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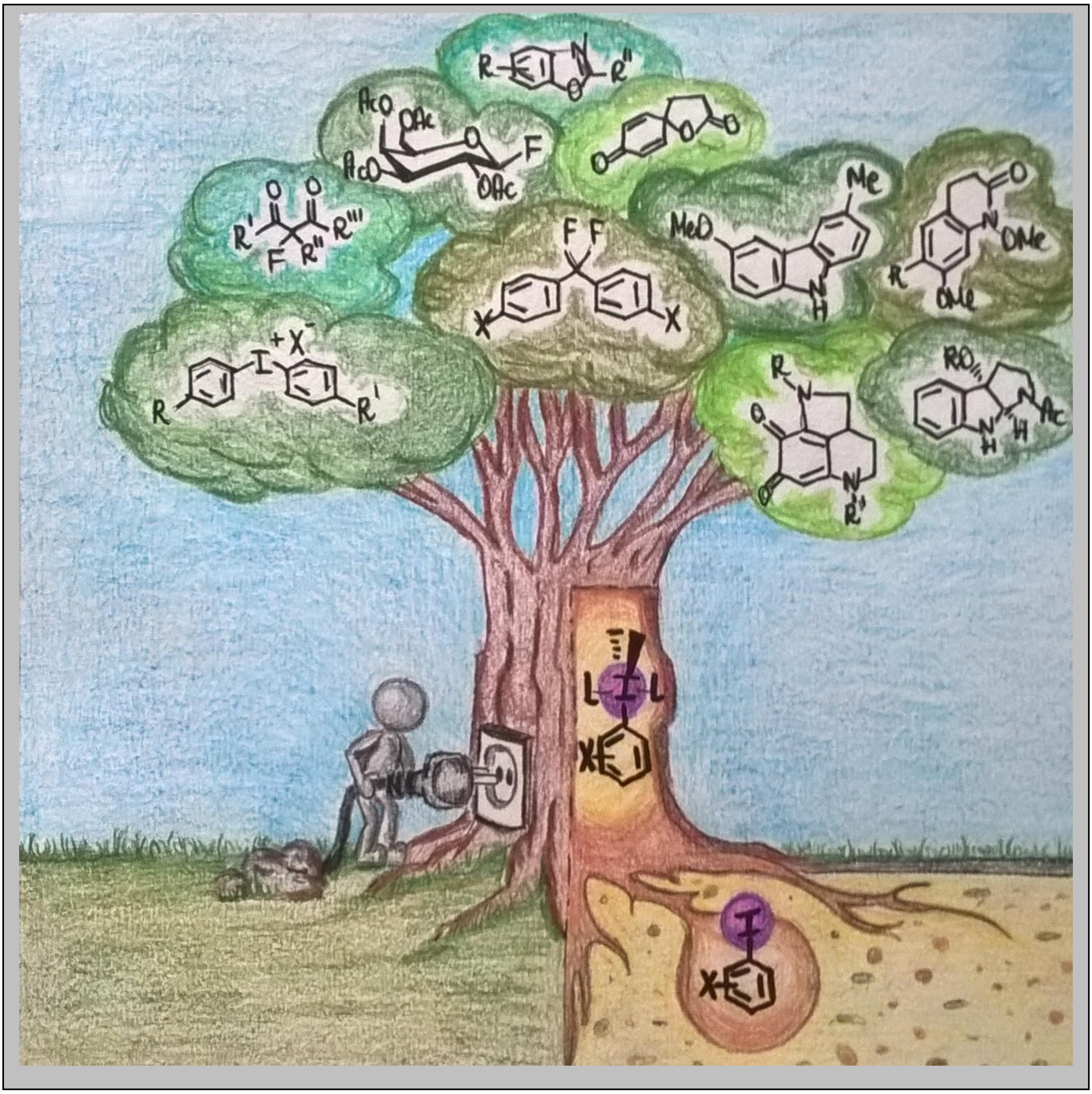
Hypervalent Iodine Reagents by Anodic Oxidation: a Powerful Green Synthesis

Mohamed Elsherbini,[a] and Thomas Wirth*[a]



Abstract: The anodic oxidation of aryl iodides is a powerful method for the synthesis of hypervalent iodine reagents, which eliminates the necessity to use expensive or hazardous chemical oxidizing reagents. The hypervalent iodine reagents generated at the anode are successfully used as either in-cell or ex-cell mediators for different valuable chemical transformations such as fluorinations and oxidative cyclizations. More recently, recyclable mediators and catalytic protocols have been developed.

