Electrochemical Oxidative Syntheses of NH-Sulfoximines, NH-Sulfonimidamides and Dibenzothiazines via Anodically Generated Hypervalent Iodine Intermediates

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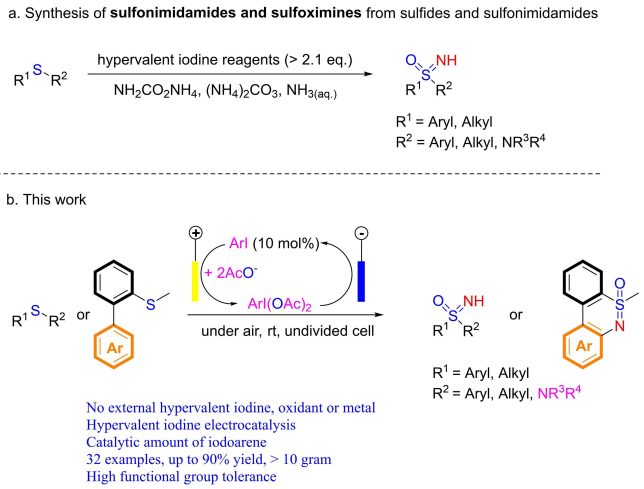
Herein, we report a general method for the synthesis of NH-sulfoximines and NH-sulfonimidamides through direct electrochemical oxidative catalysis involving an iodoarene(I)/iodoarene (III) redox couple. In addition, dibenzothiazines can be synthesized from [1,1′-biaryl]-2-sulfides under standard conditions. Notably, only a catalytic amount of iodoarene is required for the generation in situ of an active hypervalent iodine catalyst, which avoids the need for an excess of a hypervalent iodine reagent relative to conventional approaches. Moreover, this protocol features broad substrate scope and wide functional group tolerance, delivering the target compounds with good-to-excellent yields even for a scale of more than 10 g.

Introduction

Electrochemical synthesis has been recognized as fascinating sustainable chemistry due to no need for stoichiometric redox reagents, thereby avoiding the accompanying waste stream.[1] In the past ten years, there has been considerable progress in this research area, and the corresponding methods for constructing various types of chemical bonds, synthesizing value-added organic products, and heterocyclic compounds have been developed.[2] Among them, hypervalent iodine compounds have a wide range of applications in electrochemical synthesis.[3] Schmidt and Meinert reported the first electrochemical synthesis of (difluoroiodo)benzene($PhIF_2$).[3d] In 2019, Elsherbini and Wirth reported an electrochemical generator of hypervalent iodine reagents in flow reactors.[3e] The iodine(III) compounds generated at the anode are successfully used as mediators for different valuable chemical transformations.[4] Iodine(III)-mediated electrosynthesis is usually carried out in two steps: (1) generation of a hypervalent iodine compound and (2) addition of the substrate (ex-cell mediation).[5] Hypervalent iodine electrochemistry is used mainly in ex-cell protocols, which defeats the purpose of using electrochemistry. Therefore, an electrocatalytic one-pot method (in-cell mediation) would be more desirable, in which only a catalytic amount of the mediator is used. To date, there has been only one report of a genuinely electrocatalytic application of hypervalent iodine (III) species; thus, the development of electrocatalytic applications for hypervalent iodine(III) species remains highly rewarding.[6]

Dibenzothiazines, and NH-sulfoximines and NH-sulfonimidamides, the mono-aza analogs of sulfones and sulfonamides, respectively, are of interest as bioisosteres for drug design.[7] Recently several research groups have made progress in simplifying the imination of thioethers[8] and sulfenamides[9] to afford NH-sulfoximines and NH-sulfonimidamides (Scheme 1a). Tota et al. reported the first direct synthesis of NH-sulfoximines from sulfides using phenyliodine(III) diacetate as the oxidant and ammonium carbamate as the ammonia source.[8a] Then Chen and co-workers achieved the synthesis of dibenzothiazines from 2-biphenyl sulfides.[8e] Bolm and co-workers developed a one-pot synthesis of thiophene NH-sulfoximines from thiophenes.[8c] In 2019, Luisi and co-workers reported a facile metal-free protocol for the direct synthesis of NH-sulfonimida-



Scheme 1. Literature background.

