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# Efficient and General One-Pot Synthesis of Diaryliodonium Triflates: Optimization, Scope and Limitations

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This paper is dedicated to Professor Jan-Erling Bäckvall on the occasion of his 60th birthday.

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

**Abstract:** Symmetrical and unsymmetrical diaryliodonium triflates have been synthesized from both electron-deficient and electron-rich arenes and aryl iodides with *m*CPBA and triflic acid. A thorough investigation of the optimization, scope and limitations has resulted in an improved one-pot protocol that is fast, high-yielding, and operationally simple. The reaction has been extended to the direct synthesis of symmetrical iodonium salts from iodine and arenes, conveniently circumventing the need for aryl iodides.

**Keywords:** arenes; aromatic substitution; diaryliodonium salts; hypervalent compounds; iodine; oxidation

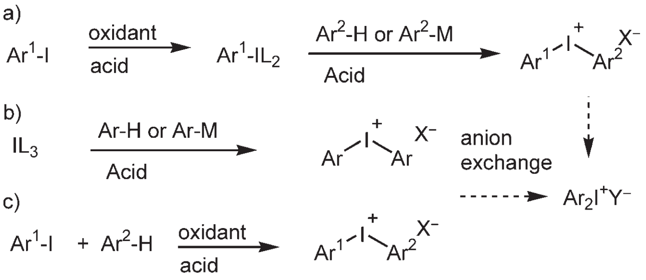
## Introduction

Hypervalent iodine compounds have recently received considerable attention as mild, non-toxic and selective reagents in organic synthesis.[1,2] Iodine(V) reagents, such as Dess–Martin periodinane and IBX, are frequently used as mild oxidants of alcohol moieties in total syntheses of natural products. IBX can also affect oxidative transformations of a variety of other functional groups.[3] Iodine(III) compounds with two heteroatom ligands, for example, (diacetoxyiodo)benzene and iodosylbenzene, are employed in oxidations of alcohols, alkenes and α-oxidations of carbonyl compounds.[4] In contrast, iodine(III) reagents with two carbon ligands have properties resembling those of metals such as Hg, Pb and Pd, and can be employed in reaction pathways that are similar to metal-catalyzed reactions.[2] As the use of transition metals in organic synthesis suffers from drawbacks like cost, toxicity and threshold values in pharmaceutical products, the interest in this type of iodine(III)-mediated reactions has recently increased considerably.[2]

Diaryl-$\lambda^3$-iodanes, also called diaryliodonium salts, are the most well-known compounds in this class. Due to their highly electron-deficient nature and hyperleaving group ability, they serve as versatile arylating agents with a variety of nucleophiles, e.g., in α-arylation of carbonyl compounds.[5,6] Their use in copper- and palladium-catalyzed cross-coupling reactions allows milder reaction conditions than in couplings with aryl halides.[7–9] Furthermore, diaryliodonium salts are used to generate benzynes[10] and serve as photo-initiators in polymerizations.[9,11]

Symmetrical diaryliodonium salts are generally preferable to unsymmetrical salts in arylation reactions. The use of unsymmetrical salts is, however, desirable when the starting materials are expensive, as the more electron-deficient aryl moiety can be selectively transferred in enolate reactions[12] whereas the more electron-rich is transferred in cross-coupling reactions.[8] Furthermore, the properties of unsymmetrical salts can be varied more easily, which is beneficial in other applications.

Synthetic routes to diaryliodonium salts typically involve 2–3 steps, with initial oxidation of an aryl iodide to iodine(III) followed by ligand exchange with an arene or an organometallic reagent to obtain the diaryliodonium salt (Scheme 1 a).[13,14] In many cases a subsequent anion exchange step is necessary, as the anion influences both the solubility and reactivity of the iodonium salt.[8] Non-nucleophilic anions, such as triflate or tetrafluoroborate, have proven superior to halide anions in many applications.[8,9] Many strategies have been reported to shorten the synthetic route towards diaryliodonium salts. Preformed inorganic iodine(III) reagents, such as iodosyl fluorosulfate, can be employed to make symmetrical iodonium salts (Scheme 1 b).[15] These reagents are, however,



**Scheme 1.** Synthetic strategies to diaryliodonium salts; M = $S(n\text{-}Bu)_3$, $B(OH)_2$, $SiMe_3$.

not commercially available. Alternatively, one-pot oxidation and ligand exchange reactions to obtain the diaryliodonium salt directly from iodoarenes and arenes can be used (Scheme 1 c). Reported methods suffer from narrow substrate scope,[16–19] or long reaction times,[18,19] need excess reagents[20] or employ toxic chromium salts.[21] The lack of general, fast and environmentally benign methods for the synthesis of diaryliodonium salts with suitable anions is cumbersome, and clearly limits their scope as reagents in organic chemistry.

