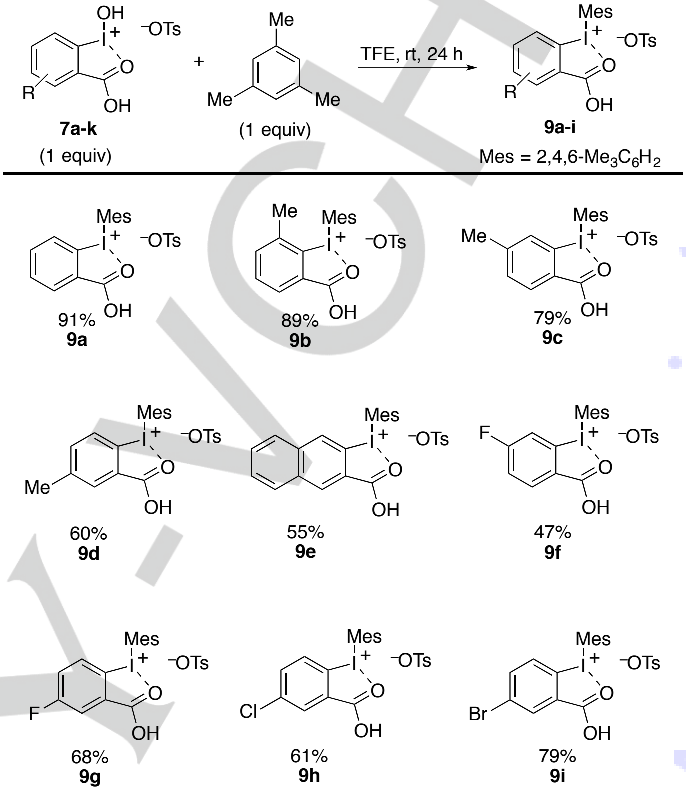


Scheme 4. One-pot synthesis of **7a**.

Similarly to Koser's reagent, the pseudocyclic benziodoxole tosylates are expected to be strong electrophiles and effective oxidants. Previously, Kita and co-worker reported that the reaction of Koser's reagent with 1,3,5-trimethylbenzene (mesitylene) in 2,2,2-trifluoroethanol gives the corresponding diaryliodonium salt at room temperature.[14] We investigated the preparation of diaryliodonium salts from compounds **7** and arenes under similar conditions. We have found that the reactions of pseudocyclic benziodoxole tosylates **7a-i** with mesitylene proceed at room temperature affording the corresponding diaryliodonium salts **9a-i** in moderate to good yields (Table 3). The structure of one of these products, diaryliodonium tosylate **9b**, was established by a single-crystal X-ray crystallography (Figure 2). The X-ray data confirmed a pseudocyclic diaryliodonium structure with a strong intramolecular interaction between iodine and oxygen atoms I(1)–O(1) = 2.7022 Å. The tosylate oxygen atom was also involved in a weak intermolecular interaction with iodine atom resulting in a pseudo square-planar coordination of the hypervalent iodine center.

The reactivity of pseudocyclic benziodoxole tosylates as oxidants toward various organic substrates is summarized in Scheme 5. For these studies we selected the readily available compound **7a** and the ortho-substituted compound **7b**. In particular, the oxidation of thioanisole **10** or arene **12** and I_2 with reagent **7a** produced the corresponding sulfoxide **11** or diiodoarene **13** in good yields. In the analogous reactions of thioanisole **10** or arene **12** with reagent **7b**, the corresponding products **11** and **13** were obtained in lower yields, probably because of partial decomposition of the reagent under reaction conditions. Partially unreacted substrates were recovered from reaction mixtures in these reactions. The oxidative α-tosyloxylation of acetophenone **14** or Hofmann rearrangement of phenylacetamide **16** with reagent **7b** afforded the corresponding products **15** or **17** in moderate to good yields. However, the same reactions using reagent **7a** gave the respective products only in very low yields. In these oxidations the reactivity of reagent **7b** is higher than reagent **7b**. We suggest that the introduction of methyl group in *ortho*-position to iodine atom may lead to destabilization of compound **7** and enhanced reactivity due to structural distortion. The effect of the *ortho* methyl group on stability and reactivity of pseudocyclic benziodoxole tosylates **7** is in agreement with the reported by Legault and coworkers experimental results and computational studies of the oxidative α-tosyloxylation of ketones.[15]

