

Sustainable Methods in Hypervalent Iodine Chemistry

Brandon Frey,[†] Asim Maity,[†] Hao Tan, Pritam Roychowdhury, and David C. Powers*

Texas A&M University, Department of Chemistry, College Station TX, 77843 USA
powers@chem.tamu.edu

Abstract

Hypervalent iodine compounds are a widely used class of metal-free oxidants that find application in organic synthesis. Due to the homology between the reactivity of hypervalent iodine and many transition metals — oxidative addition, ligand exchange, and reductive elimination can be facile for both — hypervalent iodine species find application in a variety of synthetically important organic transformations. Major limitations of these reagents include the frequent need for (super)stoichiometric loading and the intrinsically poor atom economy that results from the generation of stoichiometric quantities of iodoarene byproducts. In addition, hypervalent iodine reagents are often synthesized using metal-based terminal oxidants, which compound the resulting waste stream. Recently, substantial progress has been made to address these limitations. Here, we discuss progress towards sustainable synthetic methods for the preparation of hypervalent iodine compounds and application of those methods in the context of hypervalent iodine catalysis. The discussion is organized according to the active oxygen content, and thus atom economy, of the terminal oxidant employed. Hypervalent iodine electrochemistry and the development of recyclable iodoarenes are also discussed.

A. Introduction

Oxidation reactions, in which electron equivalents are removed from a substrate, are often critical steps in the synthesis of functional organic molecules. By definition, oxidation reactions require the use of an electron acceptor (*i.e.*, terminal oxidant). Because the reduced byproducts generated from the terminal oxidant are often lost as chemical waste, the chemical structure of the terminal oxidant dictates the sustainability of the oxidation reaction. Biological oxidation chemistry often utilizes dioxygen (O₂) as the terminal oxidant and generates water as the ultimate byproduct [1, 2]. As such, these enzymatic oxidation reactions are nearly ideal from the perspective of sustainability. Analogous utilization of O₂ as a terminal oxidant in synthetic chemistry remains a significant challenge because 1) the triplet ground state of O₂ imposes kinetic barriers to O₂ utilization [3], 2) O₂ often engages in poorly selective radical chain reactions [4], 3) the electron inventories of O₂ reduction (four-electron) and substrate oxidation (two electrons) are mismatched [5, 6]; and, 4) O₂ utilization can present safety concerns depending on the specific reaction conditions employed [7]. The challenges associated with direct O₂ utilization as a terminal oxidant in selective synthesis have stimulated the development of alternative chemical oxidants for application in specific synthetic contexts. Implicit in the use of designer chemical oxidants is an increase in the waste associated with oxidation chemistry and in turn reduced sustainability.

The principles of green chemistry articulated by Anastas *et al.* [8, 9] codify the concept of atom economy and the impact of the nature of waste on the efficiency of a chemical process. Active oxygen content, which is defined as the percent weight ratio of the oxygen transferred to

[†] These authors contributed equally to this work.

product divided by the formula weight of the reagent, can be used as a guiding parameter for evaluating the sustainability of oxidants [10]. Table 1 lists the active oxygen content and associated waste products generated from a variety of commonly encountered terminal oxidants.

Table 1. List of general oxidants in order of their respective active oxygen content [10].

$$\text{Substrate} + \text{Oxidant} \longrightarrow \text{Product} + \text{Reduced Oxidant (Stoichiometric waste)}$$

Oxidant	Active Oxygen Content (wt %)	Waste Generated
O ₂ or O ₂ / reductant ^a	100 (50)	None (H ₂ O)
H ₂ O ₂	47	H ₂ O
KMnO ₄	30.4	Mn(II) salt
NaOCl	21.6	NaCl
O ₂ / CH ₃ CHO	21.1	CH ₃ CO ₂ H
CH ₃ CO ₃ H	21.1	CH ₃ CO ₂ H
<i>t</i> BuOOH	17.8	<i>t</i> BuOH
H ₂ O ₂ -Urea	17.0	H ₂ O-Urea
KHSO ₅	10.5	KHSO ₄
<i>m</i> -CPBA	9.3	<i>m</i> -CBA
NaIO ₄	7.5	NaIO ₃
PhIO	7.3	PhI
NaBO ₃ ·4H ₂ O	7.2	NaBO ₂
Oxone ^b	2.6	K ₂ S ₂ O ₈ ·KHSO ₄ ·K ₂ SO ₄

^aThis analysis assumes the reduced byproduct is H₂O. If chemical reductants are employed (*i.e.*, H₂, NADH, CH₃CHO, etc.) the active oxygen content will be lower depending on the mass of the generated byproducts.

^b(2KHSO₅·KHSO₄·K₂SO₄).

While O₂ is an attractive oxidant based on its active oxygen content, chemical strategies that utilize both oxygen atoms for substrate functionalization (*i.e.*, dioxygenase reactivity) are rare [11]. More typically, O₂ utilization is accomplished in the presence of an appropriate reductant, which addresses the incongruous electron inventory of O₂ reduction and substrate functionalization. Consequently only 50% of active oxygen content of O₂ is utilized and the other 50% is lost as waste (ideally H₂O). Hydrogen peroxide (H₂O₂) is also considered a green oxidant, and has 47% active oxygen content when utilized in direct substrate oxidation chemistry with attendant generation of H₂O as the byproduct. Utilization of H₂O₂ as an oxidant in hypervalent iodine chemistry often requires acetic anhydride, to generate peracetic acid *in situ*, or the use of urea-hydrogen peroxide (UHP) adduct, both of which reduce the active oxygen content of the reagent. Other commonly encountered chemical oxidants, such as NaOCl, CH₃CO₃H, *m*-CPBA, NaIO₄, NaBO₃·4H₂O, and Oxone display significantly lower active oxygen contents. The recent renaissance of organic electrosynthesis offers an alternative strategy to sustainable oxidation chemistry: Anodic substrate oxidation provides the opportunity to avoid stoichiometric redox reagents and the associated waste streams [12]. The frequent requirement for high concentrations of supporting electrolyte can reduce the chemical efficiency of electrosynthetic approaches.

Hypervalent iodine compounds are a class of metal-free oxidants based on three-centered-four-electron I–L bonds [13, 14] that have emerged as important reagents in the functionalization of unsaturated hydrocarbons, transition metal-catalyzed chemistry, alcohol and amine oxidation,

and group transfer chemistry [15-21]. The reactivity of hypervalent iodine compounds bears some similarities to that of transition metal species — namely the accessibility of multiple stable redox states, the facility of ligand exchange steps, and the participation in bond-forming processes [15-18, 22]. Both I(III) and I(V) compounds are important oxidation states in hypervalent iodine chemistry due to their complementary reactivities. Although hypervalent iodine compounds are attractive oxidants due to the abundance of iodoarene starting materials and lower toxicity compared to transition metal catalysts, when employed as terminal oxidants hypervalent iodine reagents display poor atom economy. For example, when reduced, iodosylbenzene (PhIO) generates a stoichiometric quantity of iodobenzene and only features 7.3% active oxygen content. In addition, hypervalent iodine species are typically prepared with stoichiometric metal-based oxidants (KMnO₄, Oxone, NaIO₄, etc.) or organic peracids (*m*-CPBA, CH₃CO₃H) which amplifies the overall chemical inefficiency of using these reagents in synthesis.

The development of either 1) methods to synthesize hypervalent iodine compounds using higher active-oxygen-content reagents, or 2) methods to employ hypervalent iodine species as catalysts in tandem with oxygen-dense oxidants could provide a platform for sustainable oxidation methods for wide variety of reactions. Here, we summarize progress towards sustainable synthesis and use of hypervalent iodine compounds. We first discuss progress towards greener methods to prepare hypervalent iodine compounds and this discussion is organized by the active oxygen content of the terminal oxidant employed. Catalytic application of hypervalent iodine compounds as a way to reduce waste generation and increase energy efficiency is discussed. Electrochemistry as an alternate sustainable method for synthesis of hypervalent iodine compounds is described in the context of both synthesis of hypervalent iodine compounds and their utilization in electrocatalysis. Polymer-supported hypervalent iodine reagents and fluorous hypervalent iodine compounds, which have been developed to support reagent recycling, are also discussed. Only organic hypervalent iodine chemistry is presented; utilization of tetrabutylammonium iodide and other inorganic iodide sources will not be described.

B. Chemical Synthesis of Hypervalent Iodine Reagents

B.1. Synthesis of Hypervalent Iodine Reagents Using O₂

In concept, if hypervalent iodine reagents were generated using O₂ as the terminal oxidant, the array of chemistry that is available to these reagents could be achieved aerobically. Iodoarenes do not react directly with O₂ to afford hypervalent iodine compounds, and thus the development of aerobic methods of hypervalent iodine chemistry requires identification of an appropriate reductant to enable aerobic oxidation to be realized.

B.1.1. Synthesis of Hypervalent Iodine(III) Reagents with O₂

In 2018, Powers *et al.* reported the synthesis of hypervalent iodine reagents by intercepting reactive oxidants generated during acetaldehyde autoxidation [23]. Initial studies of the oxidation of iodobenzene (**1**) in the presence of acetaldehyde and O₂ afforded variable yields of (diacetoxyiodo)benzene (**2**, 42-91% yield), presumably due to inconsistent initiation of the aldehyde autoxidation chain reaction. Co(II) additives, which have been previously used as initiators of aldehyde autoxidation chemistry [24, 25], were found to be critical in achieving reproducible chemical yields. The developed aerobic oxidation protocol provided ready access to a wide variety of hypervalent iodine reagents (Figure 1): Oxidation of 4-substituted

iodoarenes provided access to hypervalent iodine species bearing both electron-donating and -withdrawing groups (**3-8**). Oxidation of 2-substituted iodoarenes afforded the corresponding cyclic iodanes (**9-12**) in high yields, which are an important class of reagents for hypervalent iodine mediated group transfer chemistry. Addition of external acids provided direct entry to acid-exchanged I(III) products (**13-15**) instead of the corresponding (diacetoxyiodo)benzene derivatives; for example, addition of TsOH, benzoic acid (BzOH), and trifluoroacetic acid (TFA) led to the formation of Koser's reagent (**13**), PhI(OBz)₂ (**14**), and PhI(TFA)₂ (**15**) in 84%, 48%, and 52% yields, respectively.

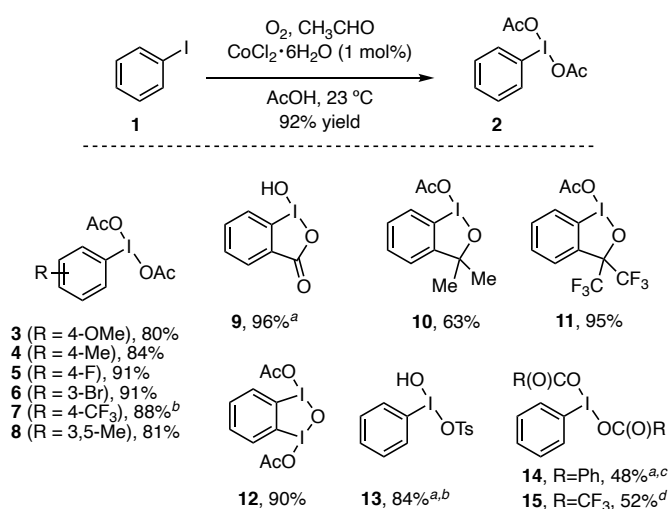


Figure 1. Aldehyde-promoted aerobic oxidation of iodoarenes provides access to a family of hypervalent iodine(III) reagents. ^aDCE as solvent, ^bin presence of TsOH·H₂O, ^cin presence of BzOH, and ^din presence of CF₃CO₂H.

A detailed investigation of the mechanism of aerobic oxidation revealed that iodoarene oxidation proceeds via a one-electron radical chain mechanism, which differs from the commonly observed two-electron oxidation / reduction reactions of these reagents [26]. The proposed mechanism was formulated based on 1) EPR spectroscopy of spin-trapped acetoxy radicals, 2) comparative Hammett analyses of aerobic oxidation and peracetic acid oxidation, 3) kinetic competition experiments, and 4) computational analysis. These data indicated that aerobic oxidation of iodobenzene (**1**) in presence of acetaldehyde and O_2 proceeds via addition of aerobically generated acetoxy radicals (**16**) to iodoarenes to generate transient iodanyl radicals **17** (Figure 2). Subsequent chain propagation by reaction with peracetic acid (**18**, an intermediate from aldehyde autoxidation) affords I(III) product (**19**) and regenerates the acetoxy radical chain carrier (**16**). Chain termination via either combination of **17** with acetoxy radical or via iodanyl radical disproportionation leads to (diacetoxyiodo)benzene (**2**).

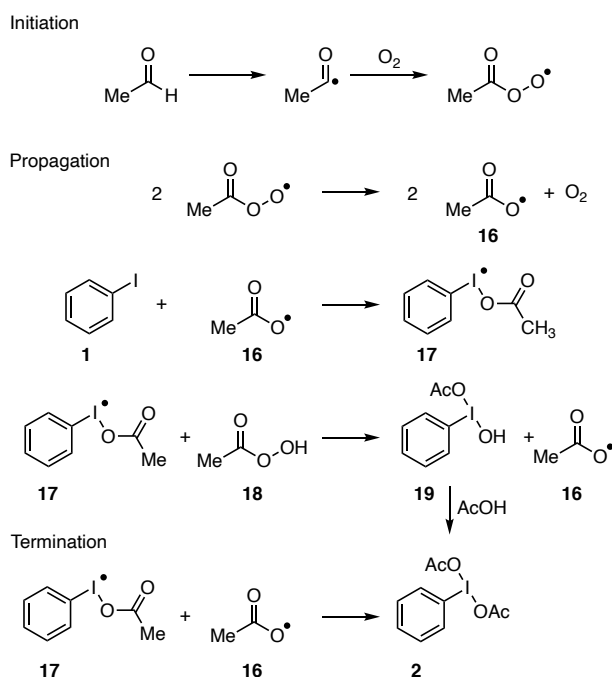


Figure 2. Aldehyde-promoted aerobic oxidation proceeds by addition of an aerobically generated acetoxy radical to iodobenzene to generate a transient iodanyl radical, which is a chain carrier in the synthesis of I(III) compounds.

B.1.2. Synthesis of Hypervalent Iodine(V) Reagents with O₂

The first aerobic synthesis of iodylbenzene (**20**) was reported by Jorissen *et al.* in 1938 [27], who demonstrated that an aerated acetaldehyde solution of iodobenzene (**1**) produced white crystals over the course of three weeks (Figure 3). These crystals were identified as iodylbenzene by iodometry.

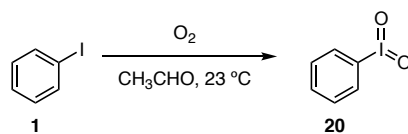


Figure 3. Upon standing for several weeks, an aerated solution of iodobenzene (**1**) in acetaldehyde resulted in the formation of crystalline iodylbenzene (**20**).

In 2018, Powers and co-workers described a strategy for the aerobic synthesis of I(V) reagents by coupling aldehyde-promoted aerobic oxidation of iodoarenes with disproportionation of the initially generated I(III) species [28]. Aerobic oxidation of iodoarenes with weakly chelating *ortho*-substituents like sulfonyl, nitro, or pyridyl were found to furnish the corresponding I(V) compounds **21-23** in good yield (Figure 4) [22, 29].

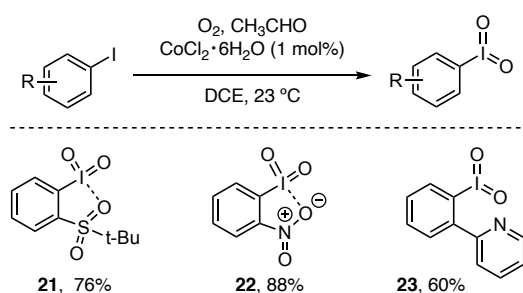


Figure 4. Aerobic synthesis of hypervalent iodine(V) reagents was achieved by coupling aldehyde-promoted aerobic oxidation iodoarenes with subsequent *in situ* disproportionation.

B.2. Synthesis of Hypervalent Iodine Reagents with H₂O₂ or UHP

H₂O₂ is considered to be an environmentally benign oxidant due to its 47% active oxygen content and the potential generation of water as the byproduct. H₂O₂ is produced via the Riedl–Pfleiderer process where 2-alkylanthraquinone is first reduced to 2-alkylhydroanthraquinone by hydrogenation and again oxidized aerobically to regenerate 2-alkylanthraquinone and H₂O₂ [30]. In spite of many advantages, decomposition of H₂O₂ to H₂O and O₂ is exothermic (–94.6 kJ/mol) [31], and the use of concentrated solutions presents significant safety hazards. Hence, H₂O₂ is typically employed as ≤30% aqueous solution. An alternative way to safely deliver H₂O₂ into the reaction is by using urea adduct of hydrogen peroxide (UHP), which is an odorless, water-soluble, crystalline solid that has an active oxygen content of 17% [32].