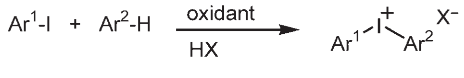
We recently communicated our preliminary results on a one-pot synthesis of diaryliodonium triflates from aryl iodides and arenes with *m*CPBA. The method was also extended to direct synthesis of diaryliodonium triflates from arenes and iodine.[22]

Herein we present a full investigation of optimization, scope and limitations of this fast, high-yielding one-pot synthesis of the title compounds. The protocol has broad substrate scope, gives both symmetrical and unsymmetrical salts and is operationally simple, which should greatly facilitate the application of these efficient, non-toxic arylation agents.

## Results and Discussion

An atom-efficient and simple one-pot synthesis of diaryliodonium salts would involve treatment of an aryl iodide with a commercially available oxidant in the presence of an arene and a suitable acid, the anion of which would end up in the iodonium salt (Scheme 2).

A screening of possible oxidants, acids and solvents that could be employed in the selected model reaction between iodobenzene (**1a**) and benzene (**2a**) to yield diphenyliodonium salts with suitable anions ($X^-$) was performed. Trifluoromethanesulfonic acid (TfOH) and boron trifluoride were deemed the most interesting acids, as they could give rise to iodonium salts with attractive anions ($X = TfO^-$ or $[BF_4]^-$) without a subsequent anion exchange step. We argued that the use of organic solvents would be practical, partly as the aryl iodide and arene would be readily soluble and partly to facilitate isolation of the salts. However, oxidation of aryl iodides to iodine(III) is often performed with inorganic oxidants like $NaBO_3$, $NaIO_4$, $CrO_3$ and $K_2S_2O_8$, which are sparingly soluble in organic solvents.

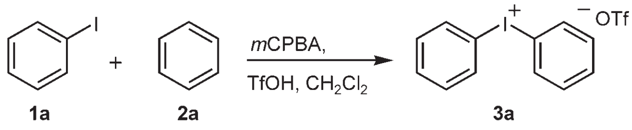


**Scheme 2.** Desired one-pot synthesis of diaryliodonium salts.

With the foreseen solubility problems, it was surprising that reactions employing potassium persulfate and boron trifluoride in dichloromethane delivered a diaryliodonium salt, albeit with a mixture of anions. This could be avoided by using triflic acid instead of $BF_3{\cdot}Et_2O$, delivering diphenyliodonium triflate (**3a**) in modest yield. Due to difficulties in isolating **3a** from the inorganic salts resulting from potassium persulfate, other oxidants were subsequently screened.

Hydrogen peroxide, which has been used as a green reagent in iodine oxidation,[23] unfortunately proved inefficient in combination with a variety of acids in our model reaction. *m*CPBA has recently been reported to oxidize **1a** to (diacyloxyiodo)benzenes,[24] which encouraged us to investigate whether this oxidant could be employed also in the direct synthesis of iodonium salts. Gratefully, initial reactions of **1a** and **2a** with *m*CPBA[25] and triflic acid in dichloromethane indeed delivered salt **3a**, and this reaction was thus investigated in detail (Table 1). The use of 2 equivalents of TfOH considerably increased the yield of salt **3a** (*cf.* entries 1 and 2). Further optimization showed that the reaction time could be decreased to only 10 min by increasing the temperature to 80 °C (entry 3), and these conditions were employed in our preliminary report. We subsequently discovered that the reactivity increased dramatically when 3 equivalents of TfOH

**Table 1.** Optimization of the synthesis of salt **3a** with *m*CPBA.[a]



| Entry | TfOH (equivs.) | *T* [°C] | Time | Yield [%][b] |
|---|---|---|---|---|
| 1 | 1.1 | r.t. | 18 h | 5 |
| 2 | 2 | r.t. | 18 h | 68 |
| 3 | 2 | 80 | 10 min | 73 |
| 4 | 3 | r.t. | 10 min | 92 |
| 5 | 3 | −25 | 10 min | 87 |
| 6 | 3 | 0 | 10 min | 79[c] |

[a] *Reaction conditions:* **1a** (1.0 equiv.), **2a** (1.1 equivs.), *m*CPBA (1.1 equivs.) and TfOH were stirred in $CH_2Cl_2$ at the indicated temperature and time.

[b] Isolated yield.