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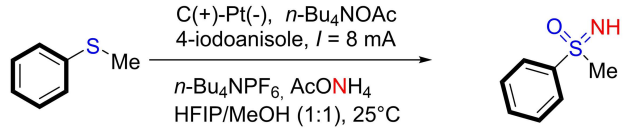
mides from sulfenamides.[9] By using excess iodosobenzene as the oxidant, a highly chemoselective N- and O-group transfer to sulfenamides was achieved in *i*PrOH. However, the utility of these methods is limited by the need to use large excesses of hypervalent iodine reagents. We speculated that hypervalent iodine species produced by electrochemical oxidation of aryl iodides could be used to oxidize sulfides to form NH-sulfoximines directly. Herein, we report that hypervalent iodine generated by anodic oxidation of an iodoarene can be directly used to synthesize NH-sulfoximines and NH-sulfonimidamides from sulfides and sulfenamides, respectively (Scheme 1d). This electrocatalytic system employs a catalytic amount of iodoarene. Furthermore, under the reaction conditions, [1,1′-biaryl]-2-sulfides can be directly transformed to dibenzothiazines.

Results and Discussion

For optimization of the reaction conditions, we used thioanisole (**1a**) as a model sulfide substrate, $AcONH_4$ as an ammonium source, *n*-Bu_4NPF_6 as a supporting electrolyte in an undivided cell (Table 1). Encouragingly, when the reaction was performed at 25 °C in 1:1 (*v*/*v*) hexafluoroisopropanol (HFIP)/MeOH at a constant current of 8 mA with an inexpensive graphite (C) anode, a Pt plate cathode, and 4-iodoanisole as the catalyst, desired NH-sulfoximine **2a** could be isolated in 84% yield (entry 1). Variation of the *para* substituent of the iodoarene decreased the yield (Table S1). Different anode materials (a Pt plate [36%] or reticulated vitreous carbon [64%]) were also less effective (entries 2 and 3). The combination of a C anode and an Mg cathode yielded none of the desired products (entry 4). Next, we investigated the effects of solvents: HFIP, MeOH, or CH_3CN alone gave only very low yields of **2a** (entries 5–7), and changing the HFIP/MeOH ratio also decreased the yield (entries 8 and 9). No product was obtained in the absence of *n*-Bu_4NOAc (entry 10). When *n*-Bu_4NOAc was replaced by AcOH, the yield of **2a** was only 21% (entry 11). Increasing or decreasing the current decreased the yield (entries 12 and 13). Alternative supporting electrolytes (*n*-Bu_4NBF_4, *n*-Bu_4NClO_4, and $LiClO_4$) were less effective than *n*-Bu_4NPF_6 (entries 14–16). Screening of other ammonium sources revealed that $NH_2CO_2NH_4$ and $NH_3 \cdot H_2O$ gave lower yields than $AcONH_4$ (entries 17 and 18); and NH_4Cl, NH_4Br, and NH_4I gave none of the desired product (entries 19–21). Methyl phenyl sulfone was obtained in the absence of iodoarenes (entry 22). Finally, in the absence of electrolyte or electric current, no **2a** was obtained (entries 23 and 24).

