

# Facile One-Pot Synthesis of Diaryliodonium Salts from Arenes and Aryl Iodides with Oxone

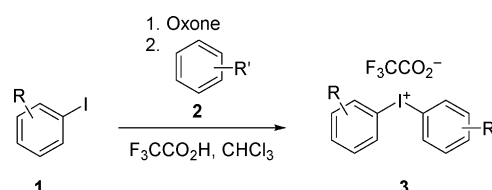
Natalia Soldatova,<sup>[a]</sup> Pavel Postnikov,<sup>[a]</sup> Olga Kukurina,<sup>[a]</sup> Viktor V. Zhdankin,<sup>[a, b]</sup> Akira Yoshimura,<sup>[b]</sup> Thomas Wirth,<sup>\*,[c]</sup> and Mekhman S. Yusubov<sup>\*,[a]</sup>

A straightforward synthesis of diaryliodonium salts is achieved by using Oxone as the stoichiometric oxidant. Slow addition is the key to obtaining good yields and purities of the reaction products, which are highly useful reagents in many different areas of organic synthesis.

Diaryliodonium salts are well-investigated compounds in organic synthesis. They are typically prepared from the corresponding iodoarenes by using oxidative reaction conditions, but iodine(III) compounds have also been used for the generation of diaryliodonium salts and most of these reactions have been summarized in Review articles.<sup>[1]</sup> These compounds have found many applications in synthesis,<sup>[2]</sup> but also in polymerizations as photoinitiators, and some of these compounds even possess biologic activities. Many different strategies have been reported for the synthesis of this compound class by various research groups<sup>[3]</sup> and us.<sup>[4]</sup>

Herein, we describe the straightforward and facile synthesis of symmetrically and unsymmetrically substituted diaryliodonium salts from arenes and iodoarenes in the presence of trifluoroacetic acid with Oxone as stoichiometric oxidant. Similar procedures have been reported by using peroxodisulfates as oxidants,<sup>[5]</sup> but Oxone is more economically viable. We have already investigated the use of Oxone in the presence of trifluoroacetic acid and found it to be more convenient in the synthesis of [bis(trifluoroacetoxy)iodo]arenes.<sup>[6]</sup> Oxone has also been used by Yakura et al. for the oxidation of iodine(I).<sup>[7]</sup> The experimental procedure used to obtain the reaction products

from iodoarenes **1** and arenes **2** is very simple. Initially, iodoarene **1** is reacted with Oxone in the presence of trifluoroacetic acid to generate [bis(trifluoroacetoxy)iodo]arenes before arene **2** is added to the reaction mixture (method A). The workup only consists of an extraction followed by recrystallization of the reaction product. The diaryliodonium compounds are obtained as the trifluoroacetate salts in very good yields (Scheme 1, Table 1). The yields of the overall transformation



**Scheme 1.** Synthesis of diaryliodonium trifluoroacetates using Oxone as a stoichiometric oxidant.

could be improved when arene **2** was added slowly over a period of several hours (method B) to the preformed [bis(trifluoroacetoxy)iodo]arenes. In other cases, the speed of arene addition did not have an influence on the outcome of the synthesis of diaryliodonium salts **3**.

By exchanging trifluoroacetic acid with trifluoromethanesulfonic acid, the corresponding diaryliodonium triflates are accessible. However, slow addition of a mixture of iodoarene **1** and arene **2** to the Oxone with trifluoromethanesulfonic acid is required for good yields in this process. Fast addition will lead to dark-colored solutions and to the formation of decomposition products. The reactions leading to symmetrical as well as unsymmetrical diaryliodonium triflates are summarized in Table 2. Recently, similar protocols have been reported for the synthesis of unsymmetrical diaryliodonium tosylates, although the synthesis consisted of two steps: firstly the oxidation to iodine(III) and secondly the generation of the diaryliodonium species.<sup>[8]</sup>

The yields in this reaction are moderate to good and all products have been purified by recrystallization from ethyl acetate/ hexane (1:10). The reaction is limited to arenes with electron-donating substituents. Even in the case of benzene as an unsubstituted arene, the yield of the arylidonium salt is quite low, as compound **4a** was isolated in only 31% yield (Table 2, entry 1). Entry 13 (Table 2) shows that also heteroaromatic iodides such as 3-iodopyridine can be employed in this reaction, leading to the diaryliodonium compound **4m** in good yield.