[c] Isolated by flash chromatography.

were employed, and **3a** could be isolated in 92% yield within 10 min at room temperature (entry 4). Under these conditions, the reaction proved completely insensitive to the temperature, giving **3a** in similar yields in the temperature range of −50 to 90°C (entry 5).[26] Changing the solvent to $Et_2O$, $CHCl_3$ or $CH_3CN$ resulted in decreased yields, whereas changes in concentration were less important.

Next, we turned our attention to the user-friendliness of the protocol, to ensure that it would be easily applicable for non-specialists. Gratefully, the reaction proved insensitive to air and moisture, which further simplified the handling. A convenient work-up and purification procedure was also developed, where the desired salt **3a** could be isolated simply by concentrating the reaction mixture followed by precipitation in diethyl ether, delivering the product in high purity without need for an anion exchange step.[27] Alternatively, flash chromatography in $CH_2Cl_2$/MeOH could be employed to give the product in slightly reduced yield (entry 6), which proved important for some other salts (*vide infra*). In this fast and operationally simple one-pot reaction, **3a** is formed directly from commercially available substrates and can be isolated with the triflate anion in high yield after a simple work-up.

## Scope and Limitations

The optimized protocol was subsequently applied to reactions of iodobenzene with various arenes to yield substituted diaryliodonium salts **3** (Table 2). Most previous protocols have been restricted to the synthesis of either electron-rich or electron-deficient iodonium salts, as the reactivity of the arenes varies dramatically with the electronic properties.[13] The arenes **2** were thus selected to investigate the formation of both electron-rich and electron-deficient salts, including heteroaryl salts.

The use of iodobenzene both as aryl iodide (**1a**) and arene (**2b**) yielded 4-iodophenyl(phenyl)iodonium triflate (**3b**) as a single regioisomer (entry 2). The other aryl halides also participated in the reaction, giving salts **3c–e** with small amounts of *ortho*-substituted product detectable by NMR (entries 3–5). The reaction of **1a** with various alkyl-substituted arenes was subsequently investigated, delivering salts **3f–j** in good yields also for sterically hindered arenes (entries 6–10). Regioselectivity became an issue with 1-bromo-3,5-dimethylbenzene (**2k**), which gave an inseparable mixture of salts **3k′** and **3k″** (entry 11).

The electron-rich arenes acetanilide (**2l**), anisole (**2m**) and thiophene (**2n**) were, as expected, very reactive under the standard conditions. By decreasing the temperature, salts **3l–n** could be obtained in excellent yields (entries 12–14). Heteroaryl salt **3n** has previously been synthesized in several steps *via* the corresponding stannane,[28] which further illuminates the efficiency and environmental friendliness of our procedure. Naphthalene and biphenyl were too reactive also at low temperatures, and failed to give any iodonium salts.[29] Electron-poor arenes, such as nitrobenzene and 2-chloropyridine, reacted sluggishly and gave salt **3b** as a by-product.[29] As the oxidation to iodine(III) intermediate is very fast (*vide supra*), this by-product might arise from an internal redox process that slowly reforms iodobenzene in the absence of a reactive arene that can participate in the ligand exchange step.

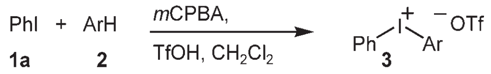
The aryl iodide scope was subsequently investigated, and the results are depicted in Table 3. 4-Bromoiodobenzene (**1b**) reacted with benzene to give salt **3c** in good yield without the *o/p*-selectivity issue described above (entry 1). Further reactions with **1b** delivered symmetrical salt **3o**, and anisole was successfully employed to give the novel salt **3p** (entries 2 and 3). The chloro-substituted substrate **1c** showed similar reactivity to **1b**, as depicted in entries 4–6.