B.2.1. Synthesis of Hypervalent Iodine(III) Reagents with H₂O₂ or UHP

There are no examples of direct oxidation of iodoarenes with H₂O₂ alone, which may be due to the spontaneous decomposition of H₂O₂ by I(III) compounds to form singlet oxygen (¹O₂) and reduced I(I) (Figure 5) [33]. H₂O₂ is often employed as an oxidant in combination with acid anhydrides and hydrohalic acids, which promote the *in situ* generation of peracids and hypohalous acids, respectively. Here, we organize presentation of H₂O₂-based methods by the type of hypervalent iodine compounds generated.

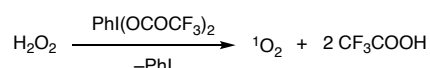


Figure 5. Hydrogen peroxide reacts with (ditrifluoroacetoxy)iodobenzene to form singlet oxygen (¹O₂) and iodobenzene (**1**).

Peracid-based oxidation of iodoarenes was first reported by Boeseken and Schneider in 1931 who synthesized (diacetoxyiodo)benzene by treatment of iodobenzene in chloroform with 55% peracetic acid [34]. In 1953, Pausacker reported a modified synthesis in which 30% H₂O₂ and acetic anhydride were stirred together at 40 °C to generate peracetic acid followed by addition of iodobenzene (**1**) to the resulting solution (Figure 6) [35]. This method avoids the use of highly concentrated peracetic acid solution and was the earliest example with H₂O₂ as the terminal oxidant for the synthesis of I(III) compounds. To date, this method is among the most widely used for the synthesis of PhI(OAc)₂ (**2**).

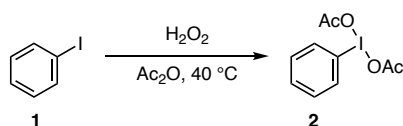


Figure 6. The combination of hydrogen peroxide and acetic anhydride generate peracetic acid *in situ*, which is responsible for oxidation of iodobenzene (**1**) to (diacetoxyiodo)benzene (**2**).

[Bis(trifluoroacetoxy)iodo]arenes are stronger oxidants than PhI(OAc)₂ due to the more electron withdrawing trifluoroacetoxy groups on the iodine center [36]. Zhdankin *et al.* reported a direct synthetic route to [bis(trifluoroacetoxy)iodo]arenes using trifluoroperacetic acid, generated *in situ* by combination of 80% H₂O₂ with trifluoroacetic anhydride [37]. Although the described procedure was more efficient than previous synthetic methods based on ligand exchange reactions of hypervalent iodine(III) compounds with trifluoroacetic acid [38, 39], silver trifluoroacetate [40], or trimethylsilyl trifluoroacetate [41], the use of such high concentration of H₂O₂ poses serious safety hazards. In 2006, Wirth *et al.* described a

modification of the procedure using UHP as the terminal oxidant, which enabled *in situ* formation of trifluoroperacetic acid, leading to efficient formation of [bis(trifluoroacetoxy)iodo]benzene (**15**), [bis(trifluoroacetoxy)iodo]toluenes (**24**, **25**), [bis(trifluoroacetoxy)iodo]arenes with electron-withdrawing substituents (**26-29**), and chiral I(III) product **30** (Figure 7) [42].

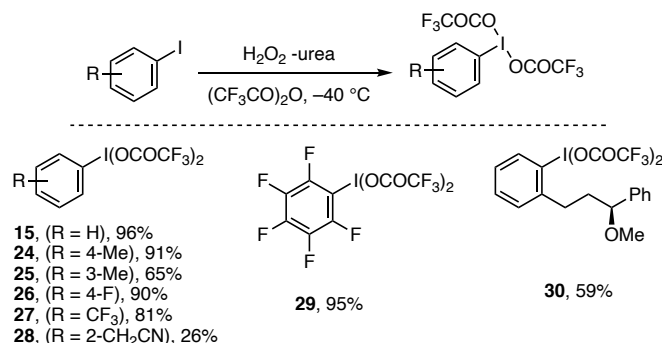


Figure 7. *In situ* generation of trifluoroperacetic acid from UHP and trifluoroacetic anhydride provides access to [bis(trifluoroacetoxy)iodo]arenes from the corresponding iodoarenes.

(Dichloroiodo)arenes, ArICl₂, are widely used reagents for the chlorination of unsaturated hydrocarbons and also as terminal oxidants for transition metal catalysis [43]. Historically, (dichloroiodo)benzene (**31**) has been synthesized by bubbling chlorine gas into a solution of iodobenzene (**1**) at a low temperature. Use of toxic and corrosive chlorine gas can be avoided using hydrochloric acid in combination with oxidants like KClO₃ [44], KMnO₄ [45], concentrated HNO₃ [45], Na₂S₂O₈ [46], CrO₃ [47], NaClO₂, or NaClO [48]. These methods suffer from (super)stoichiometric use of terminal oxidants and poor substrate scope with respect to electron withdrawing substituents on the iodoarenes. Jarnej and co-workers reported an alternative route for the synthesis of (dichloroiodo)arenes from a mixture of HCl/H₂O₂ (30% aqueous solution) in 1,1,1-trifluoroethanol (TFE) which acts both as a solvent and activator for H₂O₂ (Figure 9) [49]. In this protocol, hypochlorous acid (HOCl) is generated *in situ* and acts as the active oxidant and chlorinating agent. This method tolerates alkyl substituents (**32**, **33**) as well as electron-withdrawing groups such as carboxyl-, nitro-, and chloro substituents (**34-37**). In case of 4,4'-diiodo-1,1'-biphenyl, both the iodine centers are chlorinated to generate **38**. In the presence of electron donating groups like dimethyl, trimethyl or methoxy substituents, the corresponding (dichloro)iodoarenes (**39-41**) decompose to the chlorinated arene products.

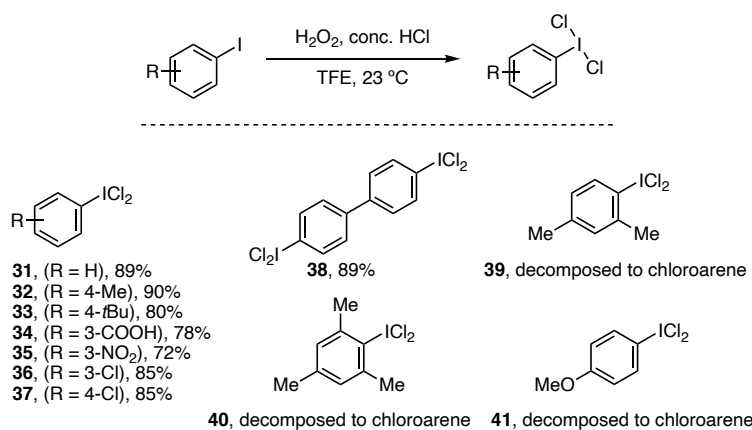


Figure 9. H₂O₂ was combined with concentrated HCl to form hypochlorous acid (HOCl) *in situ*, the active chlorinating reagent for the synthesis of (dichloroiodo)arenes from iodoarenes.

Diaryliodonium salts are typically synthesized via a two-step process involving iodoarene oxidation followed by arylation of the I(III) with a suitable arene; thus, catalysis is often limited and sustainable synthesis of these reagents is important to decrease the environmental impact. Building on the demonstration of UHP in the synthesis of iodine(III) reagents, Olofsson *et al.* developed a UHP-based synthesis of diaryliodonium triflates [50]. The authors utilized the *in situ* formation of triflic peroxide using UHP and triflic anhydride (Tf₂O) to oxidize the iodoarenes in presence of suitable arenes to furnish diaryliodonium triflates in a single step. The developed methodology was effective in synthesizing both symmetric (**42**) and unsymmetric iodonium (**43-51**) salts in good yield (42-86%) but, use of oxidatively labile substrate like anisole or pyridine led to undesired side-products or pyridine-*N*-oxides, respectively without any desired product formation (**52**, **53**) (Figure 8).

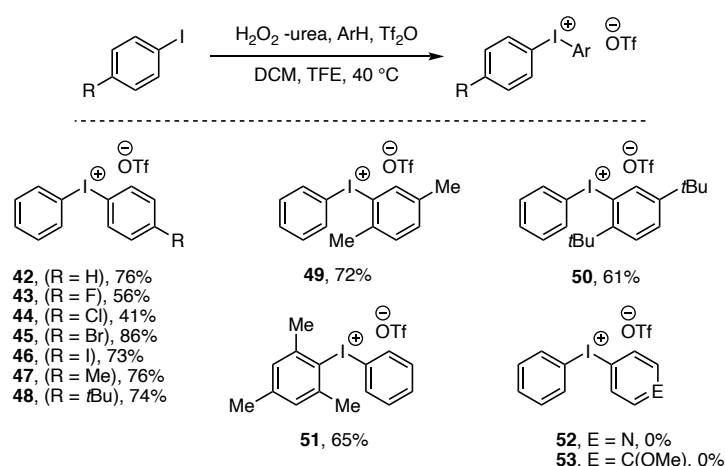


Figure 8. Diaryliodonium triflates were synthesized using urea adduct of hydrogen peroxide in a sustainable method leading to symmetric and unsymmetric iodonium salts.

B.2.1. Synthesis of Hypervalent Iodine(V) Reagents from H₂O₂ or UHP

Zhdankin and co-workers reported a two-step, one-pot strategy to access iodylarenes using H₂O₂ as the terminal oxidant by coupling *in situ* generation of peracid with subsequent disproportionation chemistry catalyzed by RuCl₃ (0.8 mol%) [51]. This method was effective in furnishing iodylarenes bearing both electron-donating (**54-57**) and electron-withdrawing groups (**58-63**), but formation of 2-iodoxybenzoic acid (IBX) from 2-iodobenzoic acid was unsuccessful (Figure 10a). When independently synthesized PhI(OAc)₂ (**2**) was treated with RuCl₃ (0.4 mol%) in an aqueous acetonitrile solution at room temperature, immediate formation of equimolar amount of iodylbenzene (**20**) and iodobenzene (**1**) were observed, which is consistent with disproportionation being operative in the synthesis of I(V) species (Figure 10b) [52].

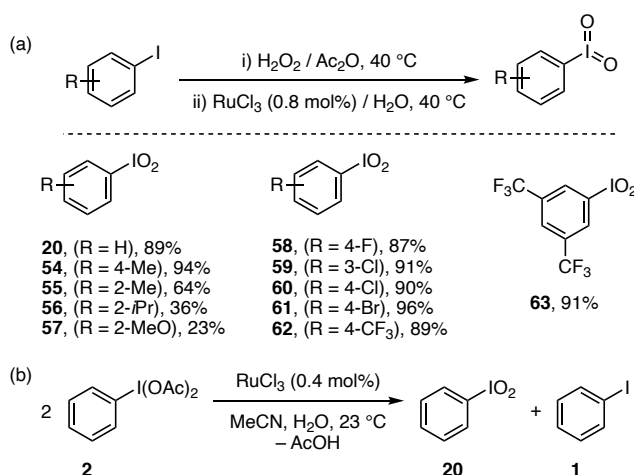


Figure 10. (a) RuCl₃-mediated disproportionation of initially formed hypervalent iodine(III) intermediates provided access to the corresponding iodylarenes. (b) Treatment of independently synthesized (diacetoxyiodo)benzene (**2**) with RuCl₃ resulted in disproportionation to equimolar amount of iodylbenzene (**1**) and iodylbenzene (**20**).

C. Electrochemical Synthesis of Hypervalent Iodine Reagents

Anodic oxidation of iodoarenes represents a conceptually attractive approach to these species, in which stoichiometric oxidants are replaced by electrical potential. Electrosynthesis can broadly be classified as either *ex cell*, in which anodic oxidation of iodoarenes is accomplished during a first step and the resulting hypervalent iodine reagents are subsequently utilized for substrate functionalization in a separate step, or *in cell*, in which anodic oxidation of iodoarenes is carried out in the presence of substrate, such as is required to achieve electrocatalysis [53]. Both I(III) and I(V) reagents have been prepared electrochemically. Due to the substantial overpotential that is typically required for the anodic oxidation of iodoarenes, hypervalent iodine electrochemistry is often limited to *ex cell* applications (*i.e.*, at the potential required to oxidize iodoarenes, many substrates participate in background oxidation).

C.1. Electrochemical Synthesis of Hypervalent Iodine(III) Reagents

The first example of electrochemical synthesis of hypervalent I(III) reagents was reported in 1960 by Schmidt and Meinert, who described the anodic oxidation of iodobenzene in the presence of silver fluoride (AgF), which acts as both the fluorine source and supporting electrolyte, to generate (difluoroiodo)benzene (PhIF₂, **65**) [54]. Subsequent reports have described difficulty reproducing this synthesis [55]. In 1994, Fuchigami and co-workers discovered that direct electrolysis of 4-iodonitrobenzene (**64**) in presence of Et₃N·3HF as the supporting electrolyte and fluorine source formed 4-(difluoroiodo)nitrobenzene (**66**) in 53% yield (Figure 11) [56]. But, electrolysis of iodobenzene and 4-iodotoluene did not lead to the desired I(III) compounds, but instead gave rise to benzylic fluorination and diaryliodonium products, respectively.

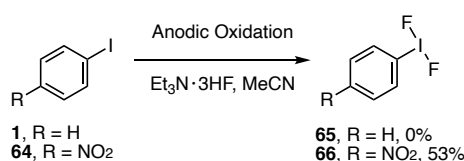


Figure 11. Electrochemical synthesis of 4-(difluoroiodo)nitrobenzene (**66**) was achieved using triethyl amine adduct of hydrogen fluoride both as the source of fluoride and the supporting electrolyte under constant current electrolysis conditions.

Hara *et al.* later discovered that by using $\text{Et}_3\text{N}\cdot 5\text{HF}$ as the supporting electrolyte and fluorine source resulted in the successful electrosynthesis of 4-(difluoroiodo)toluene (**68**) via potentiostatic electrolysis of 4-iodotoluene (**67**) at 1.5 V vs Ag^+/Ag [57]. Electrochemically generated **68** has been applied to a variety of substrate functionalization reactions including fluorination of β -dicarbonyl substrates [57], fluorocyclization of *N*-allylbenzamides [58], and vicinal difluorination of olefins (Figure 12) [59].

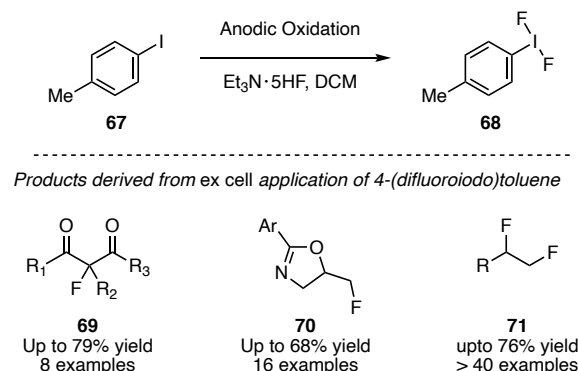


Figure 12. Electrochemical synthesis of 4-(difluoroiodo)toluene (**67**) was carried out under constant current electrolysis condition and then utilized in various *ex cell* fluorination reactions.

Ex cell electrochemistry of hypervalent iodine reagents provides a means to generate unstable, or dangerous reagents *in situ* without the need for isolation, which often leads to improved yields and safer reaction conditions [60, 61]. Nishiyama and co-workers developed anodic oxidation of iodoarenes in fluorinated solvents, such as trifluoroethanol (TFE) to afford [bis(trifluoroethoxy)iodo]benzene (**72**) [62-64]. Fluorinated alcohol solvents are known to help stabilize radical cation intermediates and consequently improve single electron oxidation events of iodoarenes at anode surfaces [36, 65-67]. While many of the I(III) reagents supported by fluorinated alkoxide ligands are not stable to isolation (with the exception of the *p*-nitro substituted derivative), these electrochemically derived reagents have been widely employed in subsequent *ex cell* substrate functionalization (Figure 13) [62-64, 68-72].

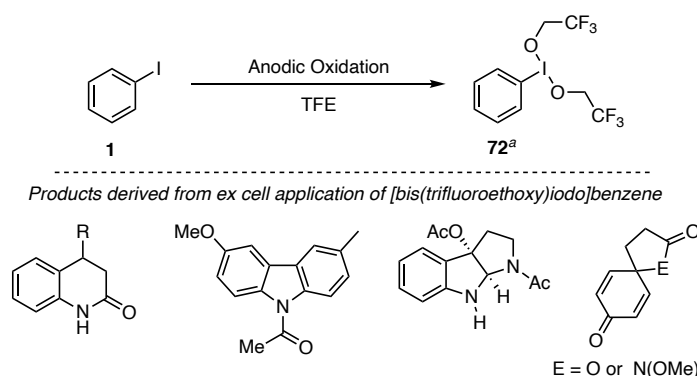


Figure 13. Fluorinated alcohol solvents such as trifluoroethanol (TFE) is used to stabilize anodically generated hypervalent iodine(III) intermediate and the resulting oxidizing solution is utilized for *ex cell* applications leading to various alkaloids, lactones and lactams. ^aOnly stable in solution, not isolable.