The reaction described here is operationally very simple, uses readily available reagents and starting materials and pro-

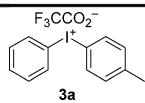
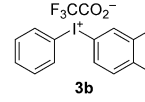
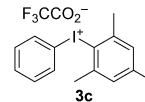
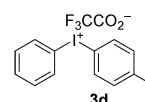
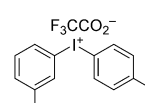
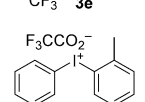
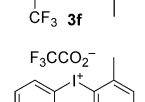
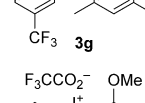
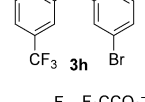
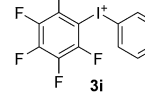
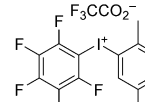
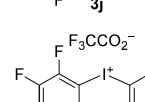
[a] N. Soldatova, P. Postnikov, Dr. O. Kukurina, Prof. Dr. V. V. Zhdankin, Prof. Dr. M. S. Yusubov  
Tomsk Polytechnic University and Siberian State Medical University  
634050 Tomsk (Russia)  
E-mail: yusubov@mail.ru  
Homepage: <http://blogs.cardiff.ac.uk/wirth/>

[b] Prof. Dr. V. V. Zhdankin, Dr. A. Yoshimura  
Department of Chemistry and Biochemistry  
University of Minnesota Duluth, Duluth, MN 55812 (USA)

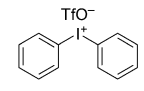
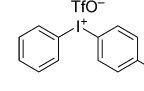
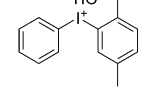
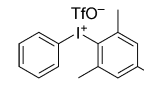
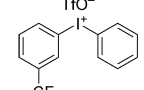
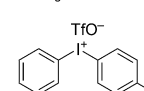
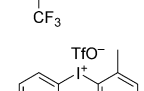
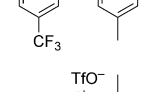
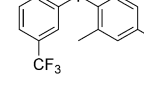
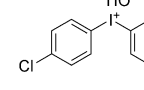
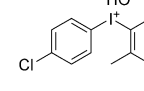
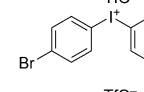
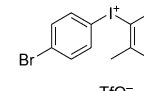
[c] Prof. Dr. T. Wirth  
School of Chemistry, Cardiff University  
Park Place, Main Building, Cardiff CF10 3AT (UK)  
E-mail: wirth@cf.ac.uk

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/open.201600129>.

© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Table 1. Synthesis of diaryliodonium trifluoroacetates.				
Entry	Iodoarene 1	Arene 2	Product 3	Yield 3 [%] (method) <sup>[a]</sup>
1	PhI	PhMe		49 (A) <sup>[b]</sup> 64 (B) <sup>[b]</sup>
2	PhI	1,2-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		80 (A)
3	PhI	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		92 (A) 94 (B)
4	PhI	PhOMe		81 (B)
5	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	PhMe		87 (B) <sup>[b]</sup>
6	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	1,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		86 (B)
7	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		89 (A) 87 (B)
8	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	4-MeOC <sub>6</sub> H <sub>4</sub> Br		94 (B)
9	C <sub>6</sub> F <sub>5</sub> I	PhMe		62 (B) <sup>[b]</sup>
10	C <sub>6</sub> F <sub>5</sub> I	1,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		59 (B)
11	C <sub>6</sub> F <sub>5</sub> I	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		74 (A) 80 (B)
12	C <sub>6</sub> F <sub>5</sub> I	PhOMe		91 (B)

[a] Method A: Addition of 2 directly after formation of [bis(trifluoroacetoxy)iodo]arene. Method B: Addition of 2 over 6 h after formation of [bis(trifluoroacetoxy)iodo]arene. [b] Small amounts (2–5%) of *ortho*-isomer were observed.