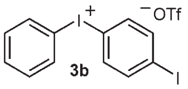
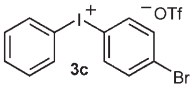
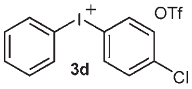
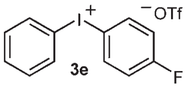
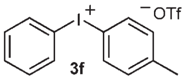
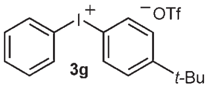
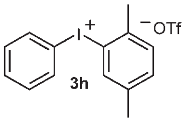
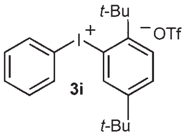
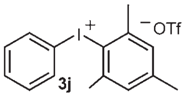
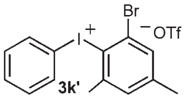
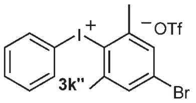
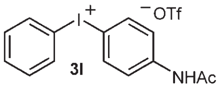
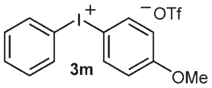
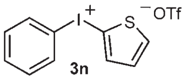
2-Iodotoluene (**1d**) is an interesting substrate, as *ortho*-substituted salts cannot be obtained selectively in reactions with iodobenzene. Iodide **1d** was hence reacted with various arenes, giving salts **3s–z** in high yields (entries 7–14). As expected, **1d** was more reactive than **1a**, but still delivered salts with high purity, including in the reaction with anisole (entry 14). Similarly, 4-iodotoluene (**1e**) was reacted with benzene and toluene, respectively, to deliver salts **3f** and **3aa** (entries 15 and 16). The reason for the moderate yield of **3aa** is unclear, as the reactivity of **1e** should be similar to **1d** (*vide supra*). *tert*-Butyl-substituted aryl iodide **1f** could also be employed, as depicted in entry 17. We experienced difficulties in precipitating salts **3g**, **3x** and **3z**, these products were instead isolated by flash chromatography.

Generally, the synthesis of electron-rich salts was easier from iodobenzene and a substituted arene than from the “reverse” reaction of a substituted aryl iodide with benzene (compare the yields of **3f** and **3g** in Tables 2 and 3). 4-Iodoanisole, 2-iodothiophene and 1-iodonaphthalene all gave black reaction mixtures, from which no product could be isolated.[29] Electron-deficient iodonium salts were, on the other hand, easily synthesized in this manner. Highly deactivated aryl iodides **1g–j**, bearing nitro, $CF_3$ or COOH substituents, all reacted cleanly with benzene, delivering salts **3ab–ae** in good yields (entries 18–21).

Pyridyliodonium salts have previously been inaccessible by acidic routes; they are usually obtained by a basic, atom-inefficient two-step procedure.[30] We were thus interested to test the performance of this substrate type in our reaction. When 3-iodopyridine was reacted with various arenes, iodonium salts were indeed obtained. However, problems with competing

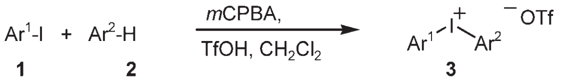
**Table 2.** Synthesis of substituted diaryliodonium salts **3** from PhI and arenes.[a]



| Entry | **2** ArH | | Salt **3**[b] | Yield [%][c] |
|---|---|---|---|---|
| 1 | **2a** | $C_6H_6$ | **3a** | 92 |
| 2 | **2b** | $C_6H_5I$ |  **3b** | 85 |
| 3 | **2c** | $C_6H_5Br$ |  **3c** | 71[d] |
| 4 | **2d** | $C_6H_5Cl$ |  **3d** | 57[d] |
| 5 | **2e** | $C_6H_5F$ |  **3e** | 92[d] |
| 6 | **2f** | $C_6H_5Me$ |  **3f** | 85 |
| 7 | **2g** | *t*-$BuC_6H_5$ |  **3g** | 86 |
| 8 | **2h** | 1,4-$Me_2C_6H_4$ |  **3h** | 66 |
| 9 | **2i** | 1,4-*t*-$Bu_2C_6H_4$ |  **3i** | 80 |
| 10 | **2j** | 1,3,5-$Me_3C_6H_3$ |  **3j** | 78 |
| 11 | **2k** | 3,5-$Me_2C_6H_3Br$ |  **3k'** | 94 |
| | | |  **3k''** | **3k'**:**3k''** = 1.2:1 |
| 12 | **2l** | $C_6H_5NHAc$ |  **3l** | 83 |
| 13 | **2m** | $C_6H_5OMe$ |  **3m** | 87 |
| 14 | **2n** | thiophene |  **3n** | 82 |

[a] *Reaction conditions:* **1a** (1.0 equiv.), **2** (1.1 equivs.), *m*CPBA (1.1 equivs.) and TfOH (2–3 equivs.) in $CH_2Cl_2$, see the Experimental Section for details.
[b] Formed with complete regioselectivity unless stated otherwise.
[c] Isolated yield.
[d] About 5% *ortho*-isomer detectable by NMR.