Having optimized the conditions for this in-cell method, we proceeded to explore its substrate scope (Scheme 2). Methyl phenyl sulfides **1** bearing an electron-withdrawing group (Br, Cl,

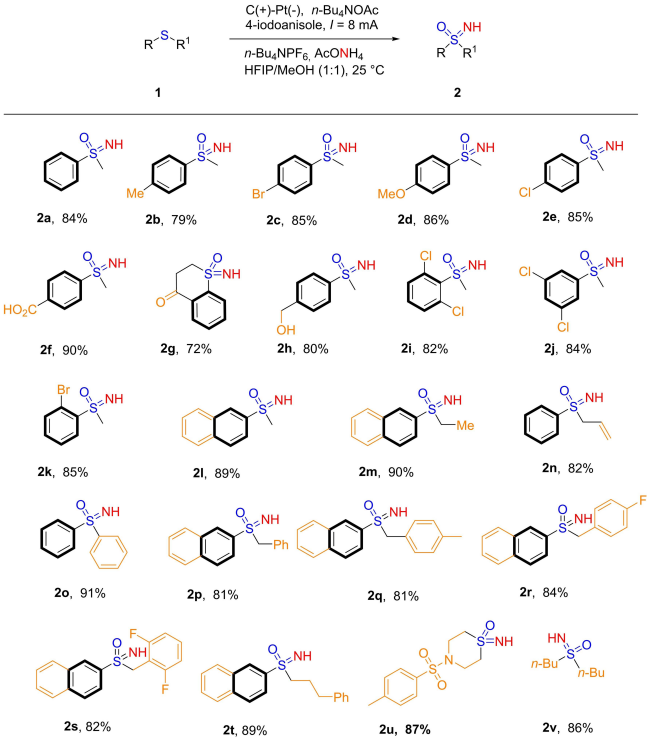
Table 1. Optimization of reaction conditions.[a]



1a **2a**

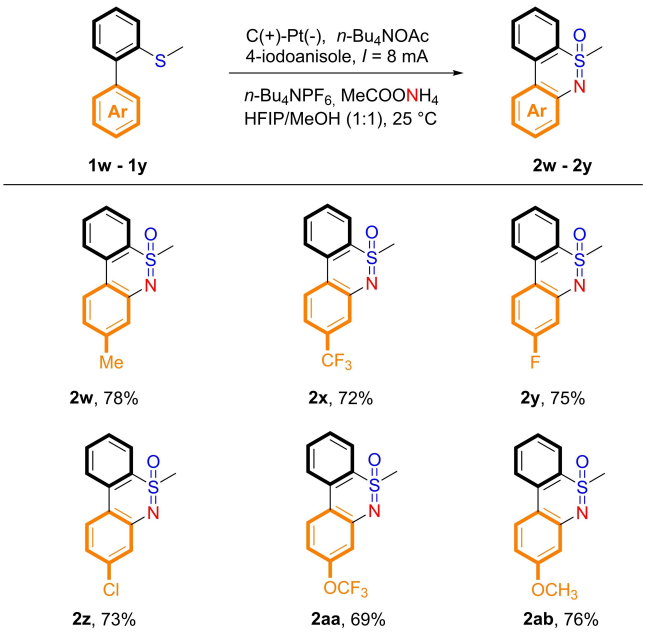
Entry	Variation from standard conditions[a]	Yield of **2a**[b] [%]
1	none	84
2	Pt anode/Pt cathode	36
3	Reticulated vitreous carbon anode/Pt cathode	64
4	C anode/Mg cathode	0
5	HFIP instead of 1:1 HFIP/MeOH	32
6	MeOH instead of 1:1 HFIP/MeOH	12
7	CH_3CN instead of 1:1 HFIP/MeOH	Trace
8	2:1HFIP/MeOH instead of 1:1HFIP/MeOH	76
9	1:2 HFIP/MeOH instead of 1:1 HFIP/MeOH	54
10	No *n*-Bu_4NOAc	0
11	AcOH instead of *n*-Bu_4NOAc	21
12	10 mA instead of 8 mA	51
13	6 mA instead of 8 mA	71
14	*n*-Bu_4NBF_4 instead of *n*-Bu_4NPF_6	71
15	*n*-Bu_4NClO_4 instead of *n*-Bu_4NPF_6	63
16	$LiClO_4$ instead of *n*-Bu_4NPF_6	12
17	$NH_2CO_2NH_4$ instead of $AcONH_4$	76
18	$NH_3 \cdot H_2O$ instead of $AcONH_4$	77
19	NH_4Cl instead of $AcONH_4$	0
20	NH_4Br instead of $AcONH_4$	0
21	NH_4I instead of $AcONH_4$	0
22	No iodoarenes	0[b]
23	No electrolyte	No reaction
24	No electric current	No reaction