Table 2. Synthesis of diaryliodonium triflates.						
TfOH and Oxone (2 eq.)		+	Arl 1 (1 eq.) Ar'H 2 (1.2 eq.)	→	TfO <sup>-</sup> Ar-I <sup>+</sup> -Ar'	4
				MeCN slow addition (6 h)		
Entry	Iodoarene 1	Arene 2	Product 4	Yield 4 [%]		
1	PhI	PhH		31		
2	PhI	PhMe		68 <sup>[a]</sup>		
3	PhI	1,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		52		
4	PhI	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		82		
5	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	PhH		33		
6	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	PhMe		51 <sup>[a]</sup>		
7	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	1,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		51		
8	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		84		
9	4-ClC <sub>6</sub> H <sub>4</sub> I	PhMe		61 <sup>[a]</sup>		
10	4-ClC <sub>6</sub> H <sub>4</sub> I	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		53		
11	4-BrC <sub>6</sub> H <sub>4</sub> I	PhMe		60 <sup>[a]</sup>		
12	4-BrC <sub>6</sub> H <sub>4</sub> I	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		61		
13	3-I-C <sub>5</sub> H <sub>4</sub> N	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>		68		

[a] Small amounts (2–5%) of *ortho*-isomer were observed.

vides pure reaction products in good yields. Synthetic applications of the diaryliodonium compounds are not provided here; electronically<sup>[9]</sup> or sterically very different substituents can react

selectively, whereas similar aryl moieties often lead to mixed results in aryl-transfer reactions.<sup>[10]</sup> Recently, even catalytic approaches involving diaryliodonium compounds have been published.<sup>[11]</sup>

In summary, we report a practically very simple, high-yielding process to make diaryliodonium triflates and trifluoroacetates in good yields by using Oxone as a cheap stoichiometric oxidant.

## Experimental Section

### Synthesis of Diaryliodonium Trifluoroacetates

#### Method A

To a solution of iodoarene **1** (1.0 mmol) in a mixture of trifluoroacetic acid (1.5 mL) and chloroform (0.5 mL), Oxone (400 mg, 1.3 mmol) was added whilst stirring at room temperature. After complete disappearance of the iodoarene (monitored by TLC), arene **2** (1.7–3.5 mmol) was added and the solution was stirred for approximately 20 h (see supporting information). A change to a dark brown color was observed. After addition of CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and H<sub>2</sub>O (5 mL), the organic layer was separated, washed with H<sub>2</sub>O (5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and the organic solvent removed under vacuum. The crude products **3** were further purified by recrystallization from EtOAc/hexane (1:10).

### Synthesis of Diaryliodonium Trifluoroacetates

#### Method B

To a solution of iodoarene **1** (1.0 mmol) in a mixture of trifluoroacetic acid (1.5 mL) and chloroform (0.5 mL), Oxone (400 mg, 1.3 mmol) was added whilst stirring at room temperature. After complete disappearance of the iodoarene (monitored by TLC), arene **2** (1.05–1.50 mmol) in CHCl<sub>3</sub> (2 mL) was added over 6 h by using a syringe pump, and the solution was stirred for approximately 20 h (see the Supporting Information). A change to a light brown color was observed. After addition of CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and H<sub>2</sub>O (5 mL), the organic layer was separated, washed with H<sub>2</sub>O (5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and the organic solvent removed under vacuum. The crude products **3** were further purified by recrystallization from EtOAc/hexane (1:10).

### Synthesis of Diaryliodonium Triflates

To a solution of trifluoromethanesulfonic acid (2.26 mmol, 339 mg, 200 μL) and Oxone (614 mg, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), a solution of iodoarene **1** (1.0 mmol) and arene **2** (1.2 mmol) in acetonitrile (2 mL) was added over 6 h by using a syringe pump. Then, Oxone (307 mg, 1 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature overnight and a color change from red–orange to pale yellow was observed. After addition of CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and H<sub>2</sub>O (5 mL), the organic layer was separated, washed with H<sub>2</sub>O (5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and the organic solvent removed under vacuum. The crude products **4** were further purified by recrystallization from EtOAc/hexane (1:10).

## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (RFBR-KO\_a 16-53-10046) and the Royal Society (IE160304). Support from the School of Chemistry, Cardiff University, is also gratefully acknowledged. We thank the EPSRC National Mass Spectrometry Facility, Swansea, for mass spectrometric data. We thank Prof. B. Olofsson, Stockholm, for valuable discussions.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** diaryliodonium triflates · diaryliodonium trifluoroacetates · iodine(III) compounds · oxidation · synthesis

- [1] a) M. S. Yusubov, A. V. Maskaev, V. V. Zhdankin, *ARKIVOC* **2011**, *i*, 370–409; b) E. A. Merritt, B. Olofsson, *Angew. Chem. Int. Ed.* **2009**, *48*, 9052–9070; *Angew. Chem.* **2009**, *121*, 9214–9234.
- [2] a) *Hypervalent Iodine Chemistry in Topics in Current Chemistry*, Vol. 373 (Ed.: T. Wirth), Springer, Berlin, **2016**; b) V. V. Zhdankin, *Hypervalent Iodine Chemistry*, Wiley, Chichester, **2014**.
- [3] a) T. Kitamura, J. Matsuyuki, H. Taniguchi, *Synthesis* **1994**, 147–148; b) M. A. Carroll, V. W. Pike, D. A. Widdowson, *Tetrahedron Lett.* **2000**, *41*, 5393–5396; c) A. Shah, V. W. Pike, D. A. Widdowson, *J. Chem. Soc. Perkin Trans. 1* **1997**, 2463–2466; d) M. Bielawski, B. Olofsson, *Chem. Commun.* **2007**, 2521–2523; e) M. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Catal.* **2007**, *349*, 2610–2618; f) M. Zhu, N. Jalalian, B. Olofsson, *Synlett* **2008**, 592–596; g) M. Bielawski, D. Aili, B. Olofsson, *J. Org. Chem.* **2008**, *73*, 4602–4607; h) L. Qin, K. D. Neumann, E. J. Linstead, K. McCauley, J. Veness, J. J. Kempinger, S. G. DiMagno, *Eur. J. Org. Chem.* **2015**, 5919–5924.
- [4] a) K. Watts, W. Gattrell, T. Wirth, *Beilstein J. Org. Chem.* **2011**, *7*, 1108–1114; b) M. Brown, M. Delorme, F. Malmedy, J. Malmgren, B. Olofsson, T. Wirth, *Synlett* **2015**, 26, 1573–1577; c) R. Edwards, W. de Vries, A. D. Westwell, S. Daniels, T. Wirth, *Eur. J. Org. Chem.* **2015**, 6909–6916; d) P. J. Stang, V. V. Zhdankin, R. Tykwinski, N. S. Zefirov, *Tetrahedron Lett.* **1991**, *32*, 7497–7498; e) V. V. Zhdankin, M. C. Scheuller, P. J. Stang, *Tetrahedron Lett.* **1993**, *34*, 6853–6856; f) P. S. Postnikov, O. A. Gusebnikova, M. S. Yusubov, A. Yoshimura, V. N. Nemykin, V. V. Zhdankin, *J. Org. Chem.* **2015**, *80*, 5783–5788.
- [5] a) M. D. Hossain, Y. Ikegami, T. Kitamura, *J. Org. Chem.* **2006**, *71*, 9903–9905; b) M. D. Hossain, T. Kitamura, *Tetrahedron* **2006**, *62*, 6955–6960.
- [6] A. A. Zagulyaeva, M. S. Yusubov, V. V. Zhdankin, *J. Org. Chem.* **2010**, *75*, 2119–2122.
- [7] T. Yakura, M. Omoto, Y. Yamauchi, Y. Tian, A. Ozono, *Tetrahedron* **2010**, *66*, 5833–5840.
- [8] T. L. Seidl, S. K. Sundalam, B. McCullough, D. R. Stuart, *J. Org. Chem.* **2016**, *81*, 1998–2009.
- [9] S. Schäfer, T. Wirth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2786–2789; *Angew. Chem.* **2010**, *122*, 2846–2850.
- [10] J. Malmgren, S. Santoro, N. Jalalian, F. Himo, B. Olofsson, *Chem. Eur. J.* **2013**, *19*, 10334–10342.
- [11] M. Reitti, P. Villo, B. Olofsson, *Angew. Chem. Int. Ed.* **2016**, *55*, 8928–8932; *Angew. Chem.* **2016**, *128*, 9074–9078.

Received: October 22, 2016

Revised: November 21, 2016

Published online on December 16, 2016