**Table 3.** Synthesis of substituted diaryliodonium salts **3** from aryl iodides **1** and arenes **2**.[a]



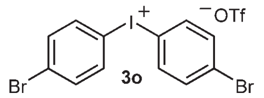
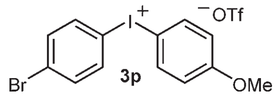
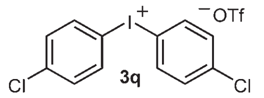
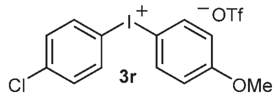
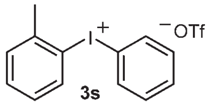
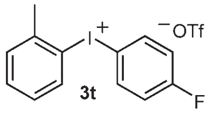
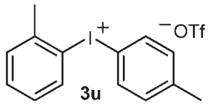
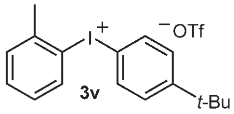
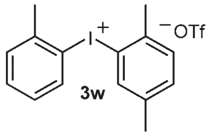
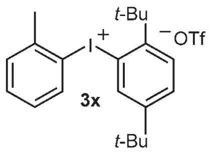
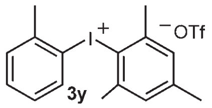
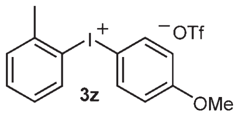
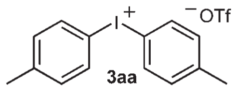
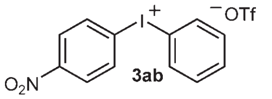
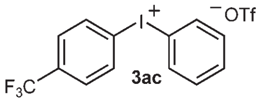
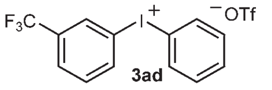
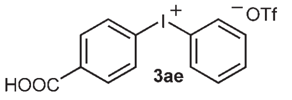
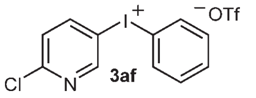
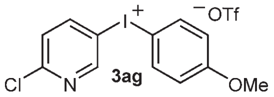
| Entry | **1** Ar$^1$I | | **2** Ar$^2$H | | Salt **3**[b] | Yield [%][c] |
|---|---|---|---|---|---|---|
| 1 | **1b** | 4-BrC$_6$H$_4$I | **2a** | C$_6$H$_6$ | **3c** | 78 |
| 2 | **1b** | 4-BrC$_6$H$_4$I | **2c** | C$_6$H$_5$Br |  **3o** | 91 |
| 3 | **1b** | 4-BrC$_6$H$_4$I | **2m** | C$_6$H$_5$OMe |  **3p** | 58 |
| 4 | **1c** | 4-ClC$_6$H$_4$I | **2a** | C$_6$H$_6$ | **3d** | 65 |
| 5 | **1c** | 4-ClC$_6$H$_4$I | **2d** | C$_6$H$_5$Cl |  **3q** | 83 |
| 6 | **1c** | 4-ClC$_6$H$_4$I | **2m** | C$_6$H$_5$OMe |  **3r** | 57 |
| 7 | **1d** | 2-MeC$_6$H$_4$I | **2a** | C$_6$H$_6$ |  **3s** | 85 |
| 8 | **1d** | 2-MeC$_6$H$_4$I | **2e** | C$_6$H$_5$F |  **3t** | 82 |
| 9 | **1d** | 2-MeC$_6$H$_4$I | **2f** | C$_6$H$_5$Me |  **3u** | 90 |
| 10 | **1d** | 2-MeC$_6$H$_4$I | **2g** | *t*-BuC$_6$H$_5$ |  **3v** | 89 |
| 11 | **1d** | 2-MeC$_6$H$_4$I | **2h** | 1,4-Me$_2$C$_6$H$_4$ |  **3w** | 62 |
| 12 | **1d** | 2-MeC$_6$H$_4$I | **2i** | 1,4-*t*-Bu$_2$C$_6$H$_4$ |  **3x** | 51[d] |
| 13 | **1d** | 2-MeC$_6$H$_4$I | **2j** | 1,3,5-Me$_3$C$_6$H$_3$ |  **3y** | 84 |
| 14 | **1d** | 2-MeC$_6$H$_4$I | **2m** | C$_6$H$_5$OMe |  **3z** | 56[d] |
| 15 | **1e** | 4-MeC$_6$H$_4$I | **2a** | C$_6$H$_6$ | **3f** | 71 |
| 16 | **1e** | 4-MeC$_6$H$_4$I | **2f** | C$_6$H$_5$Me |  **3aa** | 52 |
| 17 | **1f** | 4-*t*-BuC$_6$H$_4$I | **2a** | C$_6$H$_6$ | **3g** | 66[d] |