Table 3. Preparation of pseudocyclic diaryliodonium tosylates **9**.[a-c]



[a] Reaction conditions: a mixture of benziodoxole tosylate **7** (1 equiv) and mesitylene (1 equiv) was stirred in 2,2,2-trifluoroethanol at room temperature for 24 hours. [b] Isolated yields.

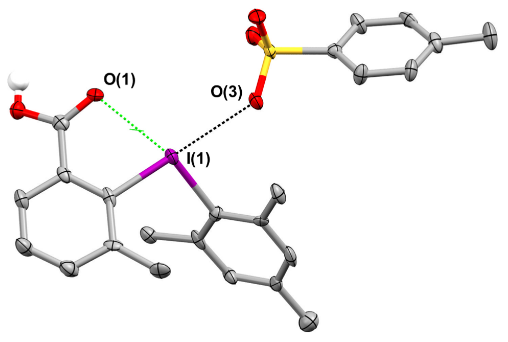
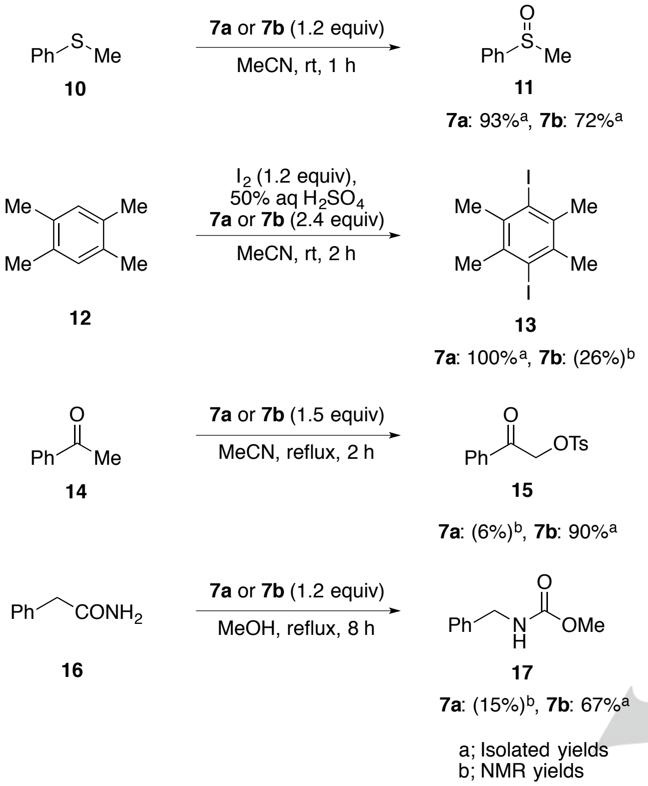


Figure 2. X-ray crystal structure of compound **9b**. Thermal ellipsoid plot of **9b** drawn to the 50% probability level. Hydrogen atoms bound to carbon atoms were removed for clarity. Selected bond lengths (Å) and angles (°): I(1)–O(1) 2.7022(44); I(1)–O(3) 2.8798(38); I(1)–C(9) 2.133(6); O(1)–I(1)–C(1) 72.15(20); O(1)–I(1)–C(9) 157.37(18); C(1)–I(1)–C(9) 100.2(2).



Scheme 5. Oxidations of organic substrates using reagents of **7a** and **7b**.