[a] Standard conditions: C anode (40 mm×10 mm×2 mm), Pt cathode (40 mm×10 mm×2 mm), *I* = 8 mA, **1a** (0.2 mmol), $AcONH_4$ (0.4 mmol), iodoarenes (0.02 mmol), *n*-Bu_4NOAc (0.2 mmol), 1:1 (*v*/*v*) HFIP/MeOH (4 mL), *n*-Bu_4NPF_6 (0.1 mol L^{-1}), 25 °C. [b] Isolated yields are reported. [c] Methyl phenyl sulfone was isolated in yields of 41%.

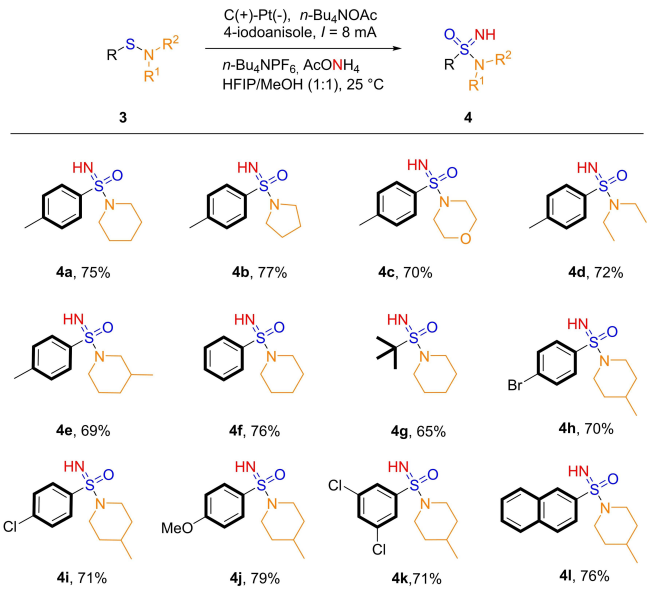


Scheme 2. Reactions of sulfides 1 to afford NH-sulfoximines 2. Standard conditions: C anode (40 mm×10 mm×2 mm), Pt cathode (40 mm×10 mm×2 mm), *I* = 8 mA, **1a** (0.2 mmol), $AcONH_4$ (0.4 mmol), iodoarenes (0.02 mmol), *n*-Bu_4NOAc (0.2 mmol), 1:1 (*v*/*v*) HFIP/MeOH (4.0 mL), *n*-Bu_4NPF_6 (0.1 mol L^{-1}), 25 °C. **2f**: 4-(Methylthio)benzaldehyde was used as the substrate.

ketone) or electron-donating groups (OMe, Me) at the *para* position of the phenyl ring gave the corresponding products in good yield (**2b**–**2e**, **2g**). Note that a substrate with a *para* aldehyde substituent gave a 90% yield of NH-sulfoximine **2f**, the product of oxidation of the aldehyde group to the corresponding acid. A substrate with an alcohol functional group was well tolerated, providing **2h** in 80% yield. The position of the substituents on the benzene ring seemed to have little influence on the yield. For example, 2,6-dichloro- and 3,5-dichloro-substituted products **2i** and **2j** were obtained in similar good yields, and the yield of *ortho*-bromo compound **2k** was the same as that of *para*-bromo compound **2c**. A 2-naphthyl derivative gave an excellent yield of **2l** (89% yield). Subsequently, we varied both the R and the R^1 groups of the sulfide. The steric bulk of the groups generally had little effect on the transformation; substrates bearing an ethyl, allyl, phenyl, or benzyl group at R^1 worked well (**2m**–**2p**), as did sulfides with substituted benzyl groups (**2q** and **2r**) or a phenylpropyl group (**2t**). Finally, dialkyl NH-sulfoximines **2u** and **2v** could also be obtained in high yields.