**Table 3.** (Continued)

| Entry | **1** Ar$^1$I | | **2** Ar$^2$H | | Salt **3**[b] | Yield [%][c] |
|---|---|---|---|---|---|---|
| 18 | **1g** | 4-$NO_2C_6H_4I$ | **2a** | $C_6H_6$ |  **3ab** | 85 |
| 19 | **1h** | 4-$CF_3C_6H_4I$ | **2a** | $C_6H_6$ |  **3ac** | 59 |
| 20 | **1i** | 3-$CF_3C_6H_4I$ | **2a** | $C_6H_6$ |  **3ad** | 63 |
| 21 | **1j** | 4-COOH-$C_6H_4I$ | **2a** | $C_6H_6$ |  **3ae** | 73 |
| 22 | **1k** | 2-chloro-5-iodopyridine | **2a** | $C_6H_6$ |  **3af** | 60 |
| 23 | **1l** | 2-chloro-5-iodopyridine | **2m** | $C_6H_5OMe$ |  **3ag** | 53 |

[a] *Reaction conditions:* **1** (1.0 equiv), **2** (1.1 equivs.), *m*CPBA (1.1 equivs.) and TfOH (2–3 equivs.) in $CH_2Cl_2$, see the Experimental Section for details.
[b] Formed with complete regioselectivity.
[c] Isolated yield.
[d] Isolated by flash chromatography.

*N*-oxidation could not be overcome by changing the reaction conditions, resulting in a mixture of iodonium salts in moderate yields. Gratefully, the more deactivated substrate 2-chloro-5-iodopyridine (**1l**) reacted with benzene and anisole to give salts **3af** and **3ag**, respectively (entries 22 and 23). Surprisingly, the isolation of these salts was facile, in contrast to the salts lacking the chloride substituent. Iodonium salts containing this aryl moiety have recently been used in an efficient total synthesis of (−)-epibatidine.[5] In that report, salt **3af** was obtained in moderate yield after several reaction steps, which was still inadequate for the preparation of salt **3ag**.[31]

The formation of iodonium salts **3** from iodoarenes **1** and substituted arenes **2** was in most cases highly regioselective, yielding salts **3** with high *para*-selectivity. Likewise, the reaction of **1a** with thiophene (**2n**) afforded only 2-substituted **3n**.

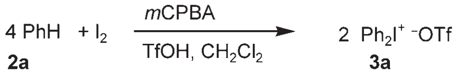
## Direct Synthesis from Arenes and Iodine

Aryl iodides are readily available but often expensive, which would make *in situ* formation of the aryl iodide an appealing extension to our developed synthesis of diaryliodonium salts.[16] Kitamura's group recently showed that (diacetoxyiodo)arenes could be formed directly from arenes and iodine in the presence of an oxidant, presumably with the corresponding aryl iodide as intermediate.[32] We thus envisioned a one-pot reaction of benzene (**2a**) and molecular iodine or lithium iodide with *m*CPBA and TfOH to give iodonium salt **3a**.

Complete transformation of molecular iodine to two iodine(III) molecules would require 3 equivalents of *m*CPBA, and we thus started our investigation with those conditions. To keep the triflic acid:product ratio to 2:1, we used 4 equivalents of TfOH, which indeed delivered salt **3a** in 45 % yield in this *one-pot, three-step reaction* (Table 4, entry 1).[33] Longer reaction time resulted in 61 % yield (entry 2), and an increase of the triflic acid:product ratio to 3:1 gave **3a** in excellent yield within 10 min at room temperature (entry 3). The use of excess *m*CPBA and benzene had a moderate effect (entries 4 and 5).

As seen in the aryl iodide reactions (*vide supra*), the reaction time could be drastically shortened by increasing the temperature, and **3a** was obtained in excellent yields with 4 equivalents of TfOH at 60 – 80 °C (entries 6 and 7). It is thus possible to choose reaction conditions depending on which parameter is deemed most important; time, reagent amount or temperature, which should be of interest when scaling up the reaction.