The anodic oxidation of iodoarenes can also be used to electrochemically synthesize diaryliodonium salts. In 1967, Miller and Hoffmann disclosed that potentiostatic electrolysis of iodobenzene at 1.65 V vs Ag^+/Ag , in acetonitrile, with lithium perchlorate as the supporting electrolyte afforded (4-iodophenyl)(phenyl)iodonium perchlorate in 45% yield [73]. Similarly,

electrolysis of iodobenzene and 4-iodotoluene in the presence of benzene resulted in diphenyliodonium perchlorate (32% yield) and (4-methylphenyl)(phenyl)iodonium perchlorate (56% yield), respectively. Wendt and co-workers later investigated the mechanism of diaryliodonium formation. Because benzene does not oxidize below 1.9 V vs Ag^+/Ag , they concluded that iodoarenes are oxidized at the anode surface [74].

In 2000, Peacock and Pletcher reported a method to expand the scope of diaryliodonium salts that could be prepared electrochemically [75, 76]. By using a mixture of acetic acid, acetic anhydride, and sulfuric acid as the reaction solvent, anodic synthesis of iodonium salts (**75**) was extended to electron rich iodoarenes and arene coupling partners (Figure 14). In addition, both symmetric and asymmetric iodonium salts were synthesized. Due to the substantial overpotential for anodic oxidation of iodoarenes, many functional groups were still found to be incompatible with the developed conditions. Electron-withdrawing substituents on the iodoarene (**73**) increased the onset potential beyond the solvent window and thus prevented initial anodic oxidation. Electron-donating substituents on the iodoarene, such as 4-methoxy, decreased the onset potential for iodoarene oxidation, however, gave rise to side reactions, such as anisole sulfonation by sulfuric acid. With respect to the arene coupling partner (**74**), electron-withdrawing substituents decreased yields due to decreased nucleophilicity and electron-rich arene coupling partners were limited due to direct anodic oxidation and subsequent radical polymerization.

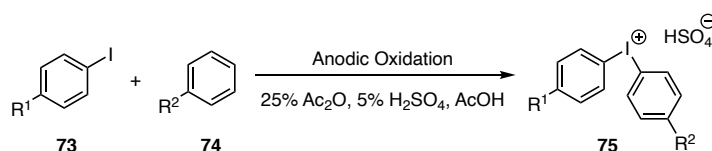


Figure 14. Electrochemical synthesis of both symmetric and unsymmetric diaryliodonium bisulfates under constant current conditions.

One challenge in utilizing electrochemically derived hypervalent iodine reagents for substrate functionalization is the need to remove the iodoarene byproducts and electrolyte from the reaction product. To address this, Francke and coworkers developed low-molecular-weight, charged iodoarenes as potential *ex cell* mediators in which the supporting electrolyte and the iodoarene mediator were combined [77-79]. The first examples developed were quaternary ammonium substituted 4-iodoarenes. Anodic oxidation of iodoarene **76** in fluorinated solvents provided access to the corresponding hypervalent iodine compound **77**, which was subsequently utilized in *ex cell* C–N bond forming reactions such as carbazole formation (**78**), *N*-arylation (**79**) [77], and oxazole syntheses (**80**) (Figure 15) [78].

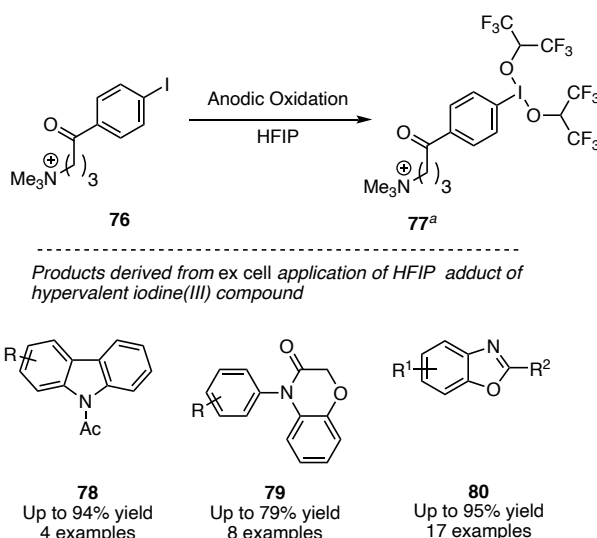


Figure 15. Iodoarene (**76**) with tetramethylammonium moiety obviates the need to use additional supporting electrolyte and acts as a mediator for C–N bond forming reactions leading to carbazoles, *N*-aryl benzoxazinones and oxazoles. “Only stable in solution, not isolable.

Francke and co-workers advanced iodophenylsulfonates (**83**, **84**) and iodobenzoates (**85–87**) as redox-active supporting electrolytes [79]. The *ex cell* reactivity of the corresponding I(III) compounds [ArI(OCH(CF₃)₂)₂] was evaluated by reaction with *N*-([1,1'-biphenyl]-2-yl)acetamide (**81**) to afford 1-(9*H*-carbazol-9-yl)ethan-1-one (**82**) (Figure 16). While both of the iodophenylsulfonate isomers **83** and **84** could be used as *ex cell* mediators for the intramolecular C–H amination reaction, iodobenzoate compounds **85–87** did not promote substrate oxidation to form carbazole **82**.

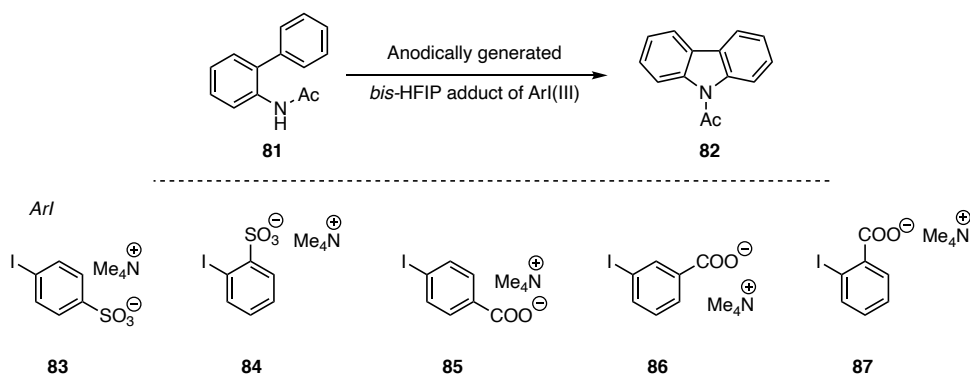


Figure 16. Tetramethylammonium salts of iodophenylsulfonates and iodobenzoates combine the roles of electrolyte and iodoarene mediator.

Flow chemistry has also been advanced as an approach to achieve anodic synthesis of hypervalent iodine reagents and utilize them in *ex cell* substrate functionalization. Flow conditions offer advantages compared to mechanical stirring, such as better mixing, more efficient heat transfer, and easy scale-up [80]. Flow systems can be especially useful in industrial settings for energy conservation [81], multistep synthesis [82] or end-to-end production [83]. Wirth and co-workers have studied the synthesis and utilization of hypervalent iodine species via flow technology [84–87]. Symmetrical and unsymmetrical iodonium salts have been synthesized by Wirth and co-workers using a microreactor with two platinum electrodes separated by a thin film (250 nm) [84]. This method was later elaborated to achieve *meta*-selective C–H arylation of anilines in an end-to-end production [85].

More recently, Wirth and co-workers extended the scope of electrochemically derived hypervalent iodine reagents generated in flow by preparing [bis(hexafluoropropoxy)iodo]arenes and utilizing them in a wide range of substrate oxidation reactions including sulfide oxidation, oxidative heterocyclization, and α -functionalization of carbonyl compounds (Figure 17) [87].

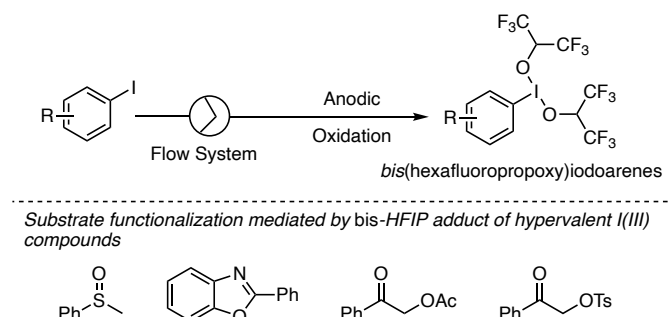


Figure 17. Anodically generated *bis*-HFIP adduct under flow condition is used for various substrate functionalization reactions.

C.2. Electrochemical Synthesis of Hypervalent Iodine(V) Reagents

Anodic oxidation of 2-iodobenzoic acid (**88**) in 0.2 M H₂SO₄ aqueous solution with a boron-doped diamond electrode produced IBX (**89**) under potentiostatic electrolysis conditions [88, 89]. This system displayed potential-dependent product selectivity: Applied potentials between 1.6–1.8 V vs SCE resulted in the formation of 1-hydroxy- λ^3 -benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**9**) while applied potentials above 1.8 V vs SCE yielded IBX (**89**) (Figure 18). The boron-doped diamond electrode was found to be important due to both its stability and the high overpotential for O₂ evolution at this electrode.

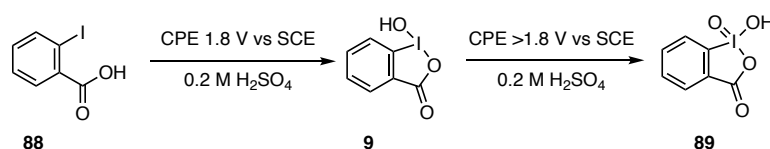


Figure 18. Electrochemical oxidation of 2-iodobenzoic acid (**88**) leads to both 1-hydroxy- λ^3 -benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**9**) and 2-iodoxybenzoic acid (**89**) under constant potential electrolysis conditions.

D. Recyclable Hypervalent Iodine Reagents

In addition to developing more sustainable oxidation protocols for the synthesis of hypervalent iodine compounds, significant effort has been made to improve iodoarene recyclability. Separation of iodoarene byproducts from the desired reaction products is often tedious, and thus iodoarenes are not typically reused. Strategies based on polymer-supported hypervalent iodine compounds, which facilitate recovery via simple filtration, and based on fluorous alkyl iodoarenes, which facilitate recovery via biphasic separations with fluorous solvents, have been developed to enable iodoarene recycling. Here we highlight the synthesis and application of polymer-supported and fluorous I(III) and I(V) reagents.

D.1. Synthesis of Polymer-supported Hypervalent Iodine(III) Reagents

Poly[4-(diacetoxyiodo)styrene] (**90**) was first prepared by Okawara via iodination of polystyrene followed by oxidation with peracetic acid [90, 91]. The loading of I(III) centers on

the polystyrene backbone was determined to be 1.99 mmol/g by iodometry. In other examples, polystyrenes that display high molecular weight (poly-(diacetoxyiodo)styrene, ~45,000) and low molecular weight (poly-(diacetoxyiodo)(α -methylstyrene), ~6000) have been converted to the corresponding hydroxy(tosyloxy)iodine(III) polymers (**91** and **92**, respectively) by treatment with *p*-toluenesulfonic acid monohydrate [92, 93]. Alternately, iodinated polymers derived from coupling between poly[(aminomethyl)styrene] and either *p*-iodobenzoic acid or *p*-iodophenylacetic acid, were oxidized with *in situ* generated peracetic acid to afford the polymer-supported (diacetoxyiodo)arenes (**93** and **94**, respectively) (Figure 19) [94]. In each of these cases, iodoarene recycling was achieved by simple filtration followed by a methanol wash of the polymer. In a similar context, highly insoluble small-molecule iodoarene mediators have also been demonstrated to be recyclable [95-98].

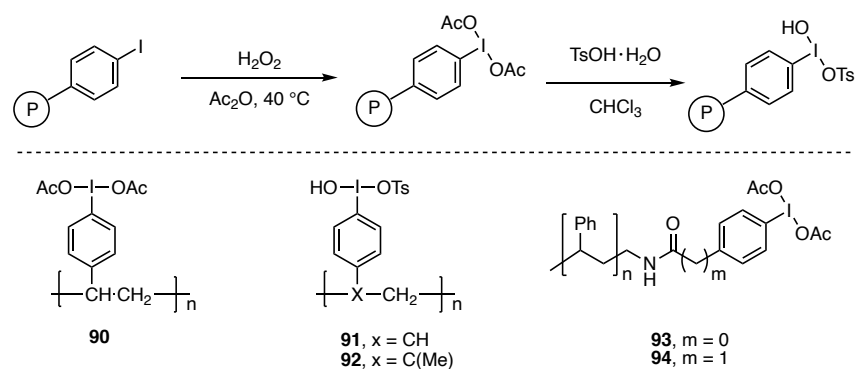


Figure 19. Synthesis of polymer-supported (diacetoxyiodo)arenes using H_2O_2 and acetic anhydride. These reagents participate in ligand exchange chemistry in presence of *p*-toluenesulfonic acid to form tosylated I(III) reagents. These reagents can be recycled by simple filtration.

D.2. Synthesis of Polymer-Supported Hypervalent Iodine(V) Reagents

IBX is poorly soluble in many organic solvents, which often necessitates the use of dimethyl sulfoxide (DMSO) as a reaction solvent. In general, it is challenging to recover the corresponding I(III) byproduct (*i.e.*, **9**) from these reaction conditions [99, 100]. To alleviate the need for DMSO as solvent, Mülbaier and Giannis developed silica-immobilized IBX reagent **95** (0.4 mmol/g) by tethering the appropriate iodoarene via a phenoxide linker (Figure 20) [101]. Oxidation to the corresponding immobilized I(V)-based material was accomplished with Oxone. Oxidation of alcohols was achieved in good yield by **95** in THF instead of DMSO, the solvent required for IBX-mediated alcohol oxidation. Polychloromethyl styrene- [102] and multiwalled carbon nanotubes (MWCNT)-supported for I(V) reagents (**96** and **97**, respectively) have also been synthesized [103]. Similarly, amide linkages have been used to prepare polymer-supported I(V) reagents **98-101** [104, 105].

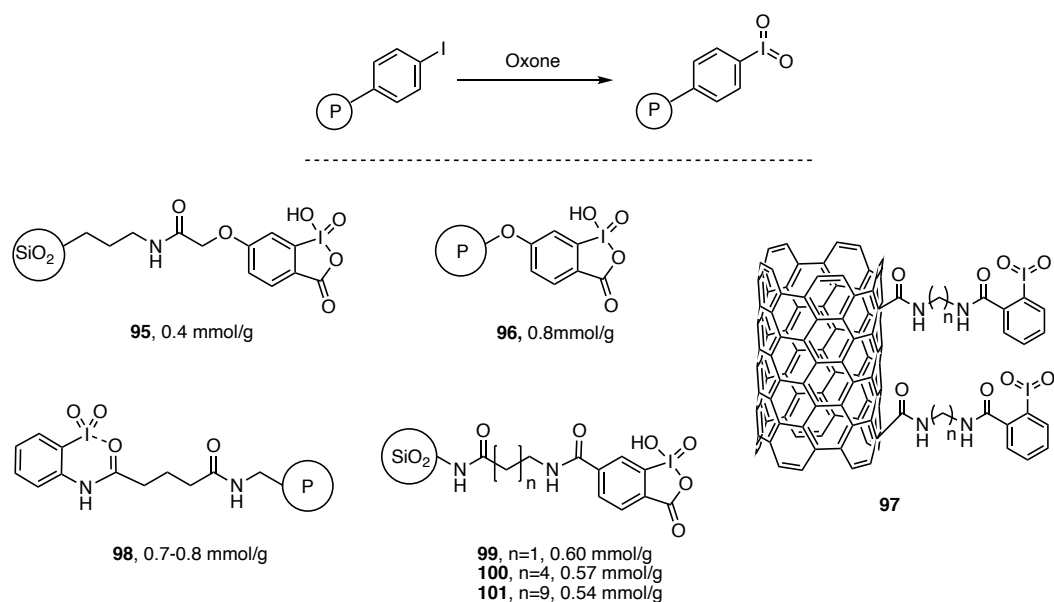


Figure 20. Examples of polymer-supported hypervalent iodine(V) reagents that facilitate recycling of the corresponding iodoarenes after substrate functionalization.

Yakura and co-workers reported magnetic nanoparticle-supported iodoarene **103** for the catalytic oxidation of phenols (**102**) to form *p*-quinones (**104**) and demonstrated recovery by application of an external magnetic field (Figure 21a) [106]. Kirsch and co-workers also reported solid-supported iodoarene catalysts **106** and **107** and for catalytic oxidation of secondary alcohols (**105**) to ketones (**108**) in the presence of Oxone and demonstrated that the recovered catalyst was catalytically active up to 5 cycles (Figure 21b) [107]. For additional discussion of iodoarene catalysis, see Section E.