1. Introduction

Hypervalent iodine reagents are widely used in modern organic synthesis.[1–4] These reagents have tremendous synthetic applications, including difuncionalization of olefins and cyclopropanes,[5–7] oxidative couplings,[8–10] phenol dearomatizations,[11,12] oxidative formation of heterocycles,[13–16] aminations,[17,18] halogenations,[19–21] arylations,[22–24] and rearrangements.[25–28] In addition, a wide range of stereoselective transformations was achieved with high degree of stereo-control using chiral hypervalent iodine reagents and catalytic systems of chiral iodoarenes and terminal oxidants.[29–31] Moreover, they are valuable reagents for the generation of carbon and heteroatom radicals where under appropriate conditions they can act as single electron oxidants.[32,33] The popularity of hypervalent iodine reagents in organic synthesis is not only due to their diverse reactivities and easy accessibility, but also for being milder and environmental friendly alternatives for heavy metal oxidants. Nevertheless, their preparation typically requires the use of an excess of expensive or hazardous oxidants such as *m*-chloroperbenzoic acid, peractic acid, oxone, hydrogen peroxide, and selectfluor,[34] which makes the whole process cumbersome. Hence, the electrochemical generation of hypervalent iodine reagents through the anodic oxidation of iodine(I) precursors is a feasible alternative leading to more sustainable reactions. Indeed, organic electrochemistry[35–40] is currently a highly active area of research. The intrinsic sustainability of the electrochemical methods (due to replacement of oxidizing and reducing agents with electric current), scalability, mild conditions, and chemoselectivity provides a reliable alternative to conventional methods. This review covers the electrochemical synthesis of hypervalent iodine reagents and their applications as in-cell and ex-cell mediators in various chemical transformations.

Mohamed Elsherbini was born 1980 in Mansoura, north of Egypt. He completed his PhD in 2014 at Mansoura University under the supervision of Prof. Hanafi H. Zoorob and Prof. Wafaa S. Hamama. His doctoral studies were on the synthesis of biologically active selenium-containing heterocycles. After working as a chemistry lecturer at the Saudi Mining Polytechnic, he moved to Cardiff University in 2016 to join the group of Prof. Thomas Wirth, where he is currently doing research in the chemistry of hypervalent iodine reagents and organic electrochemistry.

Thomas Wirth is professor of organic chemistry at Cardiff University. After receiving his PhD from TU Berlin, he stayed at Kyoto University as a JSPS fellow. Then he worked independently at the University of Basel before taking up his current position at Cardiff University in 2000. He was awarded the Werner-Prize from the New Swiss Chemical Society, the Wolfson Research Merit Award from the Royal Society and the Bader-Award from the Royal Society of Chemistry. In 2016 he was elected as a fellow of The Learned Society of Wales. His main interests of research concern stereoselective electrophilic reactions, oxidative transformations with hypervalent iodine reagents and flow chemistry performed in microreactors.

2. Electrochemical Generation of Hypervalent Iodine Reagents

2.1. Electrochemical Synthesis of Diaryliodonium Salts

Diaryliodonium salts are an important class of hypervalent iodine reagents with two carbon ligands and a negative counter ion. They are typically air and moisture stable solids. Diaryliodonium salts are strong oxidizing agents and also powerful electrophiles finding wide applications in organic synthesis as efficient electrophilic aryl sources. Coupling reactions with oxygen, sulfur, nitrogen or carbon nucleophiles enable the synthesis of a large range of organic compounds.[2] In addition, they are valuable aryne precursor molecules.[41]

The acid-catalyzed coupling of arenes with preformed hypervalent iodine reagents represents the general two-step approach for the synthesis of symmetrical and unsymmetrical diaryliodonium salts.[42] Recently, flow and one-pot procedures for the synthesis of unsymmetrical diaryliodonium salts have been reported.[43,44]

The electrochemical anodic oxidation of iodoarenes in the presence of arenes is a sustainable, single-step approach for the generation of diaryliodonium salts. This transformation was first described by Miller and Hoffmann in 1966.[45] The authors studied

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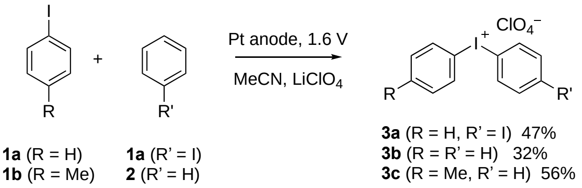
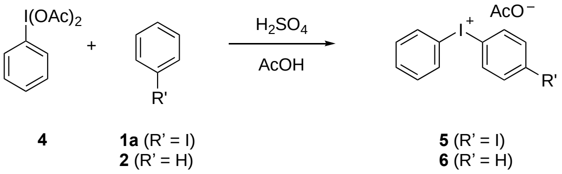
the potentiostatic oxidation of iodobenzene (**1a**), which was dissolved in a 0.5 *M* lithium perchlorate-acetonitrile solution and electrolyzed at 1.65 V (vs Ag/$AgNO_3$) in a three-compartment cell equipped with a platinum foil anode. After passing 1.78 C/mol through the cell, 4-iodophenyliodonium perchlorate (**3a**) was isolated in 47% yield. A similar oxidation of iodobenzene (**1a**) or 4-iodotoluene (**1b**) in the presence of benzene lead to the formation of the corresponding diaryliodonium perchlorates (**3b**, **3c**) as the major products.

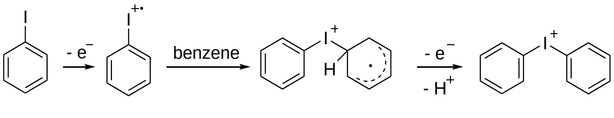


Scheme 1. First electrochemical synthesis of iodonium salts.[45]

As benzene is not oxidized below 1.9 V, the iodonium salts **3** must result from the oxidation of the aryl iodide which is then reacting with benzene. Wendt and co-workers[46] studied the above transformation in depth to gain a better understanding of the reaction mechanism. Their polarographic and kinetic studies of the anodic oxidation of iodobenzene in the presence of benzene over a gold electrode showed that the rates of formation of 4-iodophenyliodonium salt **5** and diphenyliodonium salt **6** are approximately equal indicating that the coupling reaction is unselective on gold anodes. This is in contrast to the homogeneous acid-catalyzed coupling reactions (Scheme 2) which are known to be very selective with the relative rates of the reaction to **5** and to **6** being ~1:30. These results rule out the assumption that the electrochemical coupling might go through the initial formation of iodine (III) species, which then couples to the arene after diffusing away from the electrode surface. This clearly indicates that the anodic formation of the iodonium salts is a heterogeneous process probably via radical cation formation taking place on the electrode surface represented by the mechanism shown in Scheme 3.