**Table 4.** Synthesis of salt **3a** directly from benzene and iodine.[a]



$$4\,PhH + I_2 \xrightarrow[TfOH,\ CH_2Cl_2]{mCPBA} 2\,Ph_2I^+\,{}^-OTf$$

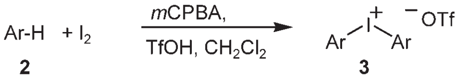
| Entry | **2a** [equivs.] | *m*CPBA [equivs.] | TfOH [equivs.] | *T* [°C] | Time | Yield [%][b] |
|---|---|---|---|---|---|---|
| 1 | 4.1 | 3 | 4 | r.t. | 10 min | 45 |
| 2 | 4.1 | 3 | 4 | r.t. | 20 h | 61 |
| 3 | 4.1 | 3 | 6 | r.t. | 10 min | 92 |
| 4 | 4.1 | 4 | 4 | r.t. | 21 h | 72 |
| 5 | 10 | 4 | 4 | r.t. | 22 h | 81 |
| 6 | 4.1 | 3 | 4 | 60 | 10 min | 92 (87) |
| 7 | 4.1 | 3 | 4 | 80 | 10 min | 93 (80) |
| 8 | 4.1 | 3 | 3 | 80 | 10 min | 46 |
| 9[c] | 10 | 3 | 3 | 80 | 10 min | (51) |
| 10[c] | 10 | 4 | 4 | 80 | 10 min | (66) |
| 11[c] | 10 | 6 | 6 | 80 | 10 min | (72) |

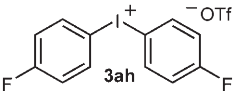
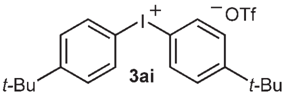
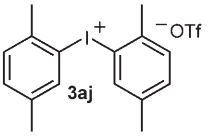
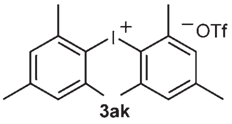
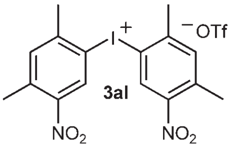
[a] *Reaction conditions:* $I_2$ (1.0 equiv.), **2a**, *m*CPBA and TfOH were stirred in $CH_2Cl_2$ at the indicated temperature and time.

[b] Isolated yield. Numbers in () are results obtained by flash chromatography.

[c] LiI (1 equiv.) was used instead of $I_2$.

**Table 5.** Direct synthesis of salts **3** from arenes and iodine.[a]



| Entry | **2** (ArH) | Product[b] | Yield [%][c] |
|---|---|---|---|
| 1 | **2a** ($C_6H_6$) | **3a** | 93 |
| 2 | **2c** ($C_6H_5Br$) | **3o** | 64 |
| 3 | **2d** ($C_6H_5Cl$) | **3q** | 57 |
| 4 | **2e** ($C_6H_5F$) |  **3ah** | 71 |
| 5[d] | **2f** ($C_6H_5Me$) | **3u:3aa** ratio 3:1 | 52 |
| 6[d] | **2f** ($C_6H_5Me$) | **3u** | 31 |
| 7 | **2g** (*t*-Bu$C_6H_5$) |  **3ai** | 78 |
| 8 | **2h** (1,4-$Me_2C_6H_4$) |  **3aj** | 47 |
| 9 | **2j** (1,3,5-$Me_3C_6H_3$) |  **3ak** | 52 |
| 10 | **2o** (4-nitro-*m*-xylene) |  **3al** | 24 |

[a] *Reaction conditions:* $I_2$ (1.0 equiv.), **2** (4–10 equivs.), *m*CPBA (3–4 equivs.) and TfOH (4 equivs.) in $CH_2Cl_2$, see the Experimental Section for details.

[b] Formed with complete regioselectivity apart from entry 5.

[c] Isolated yield.

[d] Reaction conditions in entry 5: room temperature for 2 h; entry 6: 0 °C for 1 h.

Further investigation showed that a decreased amount of triflic acid to three equivalents lowered the yield considerably (*cf.* entries 7 and 8). Lithium iodide could successfully be employed as iodine source, although an excess of reagents was needed to give useful yields of **3a** (entries 9–11).[34]

This efficient synthesis of diaryliodonium salts was subsequently applied to other arenes (Table 5). The aryl halides **2c–e** gave symmetric salts **3o**, **q**, **ah** with complete *para*-selectivity (entries 2–4). Toluene (**2f**) yielded a mixture of salts **3u** and **3aa** with 3:1 regioselectivity favouring *ortho*-iodination (entry 5). The regioselectivity was higher at lower conversions, and pure **3u** was obtained after one hour at 0 °C (entry 6). *tert*-Butylbenzene (**2g**) proved to be an excellent substrate and delivered salt **3ai** in 78 % yield (entry 7). Other alkyl-substituted arenes, such as *p*-xylene (**2h**) and mesitylene (**2j**), gave salts in moderate yields (entries 8 and 9). Even highly functionalized, deactivated arene **2o** participated in the reaction to give salt **3al** (entry 10). Electron-rich arenes like anisole (**2m**) and thiophene (**2n**) were too reactive under these conditions, only giving black by-products. Unfortunately, all attempts to obtain unsymmetrical salts by using two different arenes in the reaction resulted in product mixtures.[35]