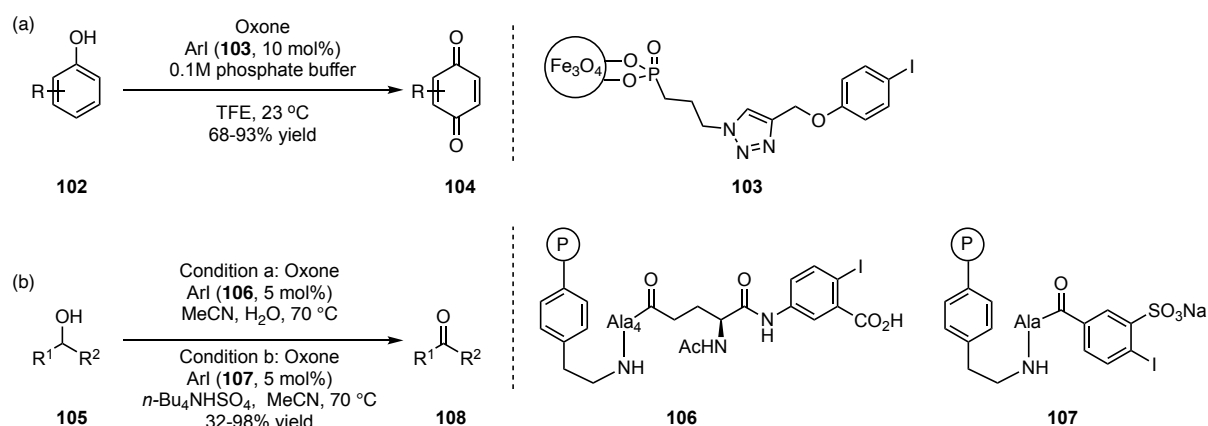


Figure 21. Oxone is used as a terminal oxidant for (a) magnetic nanoparticle-supported iodoarene (**103**) catalyzed phenolic oxidation and (b) polymer-supported iodoarene (**106** and **107**) catalyzed oxidation of secondary alcohols to ketones. While **103** is recovered by application of an external magnetic field, **106** and **107** were recycled by filtration after the reaction with $\geq 95\%$ recovery.

D.3. Fluorous Hypervalent Iodine(III) Reagents

Fluorous hypervalent iodine reagents have also been developed to enable extraction-based recovery of iodoarene byproducts. Since the first synthesis of hypervalent iodine reagents with fluoroalkyl substituents in 1971 [108], these reagents have proved to be useful due to their high lipophobicity and hydrophobicity. In 2003, Gladysz and co-workers developed a series of hypervalent iodine reagents with fluoroalkyl substituents **110-113**, which were prepared by

oxidation with $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ [109]. This family of hypervalent iodine reagents participated in the oxidation of hydroquinones **109** to generate *p*-quinones **114** (Figure 22). The resulting iodoarene byproducts displayed high fluororous-phase affinity, which facilitated separation and recycling.

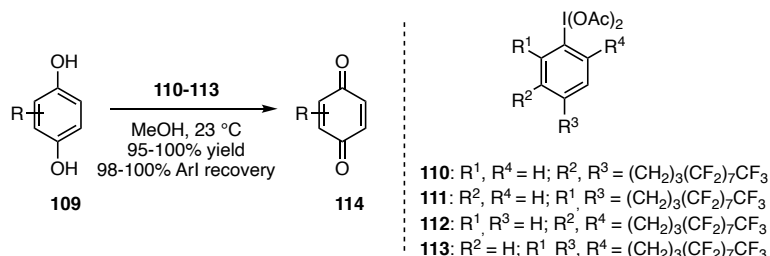


Figure 22. Fluororous hypervalent iodine mediated oxidation of hydroquinone led to high yield of benzoquinone. Iodoarene byproducts were recovered by fluororous-phase extraction with $\text{CF}_3\text{C}_6\text{F}_{11}$.

In 2006 Gladysz and co-workers reported a family of hypervalent iodine reagents (**115**) derived from fluororous alkyl iodides and applied them in alcohol oxidation chemistry (Figure 23a) [110]. Fluororous extraction enabled repeated use and recovery; three cycles achieved with high recovery of alkyl iodides. More recently, polyfluorinated hypervalent iodine reagents have been utilized towards the synthesis of sulfoximines from sulfides under mild conditions [111, 112]. Wirth and co-workers developed oxidation of sulfides (**116**) with hypervalent iodine compound **117**, catalyzed by $\text{Fe}(\text{acac})_3$ in acetonitrile, to afford *N*-substituted sulfoximines (**118**) (Figure 23b) [111]. Using the (diacetoxyiodo)arene **119** and TPGS-750-M as a surfactant allowed for formation of *N*-H sulfoximines (**120**) from **116** in aqueous media (Figure 23c) [112].

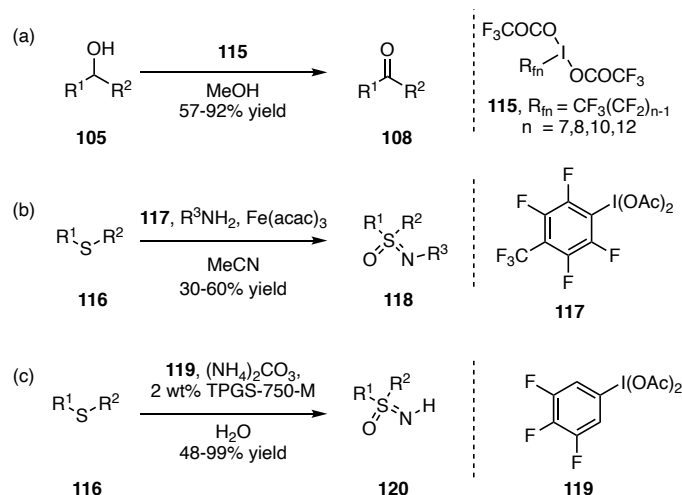


Figure 23. Fluororous hypervalent iodine compounds can be utilized for the oxidation of (a) alcohols to ketones, (b) sulfides to *N*-substituted sulfoximines, and (c) sulfides to *N*-H sulfoximines.

E. Catalytic Application of Hypervalent Iodine Compounds

Hypervalent iodine catalysis utilizes selective *in situ* oxidation of substoichiometric amounts of iodoarenes to accomplish hypervalent iodine mediated substrate functionalization chemistry. Catalysis inherently reduces the iodoarene waste that is generated by hypervalent iodine reagents. The central challenge in achieving hypervalent iodine catalysis is the selective oxidation of the iodoarene catalyst in the presence of oxidatively labile substrates. Here we highlight recent progress in hypervalent iodine catalysis, and as above, organize the presentation by the nature of the terminal oxidant employed. The examples presented are not

exhaustive, but have been selected to highlight different approaches to achieving hypervalent iodine catalysis.

E.1.1 Catalytic Hypervalent Iodine(III) Reactions Using O₂

Miyamoto and co-workers developed iodoarene-catalyzed aerobic glycol cleavage and Hofmann rearrangement chemistry under isobutyraldehyde autoxidation conditions [113]. Using pentamethyliodobenzene (**122**) as catalyst, oxidative C–C cleavage of various diols (**121**) was achieved forming ketones **123** (Figure 24a). Notably, this aerobic oxidation condition was effective for glycol scission of cyclic *trans*-diols, which can be difficult to achieve using common oxidants like NaIO₄. The authors also carried out Hofmann rearrangement of carboxamides **124** to form carbamates **125** using the same catalysis conditions (Figure 24b). This was an improvement over existing protocols that use *m*-CPBA as the terminal oxidant because aromatic amides undergo background oxidation with *m*-CPBA to form *N*-oxides [114]. The reported hypervalent iodine catalysis can also be performed using air, in place of O₂, without significant decrease in yield.

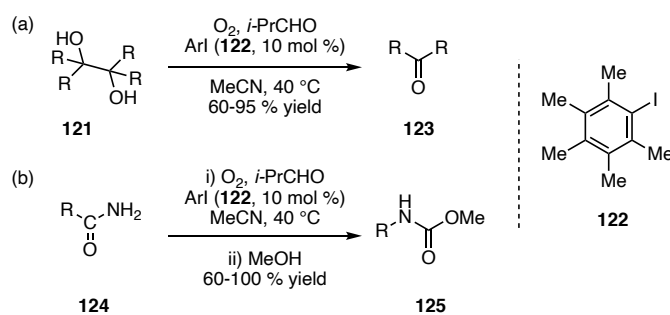


Figure 24. Aerobically generated hypervalent iodine(III) intermediates are applied to (a) oxidative C–C cleavage and (b) Hofmann rearrangement reactions using O₂ as the terminal oxidant.

Contemporaneously, Powers *et al.* utilized aerobically generated I(III) reagents (Figure 1) derived from acetaldehyde autoxidation in catalytic C–H amination, carbonyl α -functionalization, and spirocyclization reactions [23]. C–H amination was achieved using catalytic amount of 1,2-diiodobenzene (**127**) [115] with O₂ as the terminal oxidant to furnish *N*-methoxy-4-methyl-*N*-phenylbenzenesulfonamide (**128**) from benzene and amine **126** (Figure 25a). Similar reaction conditions resulted in aerobic bromination of ethyl acetoacetate (**129**) and aerobic spirocyclization of *N*-methoxy-3-(4-methoxyphenyl)propenamide (**131**) to form **130** and **132** respectively (Figure 25b–c). Control reactions in the absence of iodoarene did not furnish products in any of the reactions in Figure 25, which demonstrates that reactive intermediates from aldehyde autoxidation are not directly involved in substrate functionalization.

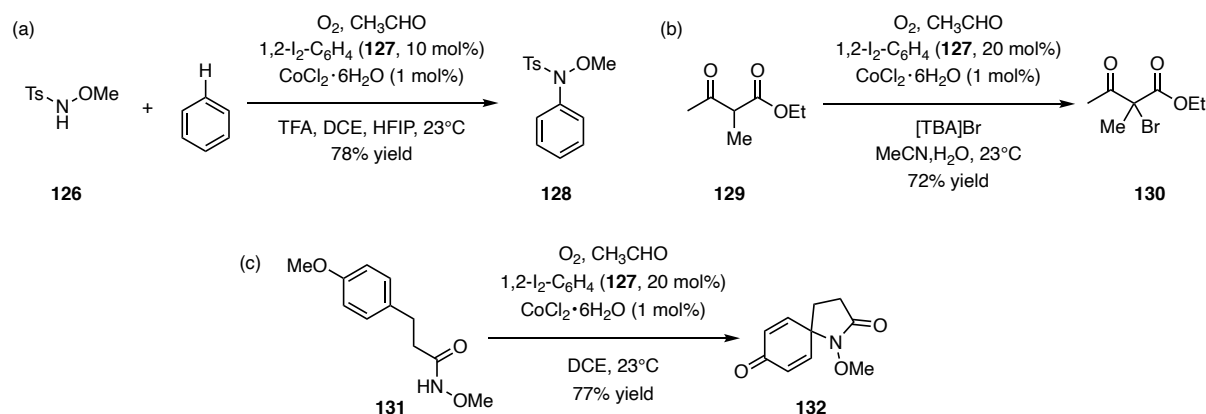


Figure 25. Utilization of aerobically generated hypervalent iodine(III) reagents are exemplified in the context of (a) C–H amination, (b) aerobic halogenation, and (c) spirocyclization using O_2 as terminal oxidant.

Similar aldehyde-promoted aerobic oxidation catalysis was reported by Sen and co-workers, who demonstrated the synthesis of substituted 1,3,4-oxadiazole **135** from *N'*-anilidene acetohydrazines **133** using 4-iodoanisole (**134**) as catalyst (Figure 26) [116].

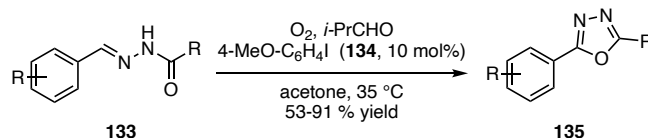


Figure 26. Synthesis of substituted oxadiazoles were carried out using O_2 as the terminal oxidant and 4-iodoanisole as the catalyst.

E.1.2 Catalytic Hypervalent Iodine(V) Reactions Using O_2

In 2018, Powers and co-workers utilized *in situ* aerobic synthesis of (2-*tert*-butylsulfonyl)iodylbenzene (**21**, Figure 4) from (2-*tert*-butylsulfonyl)iodobenzene (**136**) to accomplish hypervalent-iodine-catalyzed alcohol oxidation [28]. Secondary alcohols were oxidized to ketones, whereas primary alcohols were oxidized to carboxylic acids because initially generated aldehydes were further oxidized under aldehyde autoxidation conditions (Figure 27a). Oxidative C–C cleavage was observed for 1,2-diols, which is characteristic of the reactivity of Dess-Martin Periodinane (DMP) (Figure 27b).

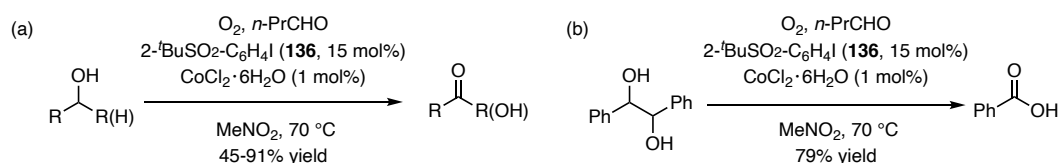


Figure 27. (a) Aerobically generated (2-*tert*-butylsulfonyl)iodylbenzene (**21**) was applied for oxidation of primary alcohols to carboxylic acids and secondary alcohols to ketones. (b) (2-*Tert*-butylsulfonyl)iodobenzene (**136**) catalyzed oxidative cleavage of hydroxybenzoin was realized under aldehyde autoxidation condition to form benzoic acid, analogous to DMP chemistry.

E.2 Catalytic Hypervalent Iodine Reactions Using Peracid Oxidants

Peracid oxidants are among the most utilized terminal oxidants in hypervalent iodine catalysis. Use of peracetic acid as a terminal oxidant generates acetic acid as the only byproduct. While less oxygen dense, *m*-CPBA has also become a popular terminal oxidant in hypervalent iodine catalysis. Because 1) similar reactions have been accomplished using peracetic acid and *m*-

CPBA as terminal oxidants, and 2) the chemical structures of these reagents are similar, hypervalent iodine catalysis using either peracid will be presented together here.

Carbonyl α -Functionalization. Some of the first examples of hypervalent iodine(III) catalysis utilized iodobenzene as a catalyst and *m*-CPBA as the terminal oxidant to achieve the α -oxidation of carbonyl compounds (*i.e.*, conversion of **137** to **138**, Figure 28) [117]. Addition boron trifluoride diethyl etherate (BF₃·Et₂O), which was proposed to both induce the enolization of carbonyl starting materials and promote ligand exchange at the *in situ* generated (diacetoxyiodo)benzenes, was found to be essential for the α -acetoxylation. Following the discovery of α -acetoxylation of ketones by Ochiai and co-workers, several research groups have reported additional examples of α -acetoxylation [118], as well as α -tosyloxylation [119-121], α -phosphoryloxylation [122], and α -fluorination reactions [123, 124].

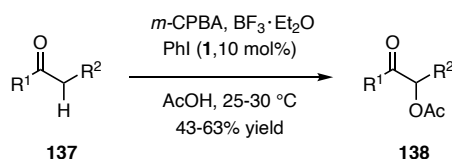


Figure 28. α -Functionalization of carbonyl compounds is exemplified by catalytic α -acetoxylation of ketones via hypervalent iodine intermediates generated using *m*-CPBA.

Catalytic enantioselective α -oxidation reactions can be accomplished with chiral iodoarenes and *m*-CPBA as the terminal oxidant. In 2007, Wirth and co-workers reported the first catalytic, enantioselective α -tosyloxylation of **137** using chiral iodoarene **139** with *p*-toluenesulfonic acid as the tosylate source to form **141** (Figure 29, condition a) [125]. In contrast to the previously developed method, which used stoichiometric chiral I(III) to accomplish enantioselective α -tosyloxylation and required a reaction temperature of -30 °C for optimum enantioselectivity [126], the catalytic reaction was performed at room temperature to overcome slow reaction kinetics (lower enantioselectivity was observed). The triazole-substituted chiral iodoarene catalyst **140** was later identified to provide similar α -tosyloxylation with higher yields as well as increased enantioselectivity (Figure 29, condition b) [127-131]. Enantioselective α -fluorination of carbonyl compounds has also been accomplished by using chiral iodoarenes and replacing the tosylate nucleophile with triethylamine hydrogen fluoride as fluorine source [132, 133].