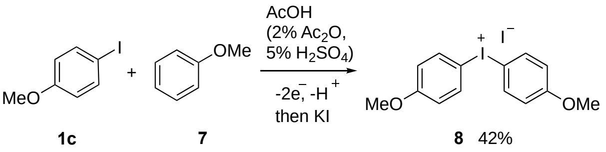
Scheme 2. Coupling of (diacetoxyiodo)benzene **4** with benzene and iodobenzene.[46]



Scheme 3. Proposed mechanism of the anodic oxidation of PhI and arene coupling.[46]

Peacock and Pletcher[47,48] proved the synthetic feasibility and generality of the above reaction with alkyl-substituted aryliodides and arenes, where both symmetrical and unsymmetrical diaryliodonium salts can be obtained in good yields in a one-step anodic oxidation/coupling sequence. The galvanostatic electrolysis was performed in an undivided cell at a carbon felt anode and a graphite rod cathode in acetic acid-acetic anhydride-sulfuric acid medium. The diaryliodonium salts have been obtained in yields between 48 and 92%.

A limitation of this protocol is that it cannot be applied for aryl iodides and arenes containing easily oxidizable functional groups. Moreover, the introduction of electron withdrawing groups such as the nitro group into the aryl iodide increase their oxidation potentials which negatively affects the reaction. The predominance of other anodic oxidations and electrode passivation are observed. The introduction of electron withdrawing groups into the arene counterpart has a similarly negative effect on the coupling step due to the decrease of the arene nucleophilicity. Thus, attempts to couple 4-nitroiodobenzene and toluene or 4-iodotoluene and nitrobenzene were unsuccessful. On the other hand, the introduction of electron donating groups into the aryl iodides and arenes is expected to decrease the oxidation potentials of the aryl iodides and increase the nucleophilicity of the arenes, which could improve the reaction efficiency. Indeed, 4,4'-dimethoxydiphenyliodonium salt (**8**) is formed in 42% from the electrolysis of 4-methoxyiodobenzene (**1c**) and anisole (**7**) in acetic acid containing 2% acetic anhydride and 5% sulfuric acid (Scheme 4). The stability of the electron-rich arenes in the reaction medium is, however, a major issue as anisole undergoes sulfonation. Increasing the percentage of acetic anhydride to 25% led to quantitative sulfonation of anisole within a few minutes, whereas replacing sulfuric acid by HBF_4 lead to acylation of anisole.



Scheme 4. Electrochemical synthesis of 4,4'-dimethoxydiphenyliodonium salt **8**.[48]

Using an electrochemical microreactor[49–53], Wirth *et al.*[54] developed a flow protocol for the synthesis of diaryliodonium salts. The microreactor consists of two platinum electrodes separated by a thin (250 µm) fluorinated ethylene propylene (FEP) foil containing a channel of 23 µL volume (Figure 1). The substrates (iodoarene/arene) solution in $MeCN/Ac_2O/H_2SO_4$ mixture were injected via a syringe pump (80 µL/min) through the reactor inlet, the reaction mixture was electrolysed under constant current (30 mA) and the reaction mixture collected from the reactor outlet into a solution of potassium iodide where the diaryliodonium salts were precipitated in the form of iodides, which are then collected by filtration. This methodology achieves the diaryliodonium salts in moderate to good yields (18 – 72%) with a minimal workup opening the way for an easy scale up.

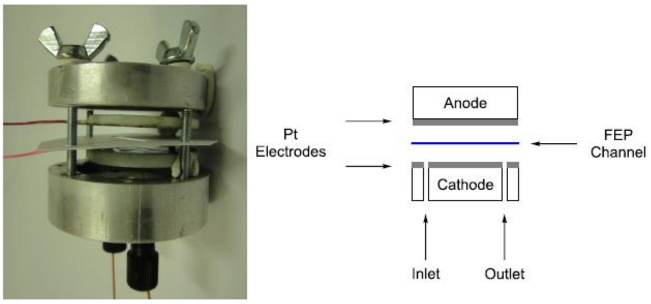
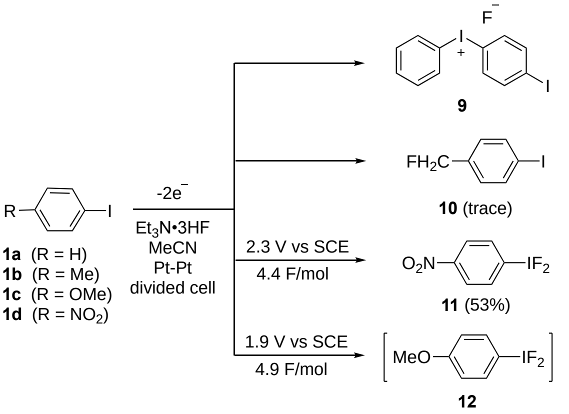