Scheme 3. Reactions of [1,1′-biaryl]-2-sulfonamides **1w**–**1y** to afford dibenzothiazines **2w**–**2y**. Standard conditions: C anode (40 mm×10 mm×2 mm), Pt cathode (40 mm×10 mm×2 mm), I = 8 mA, **1a** (0.2 mmol), $AcONH_4$ (0.4 mmol), 4-iodoanisole (0.02 mmol), *n*-Bu_4NOAc (0.2 mmol), 1:1 (*v*/*v*) HFIP/MeOH (4.0 mL), *n*-Bu_4NPF_6 (0.1 mol L^{-1}), 25 °C, 6 h.



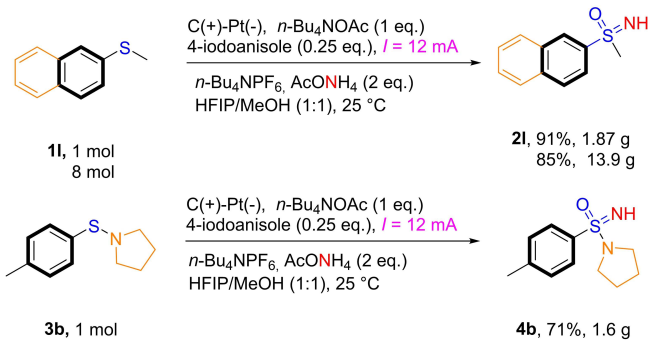
Scheme 4. Reactions of sulfenamides **3** to afford NH-sulfonimidamides **4**. Standard conditions: C anode (40 mm×10 mm×2 mm), Pt cathode (40 mm×10 mm×2 mm), I = 8 mA, **1a** (0.2 mmol), $AcONH_4$ (0.4 mmol), iodoarenes (0.02 mmol), *n*-Bu_4NOAc (0.2 mmol), 1:1 (*v*/*v*) HFIP/MeOH (4.0 mL), *n*-Bu_4NPF_6 (0.1 mol L^{-1}), 25 °C.

To further verify the generality of our electrochemical approach, we used an [1,1′-biaryl]-2-sulfonamides as the substrate (Scheme 3). When [1,1′-biaryl]-2-sulfonamides was used, the product with dibenzothiazines was obtained. The [1,1′-biaryl]-2-sulfonamides with a substituent (e.g., Me–, OCF_3, F, Cl, OMe, CF_3) provided the corresponding benzothiazines (**2w**–**2ab**) in moderate yields.