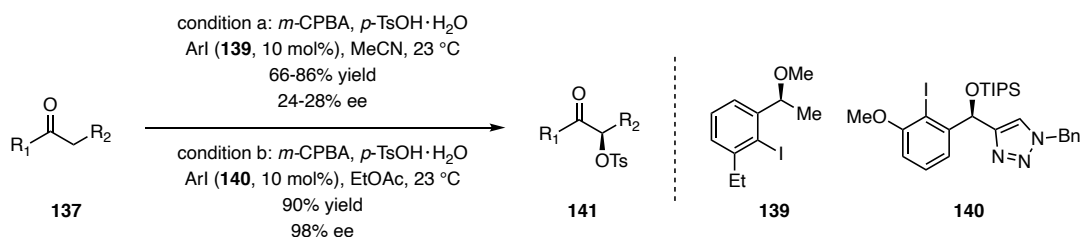


Figure 29. Enantioselective α -tosyloxylation of ketones was achieved using iodoarene catalysts bearing chiral *o*-substituents (**139** and **140**). Triazole based catalyst **140** was observed to provide increased enantioselectivity.

Spirocyclization. Hypervalent iodine catalysis has also been applied to oxidative spirocyclization chemistry (*i.e.*, the conversion of phenol **142** to spirocycle **143**, Figure 30a) [134]. Trifluoroacetic acid was found to improve the yield of spirocyclized products, which was attributed to the *in situ* formation of the stronger oxidant [bis(trifluoroacetoxy)iodo]benzene (**15**). Enantioselective examples of spirocyclization of phenolic substrates has also been studied [135-137]. Kita and co-workers reported chiral iodoarene **146** bearing an *ortho*-substituted spirobiindane backbone [135], Ishihara's group

developed a conformationally flexible C₂-symmetric iodoarene catalyst **147** [136], and Ibrahim and co-workers prepared C₂-symmetric iodoarene catalyst **148** [137], all of which promote the spirocyclization of substrate **144** to form **145** in good enantioselectivity (Figure 30b). Other catalysts including atropisomeric binaphthyl-based chiral iodides **149** have also been developed for similar spirocyclization reactions [138-148].

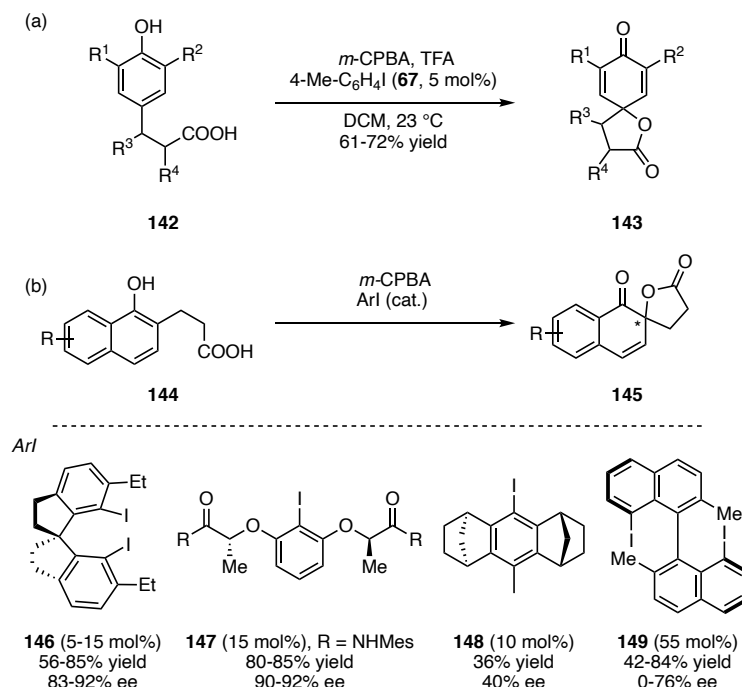


Figure 30. (a) Hypervalent iodine-catalyzed synthesis of lactones was achieved by dearomatization of 4-substituted phenolic derivatives. (b) Enantioselective spirocyclization of naphthyl propanoic acids can be achieved with various chiral iodoarenes catalysts (**146-149**).

Oxidative C–H Coupling Chemistry. In 2013, Kita and co-workers developed a hypervalent iodine-catalyzed oxidative cross-coupling reaction of aromatic sulfonanilides **150** with aromatic hydrocarbons to give the biaryl products **152** in high yields (Figure 31) [149]. While using iodobenzene as the catalyst resulted in low yields, 2,2'-diiodobiphenyl derivative **151** was found to be highly active towards the described C–C coupling chemistry.

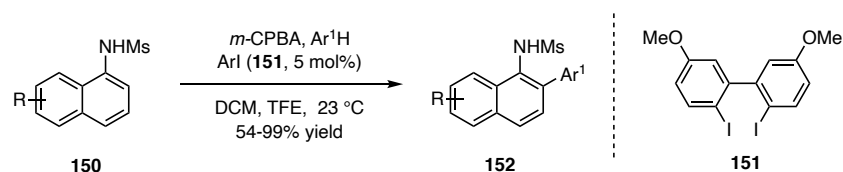


Figure 31. Hypervalent iodine-catalyzed oxidative C–C coupling with *m*-CPBA as the terminal oxidant.

Similarly, Gong and co-workers demonstrated intramolecular asymmetric oxidative C–C bond-forming chemistry, in the context of spirooxindole (**155**) synthesis from **153**, using chiral iodoarene **154** as the catalyst (Figure 32) [150]. In 2017, a computational study by Sunoj and co-workers reasoned that the observed enantioselectivity is due to the helical fold of the chiral amide arms on the iodoarene catalyst at *ortho*-positions [148].

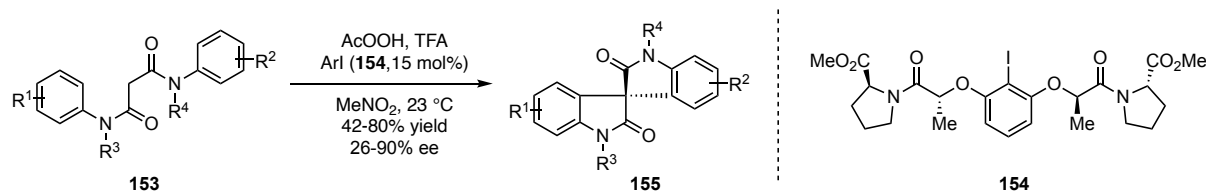


Figure 32. Asymmetric spirocyclization was achieved using chiral iodoarene catalyst **154** and peracetic acid as terminal oxidant.

Martin and co-workers reported a C(sp²)-O coupling reaction of biphenyl-2-carboxylic acids **156** in the presence of catalytic amounts of iodoarene **134** with peracetic acid as the terminal oxidant to form lactones **157** (Figure 33a) [151]. Previously, similar chemistry had been accomplished under the action of either Pt or Pd catalysts in tandem with stoichiometric hypervalent iodine(III) or Ag(I) terminal oxidants [152-158]. The authors also described formation of **160** via C(sp³)-O coupling of pyrrolobenzoxazinones **158** using 4-bromoiodobenzene (**159**) as the catalyst (Figure 33b) [151].

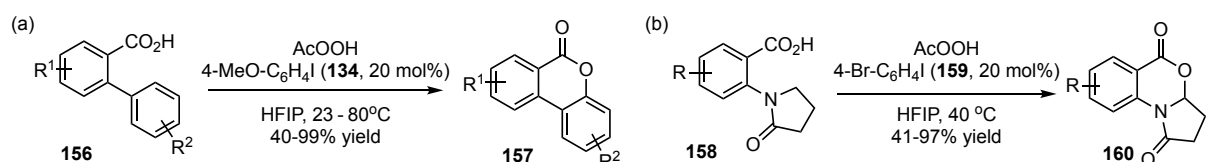


Figure 33. Iodoarene-catalyzed (a) C(sp²)-H and (b) C(sp³)-H functionalization of phenyl carboxylic acid derivatives resulted in the formation of corresponding C-O coupled lactone products.

A considerable amount of interest has focused on the development of hypervalent iodine catalysis for oxidative N-H / C-H coupling for both sp² and sp³ C-H amination [115, 159-163]. The Muñiz group reported intermolecular C-H amination (*i.e.*, the conversion of amine **161** to arylated product **162**) catalyzed by 1,2-diiodobenzene (**127**), which was identified as an exceptionally efficient catalyst that could be used in as low as 3 mol% loading (Figure 34a) [115]. The high reactivity of the corresponding μ -oxo iodine(III) species **12** was reasoned to be due to the instability of the 5-membered μ -oxo ring. Recently, Kita's group has also reported such reactivity using the 2,2'-diiodo-4,4',6,6'-tetramethyl-1,1'-biphenyl (**163**) as catalyst (Figure 34b) [164]. Similar to **12**, the μ -oxo structure of the iodine(III) species generated from **163** results in high catalytic activity; catalyst loading as low as 0.5 mol% were found to be effective.

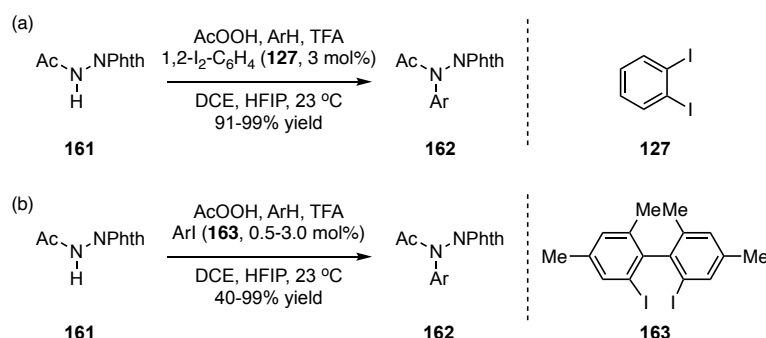


Figure 34. Hypervalent iodine-catalyzed C-H amination was achieved using (a) 1,2-diiodobenzene (**127**) and (b) 2,2'-diiodo-4,4',6,6'-tetramethyl-1,1'-biphenyl (**163**) as catalysts and peracetic acid as terminal oxidant. These reactions are proposed to proceed through μ -oxo bis-iodine(III) intermediates (e.g. **12**).

Difunctionalization of Unsaturated C-C Bonds.

Difunctionalization of olefins is one of the main classes of transformations available to hypervalent iodine compounds [165]. Achieving catalysis using peracid-based oxidants requires that the rate of iodoarene oxidation competes successfully without direct olefin epoxidation chemistry, which can be facile with peracid-based oxidants.

Oxygenation Reactions. Iodomesitylene (**165**) catalyzed *syn*-diacetoxylation of alkenes was performed using *m*-CPBA as terminal oxidant, forming vicinal diacetates (Figure 35a) [166]. These methods complement previous methods that have been developed with transition metal catalysts, including osmium [167], ruthenium [168, 169], manganese [170, 171], iron [172-174], and palladium [175, 176]. Muñiz and co-workers described an enantioselective diacetoxylation of styrenes using chiral iodoarene **168** and peracetic acid (Figure 35b) [177]. While the use of *m*-CPBA promoted significant epoxidation in this case, little background reaction was observed with peracetic acid as the terminal oxidant. The Muñiz group also demonstrated catalytic olefin diacetoxylation with iodoarene catalyst **171** bearing an *o*-pyridyl Lewis base, which proved to be kinetically superior to previous acetoxylation methods (Figure 35c) [178]. In this case, other terminal oxidants including Selectfluor, perborate, and periodate were ineffective; only peracetic acid was found to be effective. Both activated and unactivated olefins were diacetoxylation in good yields with **171**, and the increased reactivity was attributed to the stabilizing effect of pyridyl group on electrophilic iodine centers [179-181].

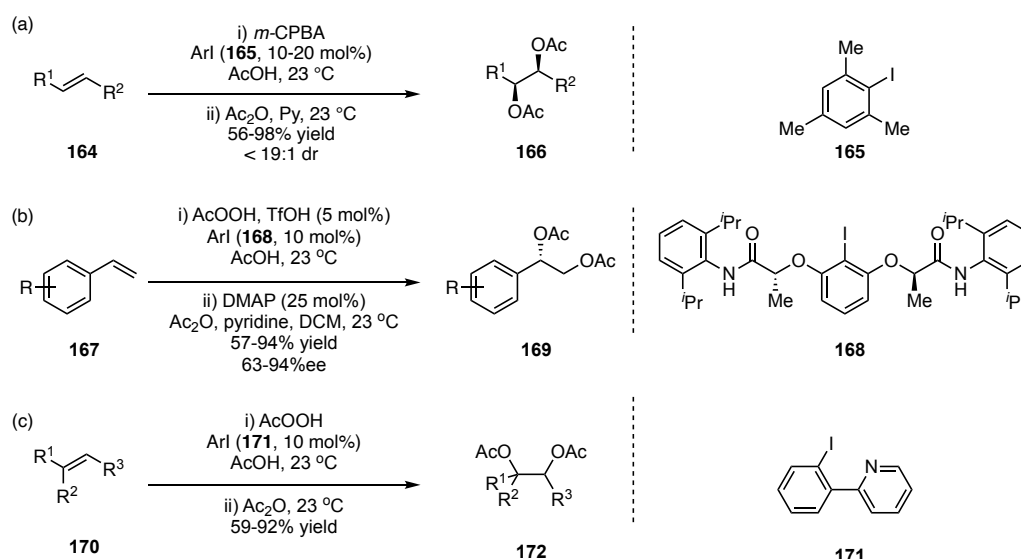


Figure 35. (a) Hypervalent iodine-catalyzed *syn*-diacetoxylation of alkenes was achieved using iodomesitylene as catalyst and *m*-CPBA as terminal oxidant. (b) Enantioselective diacetoxylation of alkenes was achieved with C₂-symmetric iodoarene catalyst **168** and peracetic acid as terminal oxidant. (c) 2-Pyridyliodobenzene catalyzed diacetoxylation of alkenes. The proximal pyridyl group was found to accelerate catalysis as compared to iodobenzene.

Fluorination Reactions. In 2016, Jacobsen and co-workers reported the enantioselective 1,2-*anti*-difluorination of alkenes with iodoarene catalyst **173**, *m*-CPBA as terminal oxidant, and an excess of Py·9HF as fluoride source (Figure 36a) [182]. The developed method is applicable to various substituted alkenes including terminal, internal, and acrylamide olefins. In the case of isolated alkenes, addition of pyridine afforded improved yields, presumably due to reduced acidity and increased nucleophilicity of fluoride ions in the reaction medium. In the same year, the Jacobsen group also reported a method for the catalytic, asymmetric, migratory geminal difluorination of β -substituted styrenes to access products bearing difluoromethylated tertiary or quaternary stereocenters using a chiral iodoarene catalyst **176** (Figure 36b) [183].

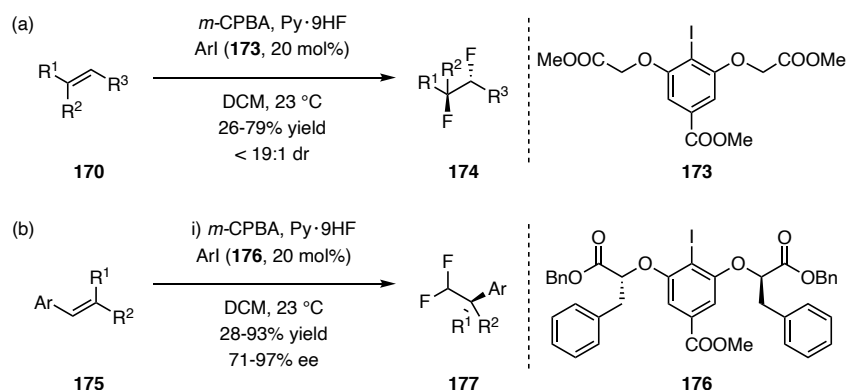


Figure 36. Asymmetric (a) vicinal difluorination and (b) gem difluorination of alkenes via chiral hypervalent iodine catalysis were achieved using *m*-CPBA as the terminal oxidant.

Amination Reactions. Iodoarene derivatives with modified chiral lactic acid side chains have emerged as effective catalysts for intermolecular diamination reactions [184]. The first hypervalent iodine-catalyzed enantioselective intermolecular diamination (*i.e.*, the conversion of **167** to **179**) was reported by the Muñiz group using iodoarene catalyst **178** (Figure 37). Background epoxidation/aminooxygenation reactions of alkenes by *m*-CPBA were reduced by changing the solvent from ethyl acetate to methyl *tert*-butyl ether (MTBE) or MTBE/HFIP mixtures, and by lowering the reaction temperature to −5 °C. With a 10 mol % catalyst loading the reaction provided 40-87% yield and up to 98% ee.

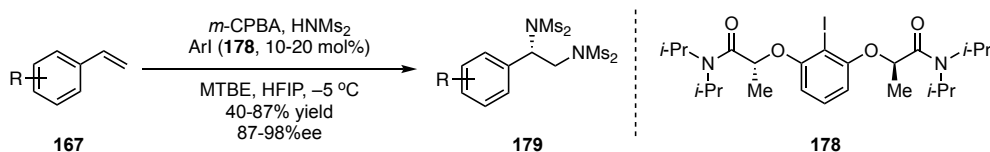


Figure 37. Hypervalent iodine-catalyzed asymmetric diamination of olefins was realized using C₂-symmetric catalyst (**178**) and *m*-CPBA as the terminal oxidant.