Figure 1. A simple multipurpose electrochemical microreactor.[54]

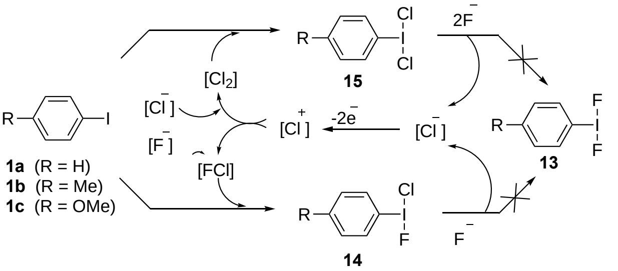
2.2. Indirect Anodic Fluorination

The first electrochemical synthesis of (difluoroiodo)benzene ($PhIF_2$) was reported in the year 1960 by Schmidt and Meinert[55] through the electrolysis of iodobenzene solution in acetonitrile in the presence of silver fluoride which acts as a supporting electrolyte and as fluorine source. However, Rozhkov[56] reported that these results were irreproducible due to the low conductivity of such a solution. In fact, the attempt to synthesize (difluoroiodo)benzene through the anodic oxidation of iodobenzene in the presence of $Et_3N{\bullet}3HF$ was unsuccessful and lead to the formation of the dimeric iodonium salt **9**.[57] Replacing iodobenzene with iodotoluene didn't lead to the desired (difluoroiodo)toluene either. Fluorination of the methyl group occurred (**10**) and decomposition products were observed. However, under the same conditions, (difluoroiodo)-4-nitrobenzene (**11**) was successfully obtained in 53% yield. Difluoride **11** was precipitated during the electrolysis and isolated in a pure form by simple filtration as a stable solid. Due to the strong electron withdrawing power of the nitro group, the anodic oxidation of 4-nitroiodobenzene (**1d**) was achieved at a highly positive potential (2.3 V vs SCE). As expected, the electron-rich 4-iodoanisol (**1c**) was oxidized at lower positive potential (1.9 V vs SCE), but the generated (difluoroiodo)-4-methoxybenzene (**12**) was much less stable and could not be isolated in a pure form (Scheme 5).



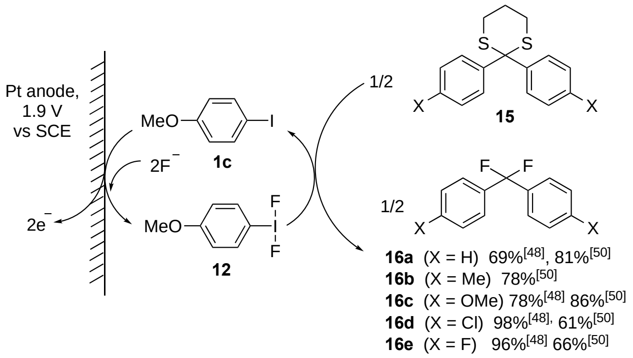
Scheme 5. Direct anodic oxidation of iodobenzene derivatives in $Et_3N{\bullet}3HF$.[57]

The difficulties accompanying the anodic oxidation of aryliodides are attributed to their relatively high oxidation potentials. This could be in principle alleviated through the indirect anodic oxidation using a mediator[58] such as chloride ions (Scheme 6). Indeed, the reaction proceeded smoothly, but forming the chlorofluorides **14** instead of the expected difluorides **13**[59].



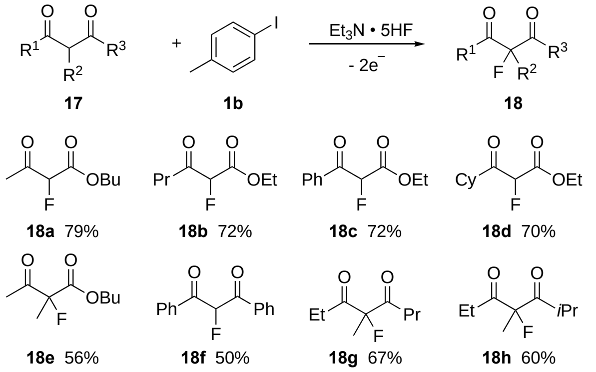
Scheme 6. Direct anodic oxidation of iodobenzene derivatives in $Et_3N{\bullet}3HF$.[59]

The electrochemically generated hypervalent iodine species **12**[57] and **14** (R = OMe) [59] were successfully used as mediators for the indirect anodic *gem*-difluorination of dithioketals. The reaction was carried out in an ex-cell manner, where the dithioketal substrates were added to the mixture after the electrolysis has been terminated. In addition, the reaction was also carried out in an in-cell manner, where the dithioketal substrates were present during the electrolysis. The in-cell mediated difluorination reaction enabled the use of aryliodides in catalytic amounts, where 5 mol% of 4-iodoanisole (**1c**) was sufficient to give the *gem*-difluorinated products **16** in high yields (Scheme 7).