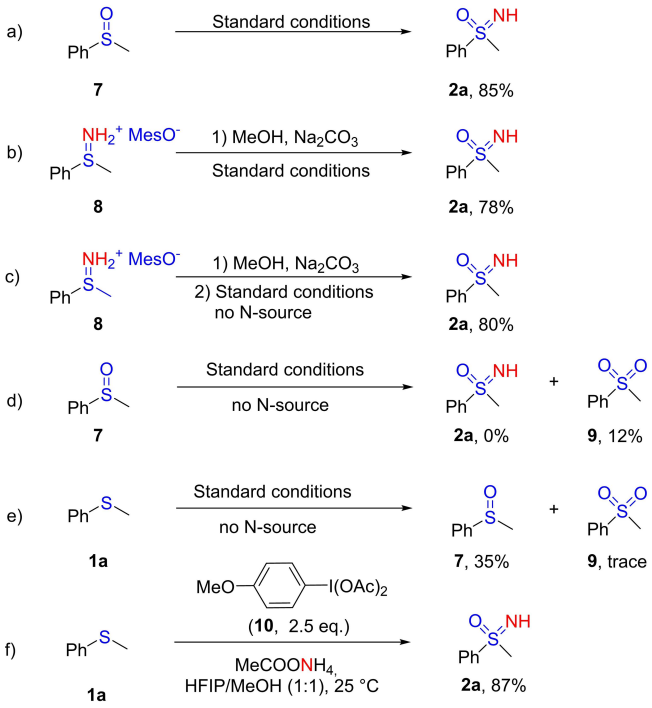
We also used this hypervalent iodine electrocatalysis method to synthesize NH-sulfonimidamides from sulfenamides **3** (Scheme 4). Initially, we focused on varying the NR^1R^2 group of the sulfenamide. Gratifyingly, the reactions were generally very clean, giving desired unprotected tertiary sulfonimidamides **4a**–**4e** in moderate isolated yields. To our delight, a benzenesulfenamide with a piperidine ring and a *t*-butyl sulfenamide with a piperidine ring also reacted smoothly to give corresponding sulfonimidamides **4f** and **4g**, respectively, in 76% and 65% yields, illustrating the broad substrate scope of this novel strategy. 4-Methylpiperidine-substituted sulfenamides **3h**–**3l**, bearing several aromatic, were investigated. Sulfonimidamides **4h**–**4j** were obtained in yields ranging from 45% to 89%. 2-Naphthyl and disubstituted phenyl substituents furnished the corresponding NH-sulfonimidamides **4l** and **4k**.

To demonstrate the practical utility of this novel electrochemical method, we carried out the reactions of **1l** and **3b** on a 1 mol scale at a constant current of 12 mA by using a commercial IKA ElectraSyn 2.0 apparatus. Products **2l** and **4b** were isolated in yields of 91% and 71% (Scheme 5). Moreover, a reaction of 8 mol of **1l** gave **2l** in 85% yield (13.9 g).

To gain insight into the reaction mechanism, we carried out a series of control experiments involving thioanisole derivatives (Scheme 6). Under the standard conditions, separate reactions of methyl phenyl sulfoxide **7** and methyl phenyl sulfilimine **8** showed complete selectivity for the formation of sulfoximine **2a** (Scheme 6a,b). Sulfilimine **8** gave **2a** even in the absence of the ammonium source (Scheme 6c). In contrast, the reaction of sulfoxide **7** in the absence of the ammonium source gave not **2a** but methyl phenyl sulfone **9** (Scheme 6d). Finally, the reaction of sulfide **1a** gave a 35% yield of the oxidation product (sulfoxide **3b**) and a trace of methyl phenyl sulfone **9** in the absence of the ammonium source (Scheme 6e). When thioanisole **1a** was reacted with 2 equiv. of ammonium acetate ($MeCOONH_4$) in the presence of 2.5 equiv. of I^{III} (**10**) in HFIP/



Scheme 5. Gram-scale syntheses of NH-sulfoximine and NH-sulfonimidamide.



Scheme 6. Control experiments.

MeOH at 25 °C, exclusive formation of the corresponding sulfoximine **2a** was observed (Scheme 6f).

Cyclic voltammograms were carried out at 100 mV s^{-1} with a 3 mm diameter glassy carbon electrode in related compounds (Figure 1). When using HFIP/MeOH (1:1) as the solvent, no obvious oxidative peak is observed (relative to the background curve 1 in Figure 1). Additionally, there is also no apparent oxidative peak is observed in the presence of 4-iodoanisole (Figure 1, curve 2). However, an oxidative peak is observed at about 1.9 V vs. Ag/AgCl in the presence of thioanisole (Figure 1, curve 3), which could be ascribed to the oxidation of thioanisole (**1a**). Another oxidative peak is observed at about 2.2 V vs. Ag/AgCl in the presence of $AcONH_4$/Bu_4NOAc/4-iodoanisole (Figure 1, curve 4),[6] which may correspond to the electrochemical generation of hypervalent iodine reagents. As expected, two