Oxidative Cleavage Reactions. In 2009, Miyamoto and Ochiai developed an efficient method for iodoarene-catalyzed oxidative cleavage of carbon–carbon multiple bonds as an alternative to ozonolysis [185]. Under these conditions, various unsaturated compounds such as cyclic alkenes, acyclic alkenes, and aryl acetylenes are selectively cleaved to afford carboxylic acids (Figure 38).

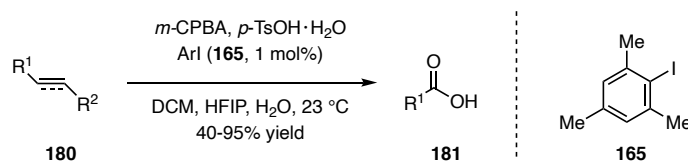


Figure 38. Iodomesitylene-catalyzed oxidative cleavage of C–C unsaturated bonds was developed as an alternative method to ozonolysis.

E.3 Catalytic Hypervalent Iodine Reactions Using Oxone

Although the active oxygen content of Oxone, in which the active oxidant is the peroxymonosulfate anion (HSO₅[−]), is lower than that of O₂ or H₂O₂, it offers several advantages, including stability, ease of transport, simple handling, controllable addition, and is nontoxic [186]. Oxone is prepared from a mixture of H₂SO₄, H₂O₂ and potassium hydroxide (KOH) [187]. Both iodine(III) and iodine(V) species can be generated from iodoarene oxidation with Oxone.

E.3.1 Catalytic Hypervalent Iodine(III) Reactions Using Oxone

Hypervalent iodine-catalyzed oxidation of phenols using Oxone as the terminal oxidant has been widely studied. Yakura and co-workers reported iodoarene (**183**) catalyzed oxidation of phenolic derivatives to form *p*-quinones **184** (Figure 39a) [188-190], and *p*-quinols **186** (Figure 39b) [191, 192], depending on the substituents at *para*-positions of **182** and **185** respectively. It was hypothesized that the *in situ* generated I(III) intermediates react with phenolic compounds to form a cationic intermediate, which is then trapped by H₂O to form the desired quinols.

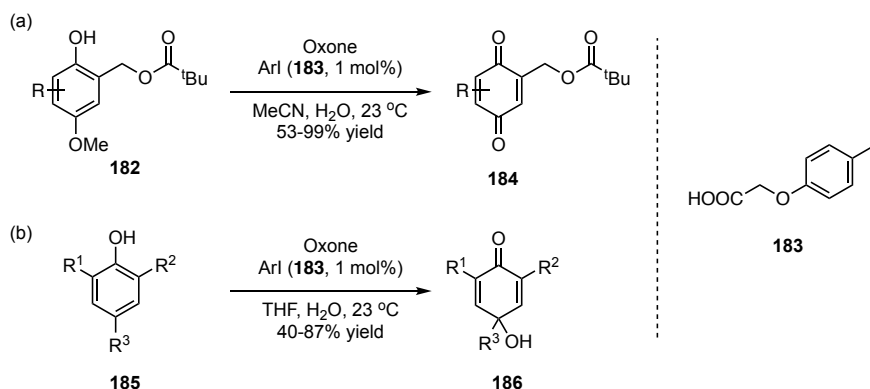


Figure 39. 2-(4-iodophenoxy)acetic acid (**183**) catalyzed oxidation of phenolic derivatives provided access to (a) *p*-quinones and (b) *p*-quinols with Oxone as the terminal oxidant.

Zhdankin and co-workers demonstrated hypervalent iodine-catalyzed Hofmann rearrangements, which had been previously accomplished by Ochiai and co-workers using *m*-CPBA as the terminal oxidant [114], could also be accomplished using Oxone as the terminal oxidant (Figure 40a) [193]. Using similar reaction conditions with 3,5-dimethyliodobenzene (**188**) as the catalyst, Zhdankin and co-workers reported cyclization of oxime **187** with alkenes or alkynes to form isoxazolines **190** or isoxazoles **191** (Figure 40b) [194]. In these reactions, *in situ* generated iodine(III) reagents oxidize oximes into nitrile oxides **189**, which then undergo [3+2] cycloaddition with alkenes or alkynes to form the corresponding heterocycles. Synthesis of substituted oxazoles **193** via cycloisomerization-amination reactions of *N*-propargyl carboxamides **192** was also realized utilizing *in situ* generated I(III) intermediate by Oxone (Figure 40c) [195].

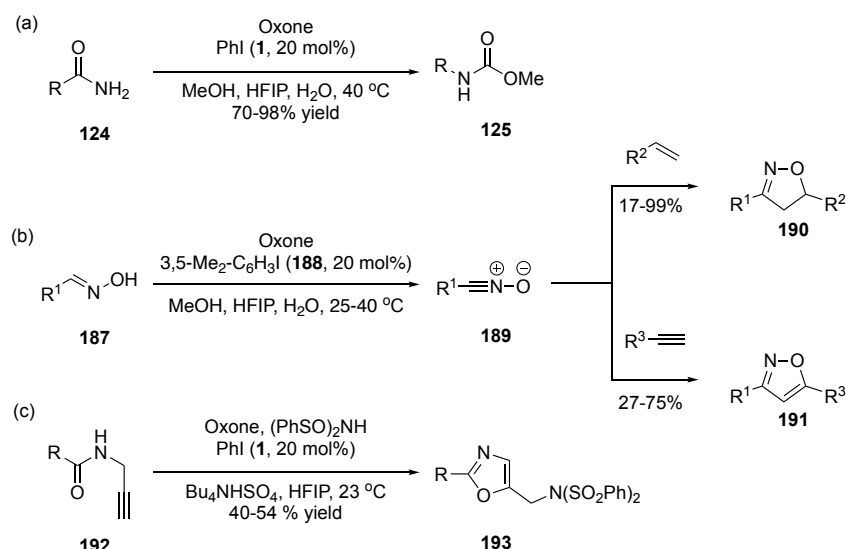


Figure 40. Oxone is often used as the terminal oxidant for various hypervalent iodine-catalyzed reactions such as (a) Hofmann rearrangement of amides, (b) [3+2] cycloaddition of alkenes or alkynes with *in situ* generated nitrile oxide, and (c) cycloisomerization-amination reactions of *N*-propargyl carboxamides.

E.3.2 Catalytic Hypervalent Iodine(V) Reactions Using Oxone

The first example of I(V) catalysis was reported by Vinod and co-workers in 2005, who reported oxidation of primary and secondary alcohols to carboxylic acids and ketones, respectively, by the *in situ* generation of IBX (**89**) from 2-iodobenzoic acid (**88**) using Oxone as the terminal oxidant (Figure 41) [196]. 1,2-Diols were also cleanly oxidized to corresponding dicarbonyls without oxidative C–C cleavage. Control reactions in the absence of catalyst resulted in no product formation.

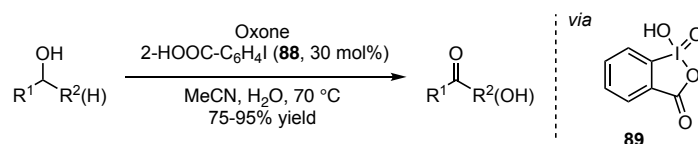


Figure 41. Catalytic oxidation of alcohols in presence of 2-iodobenzoic acid and Oxone leads to carboxylic acid from primary alcohols and ketones from secondary alcohols via the intermediacy of IBX (**89**).

The Ishihara group reported oxidation of primary and secondary alcohols with iodophenylsulfonate **194** as the catalyst (Figure 42a) [197]. It is noteworthy that a significantly lower catalyst loading (as low as 1 mol%) was achievable with sodium 2-iodobenzenesulfonate (**194**) to generate 2-iodoxysulfonic acid (IBS), which is an analogue of IBX. It was proposed that IBS might have had greater catalytic activity since the iodine(V) center has higher Lewis acidity than that of IBX due to a strong electron withdrawing sulfonate group in the *ortho*-position. Also, the oxidative rearrangement of tertiary alcohols with sodium 5-methyl-2-iodobenzenesulfonate (**196**) as catalyst was accomplished to form enones with Oxone as the terminal oxidant (Figure 42b) [198].

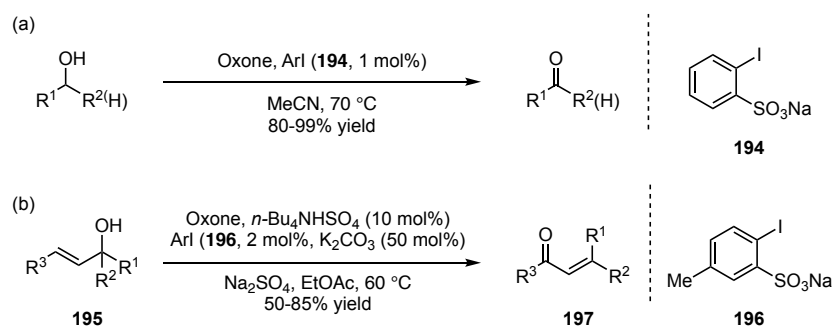


Figure 42. Iodoarene-catalyzed (a) oxidation of primary and secondary alcohols and (b) rearrangement of tertiary alcohols were performed using Oxone as the terminal oxidant. Selective oxidation of primary alcohols to aldehydes was observed.

In contrast to the I(III)-mediated oxidation of phenolic derivatives in presence of Oxone, which gave rise to 1,4-quinones (section E.3.1) [188-190], 5-methyl-2-iodobenzenesulfonate (**196**) catalyzed oxidation of phenols leads to selective *ortho*-oxidation to form 1,2-quinones via corresponding I(V) intermediate (Figure 43a) [199]. Although the reason for the selectivity remained unclear, a mechanism was proposed where the phenol-iodine(V) adduct underwent [2,3]-sigmatropic rearrangement to give the resulting 1,2-quinones. This reaction was further expanded to effect the formation of *o*-quinols (**202** and **203**) catalyzed by sodium 4,5-dimethyl-2-iodobenzenesulfonate **201** from *ortho*-substituted phenols **200** (Figure 43b) [200]. The introduction of a trialkylsilylmethyl substituent at the 2-position in this case further improved the reaction rate and selectivity for monomeric quinol product **202** over the dimerized product **203**.

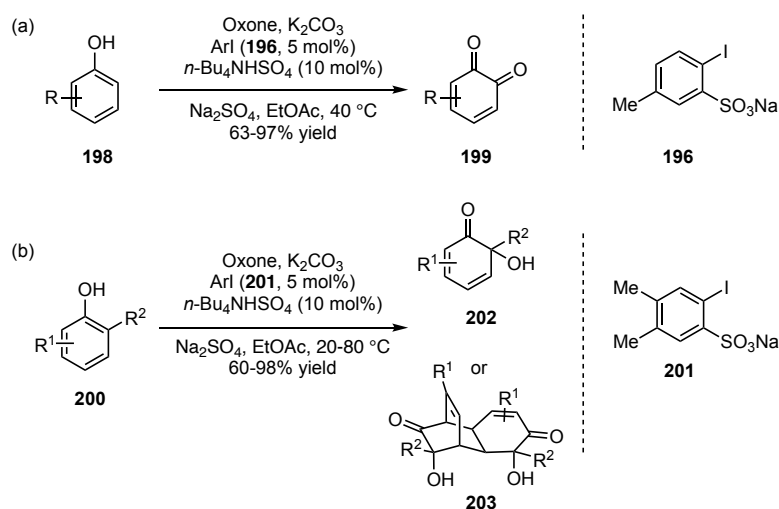


Figure 43. Catalytic oxidation of phenols by 2-iodobenzenesulfonic acid derivative and Oxone leads to (a) *o*-quinone and (b) *o*-quinol depending on the reaction conditions.

E.4 Catalytic Hypervalent Iodine Reactions Using Electrophilic Halides

Electrophilic halogen-based reagents, such as Selectfluor and *N*-bromosuccinimide (NBS), can act as terminal oxidants in hypervalent iodine catalysis. While Selectfluor oxidation generates (difluoroiodo)arenes, which are stable to isolation [201], NBS oxidation affords (dibromiodo)arenes, which are not generally stable to isolation (the presence of *ortho*-substituents that are Lewis basic can stabilize cyclic bromo-I(III) reagents) [202]. Among the oxidants discussed here, electrophilic halides are the least atom economical; the reduced

products of Selectfluor and NBS are 1-chloromethyl-1,4-diazabicyclo[2.2.2]octane and succinimide, respectively.

E.4.1 Catalytic Hypervalent Iodine(III) Reactions Using Electrophilic Halides

(Difluoriodo)arenes, generated *in situ* by the combined action of Selectfluor and hydrofluoric acid, have been applied in fluorination reactions. Moran and co-workers described the hypervalent iodine-catalyzed cyclization of *N*-allylamides to the corresponding oxazoline compounds with five- to seven-membered rings using *o*-iodoanisole (**205**) as catalyst (Figure 44a) [203]. Saito and co-workers demonstrated metal-free and catalytic fluorinative cyclization of *N*-propargyl amides to form substituted oxazoles with a similar catalysis strategy (Figure 44b) [204].

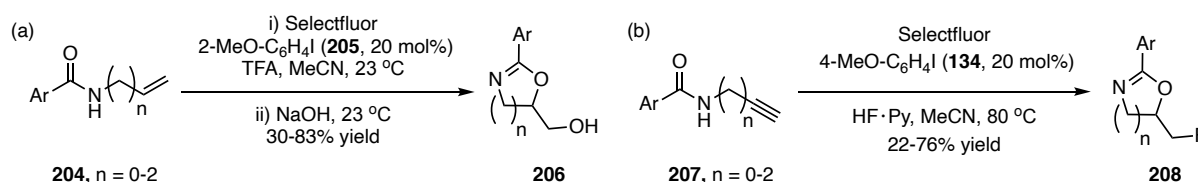


Figure 44. (a) Cyclization of *N*-allylamides in presence of Selectfluor and *o*-iodoanisole (**205**) furnished corresponding hydroxy substituted oxazoline compounds. (b) Addition of fluoride source such as pyridine hydrogen fluoride to the previous reaction condition leads fluorocyclized products **208**.

Difunctionalization of olefins can also be achieved with Selectfluor as the terminal oxidant. In 2016, Muñiz and co-workers developed an enantioselective styrene diacetoxylation reaction using chiral iodoarene **209** as catalyst (Figure 45a) [205]. The use of Selectfluor as the terminal oxidant avoided background reactions, such as epoxidation, that were observed with peracid-based oxidants. In addition, oxidation by Selectfluor generates arylfluoroiodonium species that have a more electrophilic iodine(III) center and is highly reactive towards olefins compared to other hypervalent iodine reagents like PhI(OAc)₂. Gilmour and co-workers elaborated on the developed method to achieve vicinal dichlorination of alkenes (*i.e.*, the conversion of **164** to **210**) by *in situ* generation of 4-(dichloriodo)toluene (**32**) from the I(III) fluoride species via ligand exchange reaction with cesium chloride (CsCl) (Figure 45b) [206].

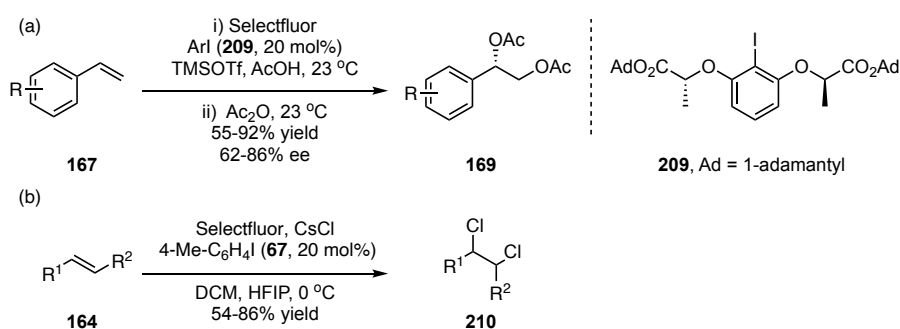


Figure 45. Selectfluor is used as a terminal oxidant for iodoarene-catalyzed (a) diacetoxylation and (b) vicinal dichlorination of alkenes.

NBS has been used for *in situ* generation of (dibromiodo)arenes, which are efficient in bromine transfer to alkenes or arenes. Braddock and co-workers reported the *in situ* synthesis of cyclic brominated hypervalent iodine intermediates from a variety of *ortho*-substituted iodoarenes (e.g. **213-217**), and found that amidine **213** was superior in the synthesis of bromolactones **212** from alkenecarboxylic acids **211** (Figure 46) [202]. Although molecular bromine has better atom economy, it failed to give rise to the formation of the expected bromoiodinane species. Instead, NBS was found to be a suitable reagent for such

transformation in good yields. Increased reaction rate and yields were obtained by increasing the nucleophilicity of the *ortho*-substituents of the iodoarene.