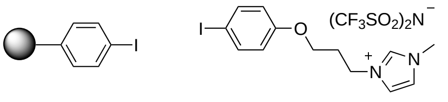
Scheme 7. Mechanism and scope of *gem*-difluorination of dithioketals.[57,59]

In the same context, Hara *et al.*[60] synthesized the valuable fluorinating agent, 4-iodotoluene difluoride (Tol-IF$_2$), electrochemically by changing the electrolyte from Et$_3$N•3HF to Et$_3$N•5HF. The electrochemically generated Tol-IF$_2$ was successfully used as an in-cell mediator for the indirect anodic fluorination of β-dicarbonyl compounds. Thus, the α-fluoro-β-dicarbonyl products **18** were obtained in good yields through the potentiostatic electrolysis (1.5 V vs Ag/Ag$^+$) of a 1:1 mixture of 4-iodotoluene (**1b**) and β-dicarbonyl substrates **17** in Et$_3$N•5HF in a Teflon PFA undivided cell. The fluorination of unsubstituted β-dicarbonyl substrates proceeded selectively to provide the monofluorinated compounds **18** as main products in good yields (Scheme 8).



Scheme 8. Indirect anodic fluorination of β-dicarbonyl compounds.[60]

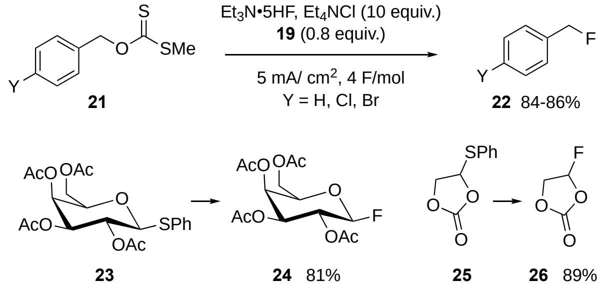
In 2010, Fuchigami *et al.* published two reports[61,62] on the indirect anodic fluorinations mediated by recyclable polystyrene-supported iodobenzene **19** and a task-specific ionic liquid **20** derived from iodophenol (Figure 2).



19 **20**

Figure 2. Recyclable iodine mediators.[61,62]

The mediator **19** was successfully applied to the indirect anodic fluorination of organosulfur compounds. Dithioketals **15** have been investigated, but also xanthates **21** or phenylsulfides **23** and **25** as shown in Scheme 9 can be efficiently fluorinated leading to products **22**, **24** and **26** in good yields. The electrolyses were performed in a mixture of Et$_3$N•5HF and Et$_4$NCl in an undivided cell under constant current conditions. The mediator **19** was easily separated from the reaction mixture and could be recycled multiple times without loss of activity.



Scheme 9. Indirect anodic fluorination of xanthates **21**, phenylsulfides **23** and **25**.[61]

The mediator **20**/ionic liquid (IL) system represents another efficient recyclable system for indirect anodic fluorination reactions, where the reaction product is extracted by an organic solvent such as diethyl ether and the recovered task specific ionic liquid (TSIL) mediator **20**/IL can be efficiently recycled without losing activity (Figure 3).[62]

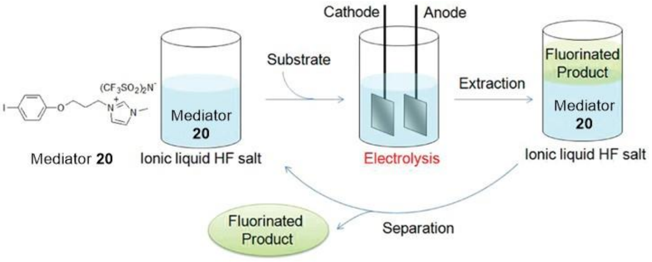
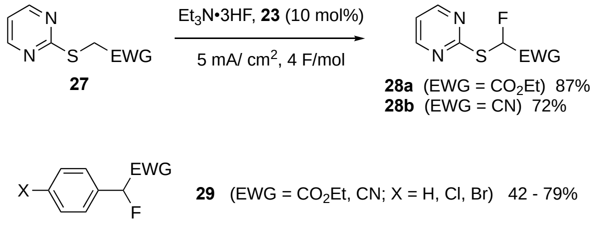


Figure 3. Use of **20** for indirect anodic fluorination.[62] (Reproduced from ref.[62] with kind permission from ACS publications)

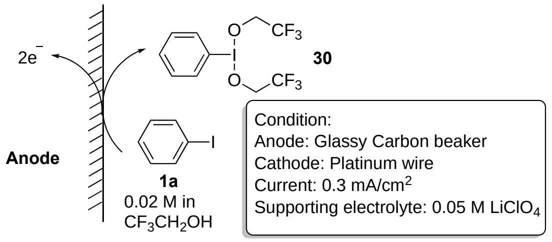
The cyclic voltammetry[63] measurements of **20** in Et$_4$NF-4HF/MeCN showed an oxidation potential of $E_{1/2}$ = 1.91 V vs SCE, which is comparable to the oxidation potentials of simple aryl iodides.[57] Several substrates such as dithioketals **15**, 2-pyrimidylsulfides **27** and substrates with activated benzylic positions were efficiently electrochemically fluorinated using this mediator system (Scheme 10). The electrolysis was carried out with constant current in a simple undivided cell equipped with platinum electrodes.