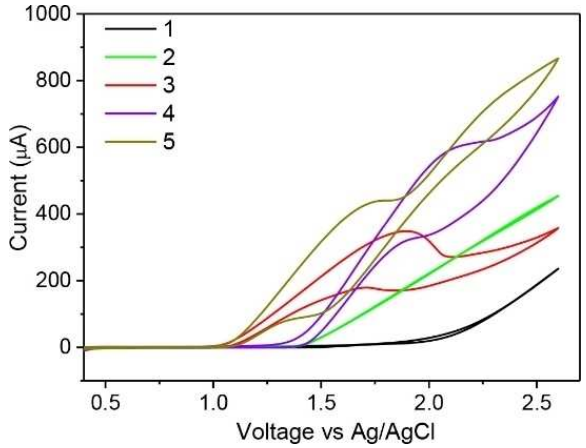
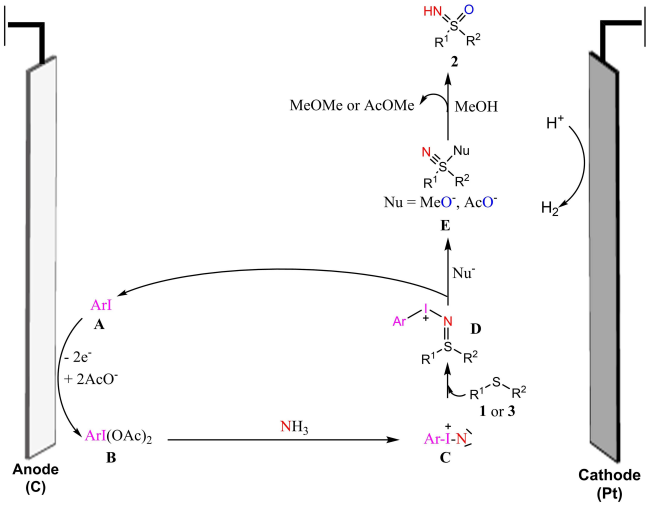


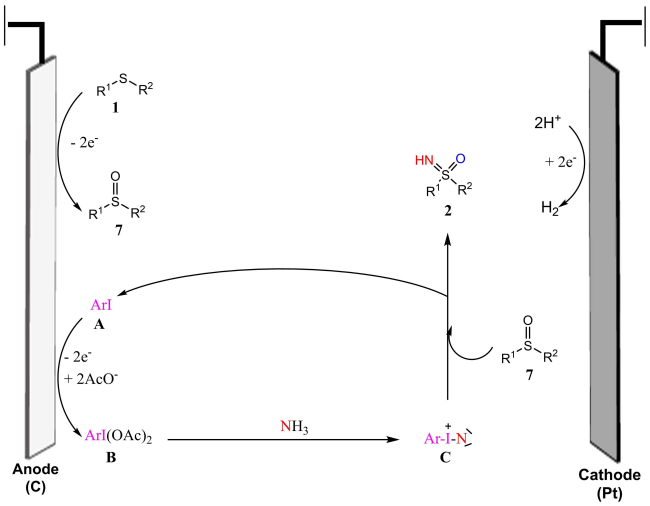
Figure 1. Cyclic voltammograms recorded at 100 mV/s with a 3 mm diameter glass carbon electrode as working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode in different electrolyte solvents: (1) background; (2) 10.0 mM 4-iodoanisole; (3) 10.0 mM Thioanisole (**1a**); (4) 10.0 mM $AcONH_4$/Bu_4NOAc/4-iodoanisole; (5) 10 mM $AcONH_4$/Bu_4NOAc/4-iodoanisole /Thioanisole.

enhanced oxidation peaks at around 1.8 V and 2.3 V vs. Ag/AgCl of curve 5 are observed when in the presence of $AcONH_4$/Bu_4NOAc/4-iodoanisole/thioanisole, indicating the efficiency of the electrochemical generation of hypervalent iodine reagents is improved.