Compared to Koser's reagent, pseudocyclic benziodoxole tosylates **7** have an additional advantage of being efficient recyclable hypervalent iodine reagents. The reduced form of reagents **7a** or **7b**, 2-iodobenzoic acid **8a** or 3-methyl-2-iodobenzoic acid **8b**, can be easily recovered from the reaction mixture in over 94% yield by a simple acid-base liquid-liquid biphasic procedure. The recovered compounds **8a** and **8b** can be re-oxidized to the 2-iodosylbenzoic acid derivatives by a standard oxidizing procedure or directly converted to tosylates **7** by treatment with Koser's reagent (Table 2).

Conclusions

In conclusion, we have reported the preparation and structural characterization of new pseudocyclic benziodoxole tosylates **7**. Single crystal X-ray crystallography of compound **7b** revealed a pseudocyclic structure with a short intramolecular interaction of 2.362 Å between oxygen and iodine in the iodoxole ring. Pseudocyclic benziodoxole tosylates readily react with various organic substrates as electrophiles or oxidants to afford the corresponding iodonium salts or the products of oxidation. Furthermore, these compounds can be used as efficient recyclable hypervalent iodine reagents. The reduced form of a pseudocyclic benziodoxole tosylate, 2-iodobenzoic acid, can be efficiently recovered from the reaction mixture by a simple acid-base liquid-liquid biphasic procedure.

Experimental Section

Preparation of 2-[hydroxy(tosyloxy)]iodobenzoic acid 7a from 2-iodosylbenzoic acid 2a and *p*-toluenesulfonic acid monohydrate: *p*-Toluenesulfonic acid monohydrate (380 mg, 2 mmol) was added at room temperature to a stirred mixture of 2-iodosylbenzoic acid (264 mg, 1 mmol) with MeCN (2 mL). The reaction was stirred at room temperature for 2 h. After completion of reaction, the solvent was removed under reduced pressure and the solid product was washed with diethyl ether several times then dried in vacuum to give 406 mg (93%) of compound **7a** as a white solid.

Ligand transfer procedure for the preparation of 2-[hydroxy(tosyloxy)]iodobenzoic acids 7 from Koser's reagent and 2-idobenzoic acids 8: Hydroxy(tosyloxy)iodobenzene (196 mg, 0.5 mmol) was added at room temperature to a stirred mixture of 2-iodobenzoic acid **8** (0.55 mmol) with CH_2Cl_2. The reaction was stirred at room temperature for 24 h. After completion of reaction, the solvent was removed under reduced pressure and the solid residue was filtered and washed with diethyl ether several times and then dried in vacuum to give final products **7**.

One-pot procedure for the preparation of 7a from 2-iodobenzoic acid 8a using *m*-CPBA in the presence of *p*-toluenesulfonic acid monohydrate: 2-iodobenzoic acid (124 mg, 0.5 mmol) and *m*-CPBA (129 mg, 0.750 mmol) were added to a solution of *p*-toluenesulfonic acid monohydrate (194 mg, 0.60 mmol) in 1.0 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 24 h. After completion of reaction, the solvent was removed under reduced pressure and the solid residue was filtered and washed with diethyl ether several times and then dried in vacuum to give 201 mg (92%) product **7a**.

Acknowledgements

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Keywords: hypervalent iodine • iodonium salts • iodine • oxidation • recyclable reagents

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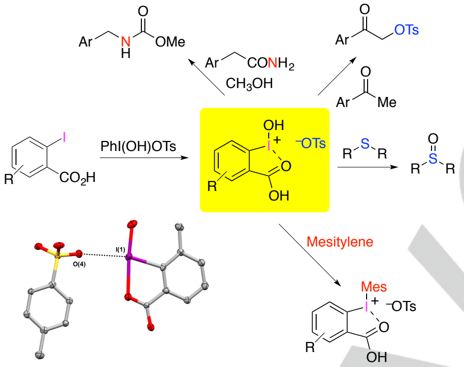

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