Scheme 10. Indirect anodic fluorination of 2-pyrimidylsulfides **27** and benzylic positions.[62]

2.3. Oxidative Heterocyclizations

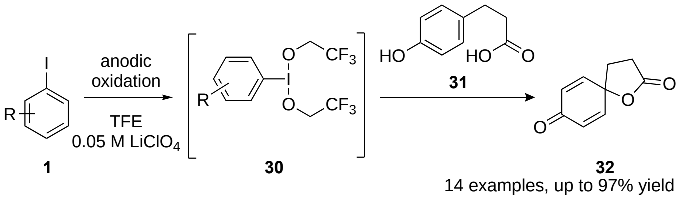
The Nishiyama group developed the electrochemically generated hypervalent iodine reagent [bis(trifluoroethoxy)iodo]benzene **30** (Figure 4) as an alternative to the commercially available reagents such as (diacetoxyiodo)benzene. The reactivity of **30** is comparable and sometimes superior to (diacetoxyiodo)benzene, which is illustrated by its successful applications in the construction of a variety of oxygen and nitrogen-containing scaffolds, natural products[64] and the oxidation of the naturally occurring xanthone derivatives (Mangostins).[65]



Condition:
Anode: Glassy Carbon beaker
Cathode: Platinum wire
Current: 0.3 mA/cm^2
Supporting electrolyte: 0.05 M LiClO$_4$

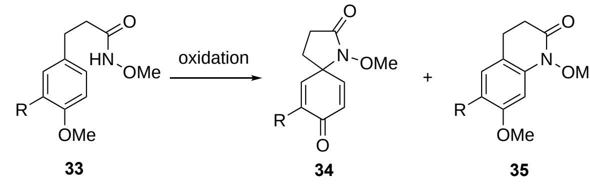
Figure 4. Electrochemical generation of the hypervalent iodine reagent **30**.[64]

Iodobenzene derivatives with different substituents were electrolyzed under constant current condition (0.3 mA/cm^2) in an undivided cell composed of a glassy carbon (GC) beaker as an anode and platinum wire as a cathode in trifluoroethanol containing LiClO$_4$ (0.05 M) as a supporting electrolyte. All the resulted hypervalent iodine reagents are only stable in the solution, except the 4-nitro substituted derivative, which can be isolated as a relatively stable solid. The oxidative efficiency of these reagents was assessed *in situ*, through the yields of the phenolic dearomatization/spirolactonization of 4-hydroxyphenylpropionic acid (**31**),[66] which was added to the reaction vessel at the end of the electrolysis (Scheme 11). The dearomatization product **32** was obtained in good yields in most cases. The iodine(III) species generated from iodobenzene proved to be the most powerful oxidant in this series, where it leads to the formation of **32** in almost quantitative yield (97%) being even superior than [bis(trifluoroacetoxy)iodo]benzene (84% yield).[67]



Scheme 11. Anodic oxidation of iodobenzenes **1** in TFE and use of the electrochemically generated iodine(III) species **30** in phenolic oxidation.[67]

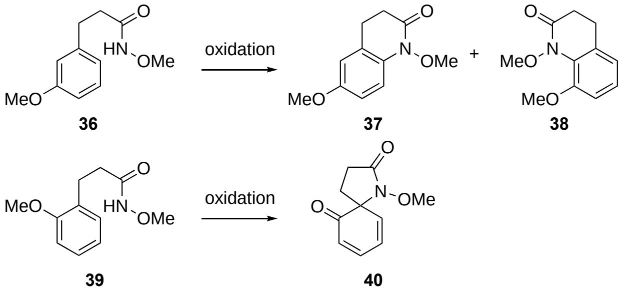
Similarly, the phenolic dearomatization/spirolactamization of the methoxyamide derivatives **33** was achieved in high yields using the electrochemically generated **30** (Scheme 12)[68], which again proved to be comparable or superior to direct anodic oxidation and [bis(trifluoroacetoxy)iodo]benzene. The spirocyclic products **34** were obtained exclusively when the substituent R is hydrogen or halogen, while in the case of strong electron-donating substituents (R = OMe) the reaction was unselective and gave a mixture of **34** and **35** in an approximately 1:1 ratio.



	R = H	R = Cl	R = Br
direct anodic oxidation	67%	45%	59%
[bis(trifluoroacetoxy)iodo)benzene	quant.	67%	75%
electrogenerated **30**	quant.	94%	89%

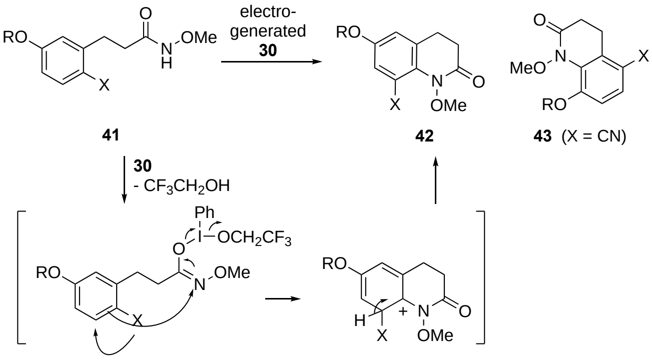
Scheme 12. Oxidation of the methoxyamide derivatives **33**.[68]

The outcome of the above reaction varies according to the position of the methoxy substituent (Scheme 13). The quinolone derivative **37** resulting from the electrophilic attack at the *para* position to the methoxy group predominates over the product of the *ortho*-cyclization **38** (ratio ~7:1). The oxidation of the *ortho*-substituted methoxyamide derivative **39** gave exclusively the spirocyclization product **40** in 92% yield using the electrogenerated iodine(III) reagent **30**.