As this one-pot reaction involves several consecutive steps and many possible sources of by-products, it is surprising that salts **3** are easily obtained in moderate to good yields. After the completion of our preliminary report another procedure for the direct synthesis of diaryliodonium triflates from iodine was published, which required heating for 72 h and a sequential anion exchange step.[19]

## Conclusions

A facile, direct synthesis of diaryliodonium triflates from the corresponding aryl iodide and arene has been developed. The products are generally obtained within one hour at room temperature, following an operationally simple procedure. The method is fast, high-yielding and has a large substrate scope. Electron-rich salts are conveniently synthesized from iodobenzene and the corresponding arene, and electron-deficient salts are formed by the reaction of a substituted aryl iodide with an arene. Alkyl-substituted iodonium salts can be formed *via* both routes in similar yields. The protocol can be extended to the synthesis of iodonium salts directly from iodine and arenes, conveniently circumventing the need for aryl iodides.

## Experimental Section

### General Experimental Conditions

The reactions were carried out in sealed tubes to allow for reaction temperatures above the boiling point of $CH_2Cl_2$, and were run without precaution to avoid moisture or air, i.e., without inert gas or dried solvent. TfOH ($\geq$99%) was stored under an argon atmosphere. New, commercially available cans of *m*CPBA were found to contain large and variable amounts of $H_2O$. The *m*CPBA needs to be dried under vacuum at room temperature for 1 h to obtain reproducible results. The percentage of active oxidizing agent in *m*CPBA was determined by iodometric titration.[36] All other chemicals were used as received without further purification. Reaction times and temperatures for each salt together with analytical data for all novel salts are given in the Supporting Information.

### General Procedure for the Synthesis of Salts 3 from Iodoarenes and Arenes

The reactions were generally performed with 2 equivalents of triflic acid, unless this resulted in by-product formation or long reaction times. *m*-Chloroperbenzoic acid (65% active oxidant, 66 mg, 0.26 mmol) and aryl iodide **1** (0.23 mmol) were dissolved in $CH_2Cl_2$ (1 mL) in a sealed tube. The arene **2** (0.26 mmol) was added and the solution was cooled to 0 °C or the tabulated temperature (if lower, see Table S4, Supporting Information) followed by dropwise addition of TfOH (40–60 μL, 0.46–0.69 mmol), resulting in a coloured solution. The reaction mixture was stirred at the indicated temperature and time (see Table S4, Supporting Information) and subsequently concentrated under vacuum (while still cold for low-temperature reactions). $Et_2O$ (1 mL) was added and the mixture was stirred at room temperature for 10 min to precipitate out an off-white solid. To ensure complete precipitation, the flask was stored in the freezer for at least 30 min before the solid was filtered off, washed with $Et_2O$ and dried under vacuum to give diaryliodonium salt **3**.

### Procedure for Electron-Rich Arenes 2m and 2n

Performed as described above apart from the fact that the arene was added at low temperature after an initial oxidation period at higher temperature with the remaining reagents present, see Table S4 (Supporting Information) for details.

### General Procedure for Direct Synthesis of Salts 3 from Arenes and Iodine

*m*-Chloroperbenzoic acid (65% active oxidant, 3–4 equivs., see Table S5, Supporting Information) and iodine (30.0 mg, 0.12 mmol) were dissolved in $CH_2Cl_2$ (1.0 mL) in a sealed tube, which resulted in a dark purple solution that was cooled to 0 °C. Arene **2** (4.1–10 equivs, see Table S5, Supporting Information) was added followed by dropwise addition of TfOH (41 μL, 0.46 mmol), resulting in a colour change to a yellow transparent solution. The solution was stirred at the indicated temperature and time (Table S5, Supporting Information). Work-up and purification was performed as described above.

## Acknowledgements

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[26] Full optimization details are given in the Supporting Information.

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[31] For the synthesis and use of **3af**, see B. Olofsson, V. K. Aggarwal, *Proc. 2nd Int. Conf. on Hypervalent Iodine,* **2006**, 47–50. The attempts to synthesize salt **3ag** are unpublished.

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[33] Iodobenzene was detected in reactions with short reaction time, supporting the assumption that iodobenzene is an intermediate in the reaction.

[34] The formation of lithium triflate complicated the isolation of salt **3a**, and purification was thus performed with flash chromatography instead of precipitation.

[35] For example, benzene + chlorobenzene; benzene + toluene or benzene + anisole.

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