A plausible mechanism for the generation of NH-sulfoximines and NH-sulfonimidamides by means of our electrochemical method is shown in Schemes 7 and 8. Based on experiments, it is likely that the two mechanisms are simultaneously occurring in the reaction system. Hypervalent iodine catalyst **B** ((4-methoxyphenyl)-iodanediyl(III) diacetate) is generated in situ via anodic oxidation of the iodoarene (**A**) in acetate-enriched HFIP under constant current electrolysis.[10] Phenyliodine(III) diacetate directly reacts with NH_3 to afford key



Scheme 7. (Path a) Proposed mechanism for electrochemical synthesis of NH-sulfoximines and NH-sulfonimidamides.



Scheme 8. (Path b) Proposed mechanism for electrochemical synthesis of NH-sulfoximines and NH-sulfonimidamides.

nitrene intermediate **C**.[8c] Then **C** is captured by the sulfide to afford sulfilimine **D**, which undergoes nucleophilic attack by an acetate anion or MeOH to afford sulfanenitrile intermediate **E** and regenerate iodoarene **A**. Intermediate **E** is attacked by MeOH to afford sulfoximines **2** (Scheme 7).

Sulfides **1** can be oxidized to sulfones **7** under electrochemical conditions (Scheme 8). Intermediate **C** react directly with the sulfoxide (**7**) afford the sulfoximine **2**.[11]

Conclusion

We have developed the first method for the preparation of NH-sulfoximines, NH-sulfonimidamides, and dibenzothiazines by means of hypervalent iodoarene-catalyzed reactions using electricity without any chemical oxidant. Highly selective one-pot transfers of NH and O were achieved with a simple ammonia source and a catalytic amount of an iodoarene. This efficient electrochemical method provides access to NH-sulfoximines, NH-sulfonimidamides, and dibenzothiazines starting from readily available sulfides, sulfenamides in yields up to 90%. Notably, the electrochemical approach is inherently safe in that the electric current can be turned off to avoid runaway reactions.

Experimental Section

(Using synthesis of **2a** as an example). An undivided cell was equipped with a carbon sheet anode (4 cm × 10 cm × 2 mm) and a platinum plate (40 mm × 10 mm × 2 mm) and connected to a DC regulated power supply. To the cell was added thioanisole **1a** (0.2 mmol), $AcONH_4$ (0.4 mmol), 4-iodoanisole (0.02 mmol), *n*-Bu_4NOAc (0.2 mmol), *n*-Bu_4NPF_6 (0.1 mol L^{-1}) and HFIP/MeOH (2.0 mL : 2.0 mL) were added. The mixture was electrolyzed using constant current conditions (~8 mA cm^{-2}) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the 1a), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of NaCl, and the product was then extracted with Dichloromethane (3 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc (*v*/*v* = 5 : 1) as eluent to afford the desired pure product **2a**.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: ammonia · electrochemical synthesis · iodine · sulfonimidamides · sulfoximines

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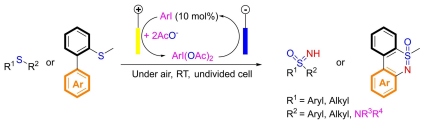
FULL PAPERS

Sprinkles of iodine: A method is reported for the direct electrochemical oxidative synthesis of NH-sulfoximines, NH-sulfonimidamides, and dibenzothiazines, respectively, with catalysis by an iodoarene(I)/iodoarene(III) redox couple. The method requires only a catalytic amount of iodoarene, and a hypervalent iodine catalyst is generated in situ from the iodoarene by anodization, which avoids the need for an excess of a hypervalent iodine reagent.



No external hypervalent iodine, oxidant or metal
Hypervalent iodine electrocatalysis
Catalytic amount of iodoarene
32 examples, up to 90% yield, > 10 g
High functional group tolerance

Dr. X. Kong, L. Lin, Dr. X. Chen, Dr. Y. Chen, Dr. W. Wang*, Prof. Dr. B. Xu**