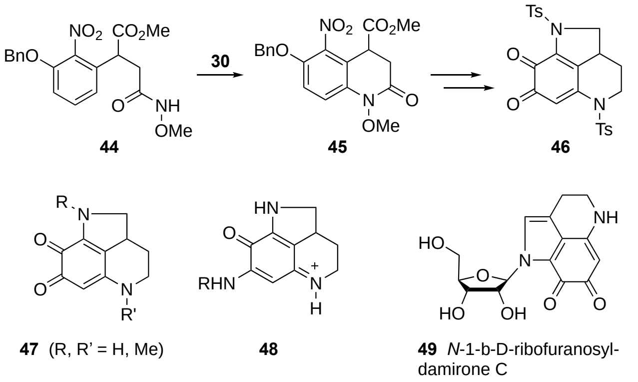
Scheme 13. Oxidation of the methoxyamide derivatives **36** and **39**.[68]

To gain access to the quinoline derivatives of type **38**, the *para*-position to the methoxy group was blocked with different substituents X (X = Cl, OAc). The modified substrates **41** were oxidized under the same reaction conditions. But still the cyclization took place predominantly at the *para*-position and quinolones **42** were the main reaction products, except for X = CN where the *ortho*-cyclized product **43** was obtained in 17% yield.[69] The formation of the quinolones **42** can be explained by the electrophilic attack at the *para*-position with concomitant migration of the substituent X as shown in Scheme 14.



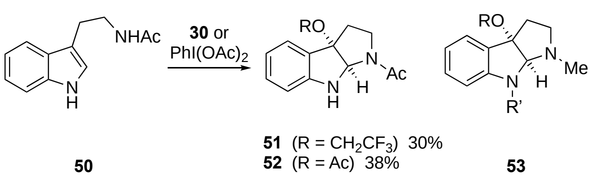
Scheme 14. Mechanism of the cyclization and rearrangement of **41**.[69]

The above quinolone synthesis was successfully applied to the construction of tetrahydropyrroloiminoquinone alkaloids.[70,71] The methoxyamide derivative **44** was smoothly transformed into the quinolone **45** in 62% yield through the oxidative cyclization by the electrochemically generated iodine(III) reagent **30**. Quinolone **45** was then transformed into the α-diketone **46** in 31% yield over 5 steps. The α-diketone **46** serves as the key intermediate for the synthesis of several tetrahydropyrroloiminoquinone alkaloids **47** – **49** (Scheme 17).[72]



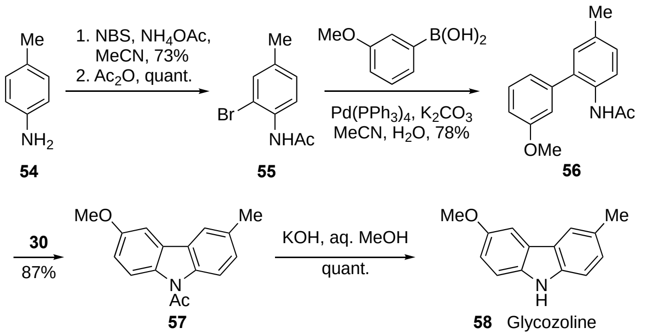
Scheme 15. Synthesis of the α-diketone **46**, a versatile key intermediate for tetrahydropyrroloiminoquinone alkaloids.[72]

Analogously, 1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]-3a-ol derivatives 51 and **52** were obtained in 30 and 38% yield, respectively, via oxidative cyclization of *N*-acetyltryptamine (**50**) mediated by the anodically generated **30**. Its acetate analogue **53** serves as a key building block in a concise synthesis of the pyrroloindol alkaloids **53** such as CPC-1 or debromoflustraminol B (Scheme 16).[73]



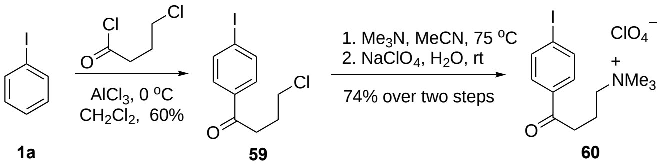
Scheme 16. Oxidative cyclization of tryptamine **50**: a concise synthesis of pyrroloindol alkaloids.[73]

In addition, the anodically generated iodine(III) reagent **30** is efficient for the oxidative cyclization of the phenyl acetanilide derivatives into the corresponding carbazoles. The reaction shows good functional group tolerance and the carbazole products were generally obtained in good yields.[74] The feasibility of this carbazole synthesis was also confirmed by its application in the synthesis of the antibacterial and antifungal naturally occurring carbazole derivative glycozoline **58** (Scheme 17).



Scheme 17. Synthesis of Glycozoline **58**.[74]

Recently, Francke *et al.* developed a novel recyclable iodine(I)/iodine (III) redox mediator for electrosynthesis.[75] The iodine(I) precursor **60** is composed of an alkylammonium group tethered to an iodophenyl moiety, which facilitates the recovery and recycling in addition to eliminating the need of supporting electrolytes. Compound **60** was synthesised from iodobenzene **1a** in 45% yield over three steps (Scheme 18).