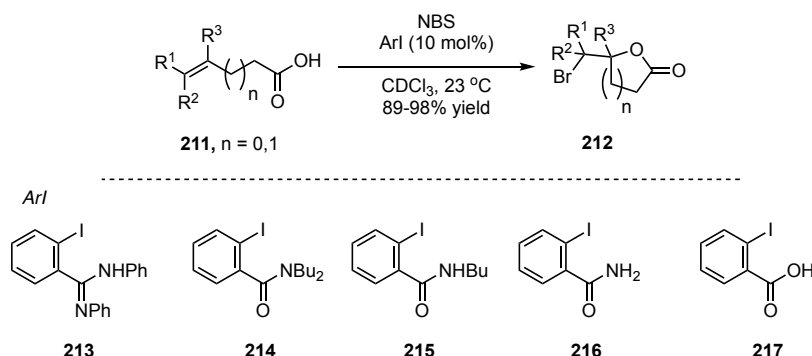


Figure 46. Bromocyclization of alkenecarboxylic acids to bromolactones was realized using (*E*)-2-iodo-*N,N'*-diphenylbenzimidamide (**213**) as catalyst and Selectfluor as terminal oxidant.

Gulder and co-workers expanded the utility of olefin functionalization catalyzed by iodoarenes using NBS as the terminal oxidant to access bromination reactions with *o*-iodobenzamide derivatives **219** and **222** as the catalysts. Specifically, 1,2-dibromination of alkenes (*i.e.*, the conversion of **218** to **220**, Figure 47a) [207] and bromocyclization of methacrylamide derivatives (*i.e.*, the conversion of **221** to **223**, Figure 47b) [208] were accomplished by the iodoarene catalysts **219** and **222**, respectively. In a similar fashion, iodoarene-catalyzed bromination followed by rearrangement of *N*-alkyl derivatives **224** was performed to access α,α -dialkylated α -alkanoate carboxylamides **225** (Figure 47c) [209] as well as the cascade bromination/rearrangement/cyclization reaction to generate β -lactams **227** from **226** (Figure 46d) [210]. The generation of bromobenziodoxolone **228**, from *o*-iodobenzamide **222** and NBS, was observed by NMR spectroscopy and ESI-MS experiments, and was proposed to be the active brominating reagent in these transformations.

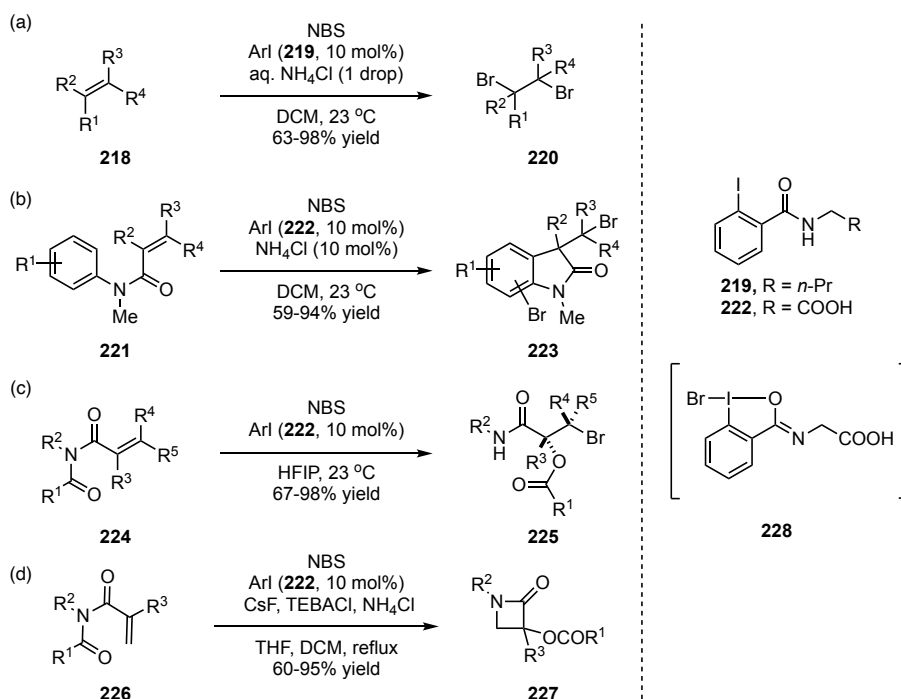


Figure 47. Hypervalent iodine-catalyzed substrate functionalizations with NBS as the terminal oxidant are exemplified in the context of (a) 1,2-dibromination of alkenes, (b) bromocyclization of methacrylamide derivatives, (c) bromination/rearrangement, and (d) cascade bromination/rearrangement/cyclization of *N*-alkyl imide derivatives. Formation of brominated hypervalent iodine intermediates is proposed in these transformations.

E.5 Hypervalent Iodine Electrocatalysis

As discussed in the context of electrochemical synthesis of hypervalent iodine reagents, *ex cell* methods require the stoichiometric generation of hypervalent iodine species, which obviates many of the potential advantages of electrochemistry vis-à-vis sustainability. *In cell* electrocatalytic methods, in which hypervalent iodine species are generated *in situ* during substrate functionalization, can be limited by the significant overpotential that is often required to anodically oxidize many iodoarenes, however, strategies to enable electrocatalysis have begun to emerge.

E.5.1 Catalytic Hypervalent Iodine(III) Electrocatalysis

In 1994, Fuchigami and co-workers reported *in cell* utilization of hypervalent iodine intermediates to accomplish 1,1-difluorination of dithioketals (*i.e.*, the conversion of **229** to **230**, Figure 48) [56]. As discussed in section C.1, Fuchigami and co-workers were only able to electrosynthesize 4-(difluoriodo)nitrobenzene upon anodic oxidation of 4-iodonitrobenzene in Et₃N·5HF (Figure 11). Since the oxidation peak potential of 4-iodonitrobenzene (2.3 V vs SCE) was higher than the potential required for the oxidation of dithioketals (2.1–2.2 V vs SCE), 4-iodoanisole was used as an electrocatalyst (1.9 V vs SCE), and resulted in selective iodoarene oxidation to form the reactive 4-(difluoriodo)anisole (**231**) *in situ*.

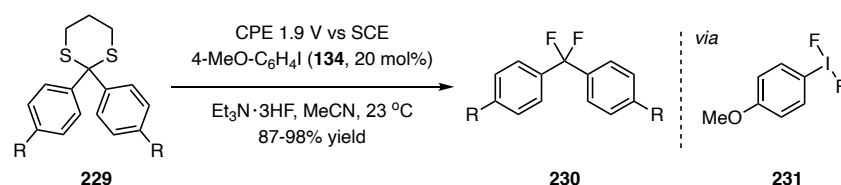


Figure 48. The first example of hypervalent iodine electrocatalysis was reported in the context of the difluorination of propane-1,3-dithiol protected carbonyl compounds **229** under constant potential conditions.

In 2019, Ackermann and co-workers reported an electrochemical co-catalytic system based on iodobenzene (**1**) and Ru-compound **233**, for the directed C–H hydroxylation of **232** to give **234** (Figure 49) [211]. The iodine(III)/ruthenium(II)-electrocatalyzed C–H functionalization was enabled by the electrochemical generation of hypervalent iodine(III) reagents. Complementary computational work indicated that the oxidation potential of iodobenzene is 200 mV lower than that of the ruthenium(II/IV) manifold, and most likely goes through anodically generated hypervalent iodine intermediates [212]. Replacement of applied potential with other oxidants, like *m*-CPBA or Oxone, under these reaction conditions, resulted in considerably inferior yield (15% and 32% respectively).

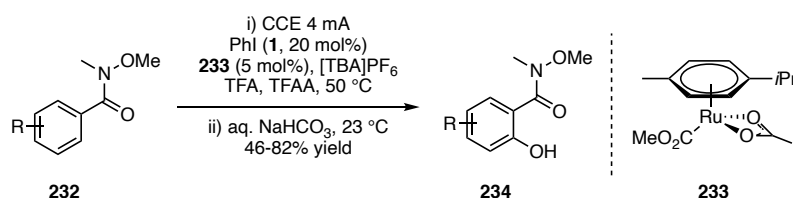


Figure 49. Iodoarene and Ru co-catalyzed C–H hydroxylation of benzamide derivatives.

In 2020, Powers and co-workers developed hypervalent iodine electrocatalysis for intra- and intermolecular C–N bond-forming reactions [213]. In the intramolecular carbazole formation, either iodoarene catalyst **134** or **163** was used depending on the substrate (Figure 50a). 4-

Iodoanisole was selected for its low onset potential and was successfully used as an electrocatalyst for electron-neutral or slightly electron-poor substrates. For more electron-poor substrates, bearing nitro- or carbonyl substituents, the more oxidizing iodoarene **163** was employed as catalyst in potentiostatic electrolysis at 1.9 V vs Ag⁺/Ag. Electron-rich substrates with methyl or methoxy substituents underwent unselective anodic oxidative degradation due to lower onset potentials compared to iodoarene catalyst. Intermolecular C–H amination was also achieved between *N*-(1,3-dioxoisindolin-2-yl)acetamide **161** and arenes using iodoarene **163** as catalyst (Figure 50b). The absence of an oxidation peak in the cyclic voltammogram (CV) for amine **161** at the high potentials required to oxidize iodoarene **163** allowed for its *in cell* utilization. Control experiments in the absence of iodoarene, acetate, or HFIP resulted in no desired products. Titration of increasing acetate concentration to iodoarene resulted in CVs with decreased reversibility and increased current response, which is indicative of trapping anodically generated I(II) intermediate by acetate ion and subsequent oxidation to I(III) intermediate (Figure 50c).

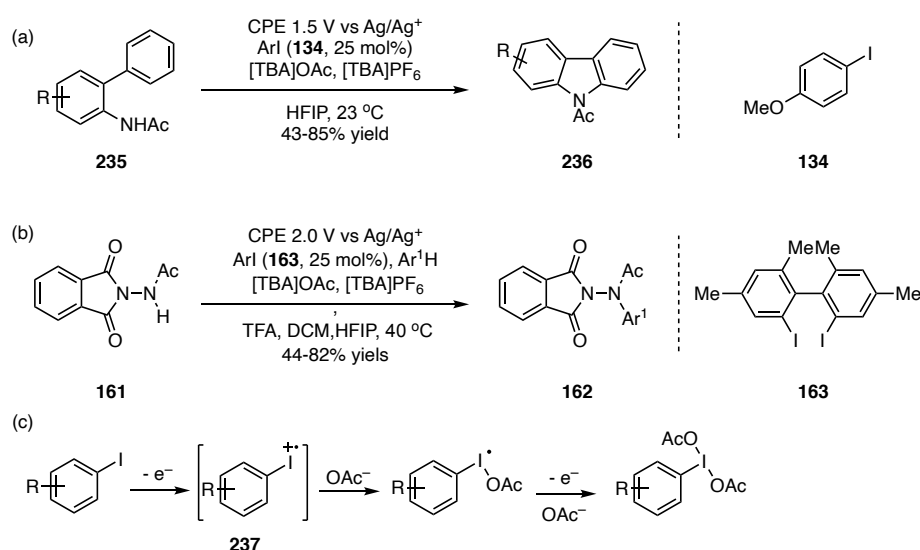


Figure 50. Anodically generated hypervalent iodine intermediates were used in (a) inter- and (b) intramolecular C–H amination reactions. (c) Stabilization of *in situ* generated I(II) intermediate (**237**) by acetate anion was proposed to enable hypervalent iodine electrocatalysis.

F. Conclusion

Hypervalent iodine compounds are an important class of oxidants in synthetic chemistry. Use of hypervalent iodine reagents is often not highly atom economical due to the low active oxygen content of these species. Advances in the sustainable synthesis of these reagents promise to impact the sustainability of the substrate functionalization reactions that can be affected by these compounds. Here, we have discussed advances in the use of environmentally benign oxidants such as O₂ and H₂O₂ in the preparation of hypervalent iodine species. In addition, significant progress has been made towards the electrochemical oxidation of iodoarenes, which avoids the need for stoichiometric terminal chemical oxidants. Polymer-supported and fluorous hypervalent iodine compounds have emerged as recyclable platforms that could reduce the waste associated with stoichiometric application of these reagents. More recently, the development of hypervalent iodine catalysis promises to significantly impact the sustainability of reaction chemistry effected at the hypervalent iodine center by enabling use of substoichiometric iodoarene loading. To fully realize the potential of hypervalent iodine catalysis, new approaches to achieving selective oxidation of iodoarenes in the presence of oxidatively labile substrates is critical. Ongoing efforts to better define the mechanistic

alternatives available for the synthesis of these species promises to impact the ongoing development of aerobic and electrochemical strategies to hypervalent iodine compounds and catalysis.

G. Acknowledgement

The authors thank the Welch Foundation (A-1907) and the National Science Foundation (CAREER 1848135) for financial support.

H. References

1. Fetzner, S. and Steiner, R.A. (2010). Cofactor-Independent Oxidases and Oxygenases. *Applied Microbiology and Biotechnology* **86**: 791–804.
2. Ho, R.Y., Liebman, J.F., Valentine, J.S. (1995). Biological Reactions of Dioxygen: An Introduction. In *Active Oxygen in Biochemistry* Springer: 1–36.
3. Borden, W.T., Hoffmann, R., Stuyver, T., Chen, B. (2017). Dioxygen: What Makes This Triplet Diradical Kinetically Persistent? *Journal of the American Chemical Society* **139**: 9010–9018.
4. Filatov, M. Reckien, W. Peyerimhoff, S.D., Shaik, S. (2000). What Are the Reasons for the Knetic Sability of a Mixture of H₂ and O₂? *The Journal of Physical Chemistry A* **104**: 12014–12020.
5. Ho, R.Y.N., Liebman, J.F., Valentine, J.S. (1995). Overview of the Energetics and Reactivity of Oxygen. In *Active Oxygen in Chemistry* ed. Foote, C.S.; Valentine, J.S.; Greenberg, A.; Liebman, J.F. Blackie Academic and Professional: 1–23.
6. McCann, S.D. and Stahl, S.S. (2015). Copper-Catalyzed Aerobic Oxidations of Organic Molecules: Pathways for Two-Electron Oxidation with a Four-Electron Oxidant and a One-Electron Redox-Active Catalyst. *Accounts of Chemical Research* **48**: 1756–1766.
7. Osterberg, P.M., Niemeier, J.K., Welch, C.J., Hawkins, J.M., Martinelli, J.R., Johnson, T.E., Root, T.W., Stahl, S.S. (2015). Experimental Limiting Oxygen Concentrations for Nine Organic Solvents at Temperatures and Pressures Relevant to Aerobic Oxidations in the Pharmaceutical Industry. *Organic Process Research & Development* **19**: 1537–1543.
8. Anastas, P. and Warner, J. (1998). *Green Chemistry: Theory and Practice* Oxford University Press.
9. Anastas, P. and Eghbali, N. (2010). Green Chemistry: Principles and Practice. *Chemical Society Reviews* **39**: 301–312.
10. Goti, A. and Cardona, F. (2008). Hydrogen Peroxide in Green Oxidation Reactions: Recent Catalytic Processes. In *Green Chemical Reactions* Springer: 191–212.
11. Campbell, A.N. and Stahl, S.S. (2012). Overcoming the “Oxidant Problem”: Strategies to Use O₂ as the Oxidant in Organometallic C–H Oxidation Reactions Catalyzed by Pd (and Cu). *Accounts of Chemical Research* **45**: 851–863.
12. Ibanez, J.G., Fitch, A., Frontana-Urbe, B.A., Vasquez-Medrano, R. (2014). Green Electrochemistry. In *Encyclopedia of Applied Electrochemistry*, Springer: 964–971.
13. Hach, R.J. and Rundle, R.E. (1951). The Structure of Tetramethylammonium Pentaoxide. *Journal of the American Chemical Society* **73**: 4321–4324.
14. Pimentel, G.C. (1951). The Bonding of Trihalide abd Bifluoride Ions by the Molecular Orbital Method. *The Journal of Chemical Physics* **19**: 446–448.
15. Zhdankin, V.V. and Stang, P.J. (2002). Recent Developments in the Chemistry of Polyvalent Iodine Compounds. *Chemical Reviews* **102**: 2523–2584.
16. Stang, P.J. and Zhdankin, V.V. (1996). Organic Polyvalent Iodine Compounds. *Chemical Reviews* **96**: 1123–1178.
17. Zhdankin, V.V. and Stang, P.J. (2008). Chemistry of Polyvalent Iodine. *Chemical Reviews* **108**: 5299–5358.
18. Yoshimura, A. and Zhdankin, V.V. (2016). Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chemical Reviews* **116**: 3328–3435.
19. Varvoglis, A. (1997). *Hypervalent Iodine in Organic Synthesis* Academic Press.
20. Wirth, T. (2003). Oxidations and Rearrangements. In *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis* Springer: 185–208.
21. Singh, F.V. and Wirth, T. (2014). Hypervalent Iodine-Catalyzed Oxidative Functionalizations Including Stereoselective Reactions. *Chemistry–An Asian Journal* **9**: 950–971.