Scheme 18. Synthesis of the ionically tagged phenyl iodide derivative **63**.[75]

The ionically tagged aryl iodide **60** is anodically oxidized in fluorinated alcohols such as trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) to the corresponding hypervalent iodine reagents **61** and **62**, respectively. A schematic representation of the anodic oxidation of **60** and the use of the generated iodine(III) species as ex-cell mediators is illustrated in Figure 5.

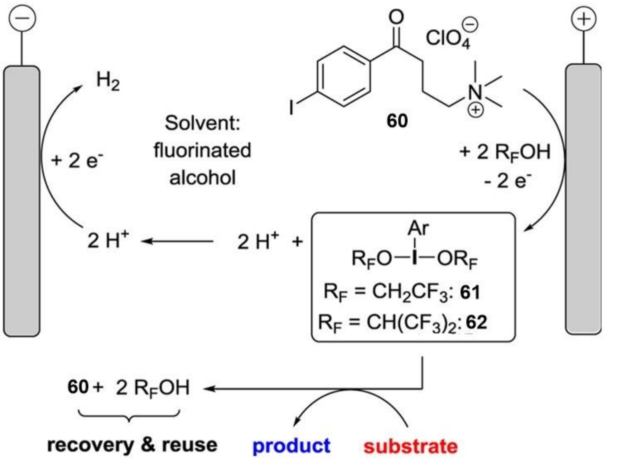
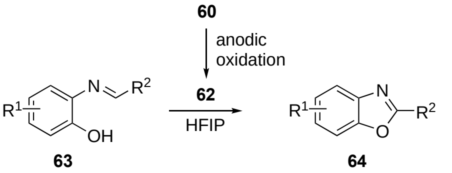


Figure 5. A iodine(I)/iodine(III) redox couple as a mediatory system for electrosynthesis.[75] (Reproduced from ref.[75] with kind permission from ACS publications).

The cyclic voltammetry (CV) measurements of a 2 mM solution of **60** in TFE and HFIP containing NBu_4ClO_4 (0.1 M) as supporting electrolyte, showed similar irreversible oxidation peaks with potentials Ep (2.12 V and 2.16 V, respectively, vs Ag/$AgNO_3$; 2.418 V and 2.458 V, respectively, vs SCE[76]). The cyclic voltammograms of the blanks showed that HFIP has higher anodic stability than TFE, hence it was the solvent of choice for further studies.

The hypervalent iodine species **62** is obtained through the electrolysis of **60** in HFIP in an undivided cell equipped with a glassy carbon anode and a platinum cathode, applying current densities of 15 mA cm^{-2} (2 F/mol). Several C–C and C–N coupling reactions were successfully achieved using the new recyclable redox mediatory system.[75]

Finally, the anodically generated hypervalent iodine reagent **62** was used as an ex-cell mediator for the indirect electrosynthesis of benzoxazoles **64** *via* oxidative cyclization of 2-(benzylideneamino)phenol substrates **63**. The reaction proceeds smoothly showing wide functional group tolerance and the benzoxazole products were obtained generally in good to excellent yields (Scheme 19)[77].



17 examples, 40 – 95%

Scheme 19. Indirect anodic synthesis of benzoxazoles **64**.[77]

3. Conclusions and Outlook

In this review, we discuss the electrochemical generation of hypervalent iodine reagents through the anodic oxidation of iodoarenes. The anodic oxidation of aryl iodides is successfully achieved under both galvanostatic and potentiostatic electrolysis conditions in either divided or undivided cells. Using electricity eliminates the necessity of terminal chemical oxidants, which minimize the waste and make the hypervalent iodine chemistry more sustainable. The electrochemically generated hypervalent iodine reagents are powerful in-cell and ex-cell mediators for several valuable chemical transformations including, fluorination and oxidative heterocyclizations. In addition, they are successfully applied in the total synthesis of several natural products. The electrochemically generated hypervalent iodine reagents have comparable or superior reactivity to the commercially available reagents such as (diacetoxyiodo)benzene. Some elegant catalytic transformations relying on the iodine(I)/iodine(III) redox cycles were developed and proved to be highly efficient. Moreover, recyclable aryl iodide mediators that can be used and easily recovered and recycled were also developed. Despite, the impressive examples presented in this short review, the literature of the electrochemical generation/application of hypervalent iodine reagents is still relatively limited, which leaves a wide field to explore the horizon of this powerful combination.

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Keywords: Hypervalent Iodine • Electrochemistry • Anodic Oxidation • Redox mediators • Fluorination

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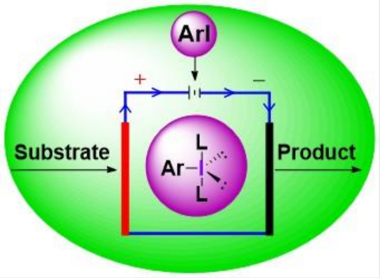
Entry for the Table of Contents

REVIEW

The anodic oxidation of aryl iodides is a powerful method for the synthesis of hypervalent iodine reagents, which eliminates the necessity to use expensive or hazardous chemical oxidizing reagents. The hypervalent iodine reagents generated at the anode can be successfully used as mediators for valuable chemical transformations such as fluorinations or oxidative cyclizations. Recyclable mediators and catalytic protocols were developed recently.



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Hypervalent Iodine Reagents by Anodic Oxidation: a Powerful Green Synthesis