22. Zhdankin, V.V. and Protasiewicz, J.D. (2014). Development of New Hypervalent Iodine Reagents with Improved Properties and Reactivity by Redirecting Secondary Bonds at Iodine Center. *Coordination Chemistry Reviews* **275**: 54–62.
23. Maity, A., Hyun, S.-M., Powers, D.C. (2018). Oxidase Catalysis via Aerobically Generated Hypervalent Iodine Intermediates. *Nature Chemistry* **10**: 200–204.
24. Larkin, D.R. (1990). The Role of Catalysts in the Air Oxidation of Aliphatic Aldehydes. *The Journal of Organic Chemistry* **55**: 1563–1568.
25. Lehtinen, C. and Brunow, G. (2000). Factors Affecting the Selectivity of Air Oxidation of 2-Ethylhexanal, an α -Branched Aliphatic Aldehyde. *Organic Process Research & Development* **4**: 544–549.
26. Hyun, S.-M., Yuan, M., Maity, A., Gutierrez, O., Powers, D.C. (2019). The Role of Iodanyl Radicals as Critical Chain Carriers in Aerobic Hypervalent Iodine Chemistry. *Chem* **5**: 2388–2404.
27. Jorissen, W.P. and Dekking, A.C.B. (1938). On the Induced Oxidation of Iodobenzene During the Oxidation of Acetaldehyde in an Atmosphere of Oxygen. *Recueil Des Travaux Chimiques Des Pays-Bas* **57**: 1125–1126.
28. Maity, A., Hyun, S.-M., Wortman, A.K., Powers, D.C. (2018). Oxidation Catalysis by an Aerobically Generated Dess-Martin Periodinane Analogue. *Angewandte Chemie International Edition* **57**: 7205–7209.
29. Cardenal, A.D., Maity, A., Gao, W.-Y., Ashirov, R., Hyun, S.-M., Powers, D.C. (2019). Iodosylbenzene Coordination Chemistry Relevant to Metal–Organic Framework Catalysis. *Inorganic Chemistry* **58**: 10543–10553.
30. Hans-Joachim, R. and Georg, P. (1999). Production of hydrogen peroxide. Google Patents: 1939.
31. Marzzacco, C.J. (1999). The Enthalpy of Decomposition of Hydrogen Peroxide: A General Chemistry Calorimetry Experiment. *Journal of Chemical Education* **76**: 1517–1518.
32. Lu, C.-S., Hughes, E., Giguère, P.A. (1941). The Crystal Structure of the Urea–Hydrogen Peroxide Addition Compound $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$. *Journal of the American Chemical Society* **63**: 1507–1513.
33. Catir, M., Kilic, H., Nardello-Rataj, V., Aubry, J.-M., Kazaz, C. (2009). Singlet Oxygen Generation from [Bis(trifluoroacetoxy)iodo]benzene and Hydrogen Peroxide. *The Journal of Organic Chemistry* **74**: 4560–4564.
34. Boeseken, J. and Schneider, G.C.C. (1931). Über den Verlauf der Oxydation der Doppelbindung mittels Peressigsäure und Perbenzoesäure. *Journal für Praktische Chemie* **131**: 285.
35. Pausacker, K. (1953). The Oxidation of Glycols by Aryl Iodosoacetates. A Kinetic Study. *Journal of the Chemical Society* 107–109.
36. Colomer, I., Batchelor-McAuley, C., Odell, B., Donohoe, T.J., Compton, R.G. (2016). Hydrogen Bonding to Hexafluoroisopropanol Controls the Oxidative Strength of Hypervalent Iodine Reagents. *Journal of the American Chemical Society* **138**: 8855–8861.
37. Zhdankin, V.V., Scheuller, M.C., Stang, P.J. (1993). A General Approach to Aryl(cyano)iodonium Triflates-Versatile Iodonium Transfer Reagents. *Tetrahedron Letters* **34**: 6853–6856.
38. Spyroudis, S. and Varvoglis, A. (1975). Dehydrogenations with Phenyliodine Ditrifluoroacetate. *Synthesis* : 445–447.
39. White, J.D., Caravatti, G., Kline, T.B., Edstrom, E., Rice, K.C., Brossi, A. (1983). Biomimetic Total Synthesis of (–)-Codeine. *Tetrahedron* **39**: 2393–2397.
40. Alcock, N.W. and Waddington, T.C. (1963). 780. Chemistry of Positive Iodine. Part II. Reactions of Iodobenzene Dichloride with Silver Salts. *Journal of the Chemical Society*: 4103–4109.
41. Zefirov, N., Safronov, S., Kaznacheev, A., Zhdankin, V. (1989). General Method for the Synthesis of Aryliodoso Derivatives Under Aprotic Conditions by the Reaction of Iodosobenzene with Substituted Trimethylsilanes. *Russian Journal of Organic Chemistry* **25**: 1807–1808.
42. Page, T.K. and Wirth, T. (2006). Simple Direct Synthesis of [Bis(trifluoroacetoxy)iodo]arenes. *Synthesis* 3153–3155.
43. Knight, D.W. and Russell, G.A. (2001). Phenyliodine(III) Dichloride. *Encyclopedia of Reagents for Organic Synthesis* :1–4.
44. Krassowska-Wiebocka, B., Prokopienko, G., Skulski, L. (1999). Biphasic Chlorination of Iodoarenes to (Dichloroiodo)arenes. *Synlett* 1409–1410.
45. Obeid, N. and Skulski, L. (2000). Novel Oxidative, Liquid-Phase Chlorination Procedures for the Preparation of (Dichloroiodo)arenes from Iodoarenes. *Polish Journal of Chemistry* **74**: 1609–1615.
46. Baranowski, A., Plachta, D., Skulski, L., Klimaszewska, M. (2000). Liquid-Phase and Biphasic Chlorination of Some Iodoarenes to Form (Dichloroiodo)arenes with Sodium Peroxodisulfate as the Oxidant. *Journal of Chemical Research* 435–437.
47. Kaźmierczak, P., Skulski, L., Obeid, N. (1999). Oxidative Chlorination of Various Iodoarenes to (Dichloroiodo)arenes with Chromium (VI) Oxide as the Oxidant. *Journal of Chemical Research, Synopses* 64–65.
48. Zhao, X.-F. and Zhang, C. (2007). Iodobenzene Dichloride as a Stoichiometric Oxidant for the Conversion of Alcohols into Carbonyl Compounds; Two Facile Methods for its Preparation. *Synthesis* 551–557.

49. Podgoršek, A. and Iskra, J. (2010). Conversion of Aryl Iodides into Aryliodine(III) Dichlorides by an Oxidative Halogenation Strategy Using 30% Aqueous Hydrogen Peroxide in Fluorinated Alcohol. *Molecules* **15**: 2857–2871.
50. Merritt, E.A., Malmgren, J., Klinke, F.J., Olofsson, B. (2009). Synthesis of Diaryliodonium Triflates Using Environmentally Benign Oxidizing Agents. *Synlett* 2277–2280.
51. Kuposov, A.Y., Karimov, R.R., Pronin, A.A., Skrupskaya, T., Yusubov, M.S., Zhdankin, V.V. (2006). RuCl₃-Catalyzed Oxidation of Iodoarenes with Peracetic Acid: New Facile Preparation of Iodylarenes. *The Journal of Organic Chemistry* **71**: 9912–9914.
52. Yusubov, M.S., Chi, K.-W., Park, J. Y., Karimov, R., Zhdankin, V.V. (2006). Highly Efficient RuCl₃-Catalyzed Disproportionation of (Diacetoxyiodo) benzene to Iodylbenzene and Iodobenzene; Leading to the Efficient Oxidation of Alcohols to Carbonyl Compounds. *Tetrahedron Letters* **47**: 6305–6308.
53. Elsherbini, M. and Wirth, T. (2018). Hypervalent Iodine Reagents by Anodic Oxidation Powerful Green Synthesis. *Chemistry—A European Journal* **24**: 13399–13407.
54. Schmidt, H. and Meinert, H. (1960). Zum Mechanismus der Elektrochemischen Fluorierung und über die Bildung von Jod-monofluorid. *Angewandte Chemie* **72**: 109–110.
55. Rozhkov, I.N. (1976). Radical-Cation Mechanism of the Anodic Fluorination of Organic Compounds. *Russian Chemical Reviews* **45**: 615–619.
56. Fuchigami, T. and Fujita, T. (1994). Electrolytic Partial Fluorination of Organic Compounds. The First Electrosynthesis of Hypervalent Iodobenzene Difluoride Derivatives and Its Application to Indirect Anodic gem-Difluorination. *The Journal of Organic Chemistry* **59**: 7190–7192.
57. Hara, S., Hatakeyama, T., Chen, S.-Q., Ishi-i, K., Yoshida, M., Sawaguchi, M., Fukuhara, T., Yoneda, N. (1998). Electrochemical Fluorination of β -Dicarbonyl Compounds Using *p*-Iodotoluene Difluoride as a Mediator. *Journal of Fluorine Chemistry* **87**: 189–192.
58. Haupt, J.D., Berger, M., Waldvogel, S.R. (2018). Electrochemical Fluorocyclization of N-Allylcarboxamides to 2-Oxazolines by Hypervalent Iodine Mediator. *Organic Letters* **21**: 242–245.
59. Doobary, S., Sedikides, A.T., Caldora, H.P., Poole, D.L., Lennox, A.J. (2020). Electrochemical Vicinal Difluorination of Alkenes: Scalable and Amenable to Electron-rich Substrates. *Angewandte Chemie* **132**: 1171–1176.
60. Lund, H. and Hammerich, O. (2001). *Organic Electrochemistry*. Marcel Dekker Inc.
61. Simonet, J. and Pilard, J.-F. (2001). Electrogenerated Reagents in *Organic Electrochemistry* ed. H Lund, O Hammerich. Marcel Dekker Inc.: 1163–1225.
62. Kajiyama, D., Saitoh, T., Nishiyama, S. (2013). Application of Electrochemically Generated Hypervalent Iodine Oxidant to Natural Products Synthesis. *Electrochemistry* **81**: 319–324.
63. Inoue, K., Ishikawa, Y., Nishiyama, S. (2010). Synthesis of Tetrahydropyrroloiminoquinone Alkaloids Based on Electrochemically Generated Hypervalent Iodine Oxidative Cyclization. *Organic Letters* **12**: 436–439.
64. Kajiyama, D., Inoue, K., Ishikawa, Y., Nishiyama, S. (2010). A Synthetic Approach to Carbazoles Using Electrochemically Generated Hypervalent Iodine Oxidant. *Tetrahedron* **66**: 9779–9784.
65. Dohi, T., Ito, M., Yamaoka, N., Morimoto, K., Fujioka, H., Kita, Y. (2009). Hypervalent Iodine(III): Selective and Efficient Single-Electron-Transfer (SET) Oxidizing Agent. *Tetrahedron* **65**: 10797–10815.
66. Dohi, T., Yamaoka, N., Kita, Y. (2010). Fluoroalcohols: Versatile Solvents in Hypervalent Iodine Chemistry and Syntheses of Diaryliodonium(III) Salts. *Tetrahedron* **66**: 5775–5785.
67. Eberson, L., Hartshorn, M.P., Persson, O., Radner, F. (1996). Making Radical Cations Live Longer. *Chemical Communications* 2105–2112.
68. Amano, Y. and Nishiyama, S. (2006). Oxidative Synthesis of Azacyclic Derivatives Through the Nitrenium Ion Application of a Hypervalent Iodine Species Electrochemically Generated from Iodobenzene. *Tetrahedron Letters* **47**: 6505–6507.
69. Faulkner, D.J. (2001). Marine Natural Products. *Natural Product Reports* **18**: 1R–49R.
70. Izawa, T., Nishiyama, S., Yamamura, S. (1994). Total Syntheses of Makaluvamines A, B, C, D and E, Cytotoxic Pyrroloiminoquinone Alkaloids Isolated from Marine Sponge Bearing Inhibitory Activities Against Topoisomerase II. *Tetrahedron* **50**: 13593–13600.
71. Amano, Y., Inoue, K., Nishiyama, S. (2008). Oxidative Access to Quinolinone Derivatives with Simultaneous Rearrangement of Functional Groups. *Synlett* 134–136.
72. Amano, Y. and Nishiyama, S. (2008). Effects of Aromatic Substituents of Electrochemically Generated Hypervalent Iodine Oxidant on Oxidation Reactions. *Heterocycles* **75**: 1997–2003.
73. Miller, L.L. and Hoffmann, A.K. (1967). The Electrochemical Formation of Carbonium and Iodonium Ions from Alkyl and Aryl Iodides. *Journal of the American Chemical Society* **89**: 593–597.
74. Hoffelner, H., Lorch, H., Wendt, H. (1975). Anodic Phenyl-Onium Cation Formation: Part II. Reaction Mechanism and Optimization for the Anodic Formation of Diphenyliodonium Cations. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **66**: 183–194.

75. Peacock, M.J. and Pletcher, D. (2001). The Synthesis of Diaryliodonium Salts by the Anodic Oxidation of Aryl Iodide/Arene Mixtures. *Journal of The Electrochemical Society* **148**: D37–D42.
76. Peacock, M.J. and Pletcher, D. (2000). The Electrosynthesis of Diaryliodonium Salts. *Tetrahedron Letters* **41**: 8995–8998.
77. Broese, T. and Francke, R. (2016). Electrosynthesis Using a Recyclable Mediator-Electrolyte System Based on Ionically Tagged Phenyl Iodide and 1,1,1,3,3,3-Hexafluoroisopropanol. *Organic Letters* **18**: 5896–5899.
78. Koleda, O., Broese, T., Noetzel, J., Roemelt, M., Suna, E., Francke, R. (2017). Synthesis of Benzoxazoles Using Electrochemically Generated Hypervalent Iodine. *The Journal of Organic Chemistry* **82**: 11669–11681.
79. Roesel, A.F., Broese, T., Májek, M., Francke, R. (2019). Iodophenylsulfonates and Iodobenzoates as Redox-Active Supporting Electrolytes for Electrosynthesis. *ChemElectroChem* **6**: 4229–4237.
80. Plutschack, M.B., Pieber, B.U., Gilmore, K., Seeberger, P.H. (2017). The Hitchhiker's Guide to Flow Chemistry. *Chemical Reviews* **117**: 11796–11893.
81. Asprion, N., Mollner, S., Poth, N., Rumpf, B. (2000). Energy Management in Chemical Industry. In *Ullmann's Encyclopedia of Industrial Chemistry* Wiley-VCH.
82. Britton, J. and Raston, C.L. (2017). Multi-Step Continuous-Flow Synthesis. *Chemical Society Reviews* **46**: 1250–1271.
83. Adamo, A., Beingessner, R.L., Behnam, M., Chen, J., Jamison, T.F., Jensen, K.F., Monbaliu, J.-C.M., Myerson, A.S., Revalor, E.M., Snead, D.R. (2016). On-Demand Continuous-Flow Production of Pharmaceuticals in a Compact, Reconfigurable System. *Science* **352**: 61–67.
84. Watts, K., Gattrell, W., Wirth, T. (2011). A Practical Microreactor for Electrochemistry in Flow. *Beilstein Journal of Organic Chemistry* **7**: 1108–1114.
85. Gemoets, H.P., Laudadio, G., Verstraete, K., Hessel, V., Noël, T. (2017). A Modular Flow Design for the meta-Selective C–H Arylation of Anilines. *Angewandte Chemie International Edition* **56**: 7161–7165.
86. Gao, W.-C., Xiong, Z.-Y., Pirhaghani, S., Wirth, T. (2019). Enantioselective Electrochemical Lactonization Using Chiral Iodoarenes as Mediators. *Synthesis* **51**: 276–284.
87. Elsherbini, M., Winterson, B., Alharbi, H., Folguez-Amador, A.A., Génot, C., Wirth, T. (2019). Continuous-Flow Electrochemical Generator of Hypervalent Iodine Reagents: Synthetic Applications. *Angewandte Chemie International Edition* **58**: 9811–9815.
88. Bystron, T., Horbenko, A., Syslova, K., Hii, K.K., Hellgardt, K., Kelsall, G. (2018). 2-Iodoxybenzoic Acid Synthesis by Oxidation of 2-Iodobenzoic Acid at a Boron-Doped Diamond Anode. *ChemElectroChem* **5**: 1002–1005.
89. Devadas, B., Svoboda, J., Krupička, M., Bystron, T. (2020). Electrochemical and Spectroscopic Study of 2-Iodobenzoic Acid and 2-Iodosobenzoic Acid Anodic Oxidation in Aqueous Environment. *Electrochimica Acta* **342**: 136080–136091.
90. Okawara, M. and Mizuta, K. (1961). Synthesis and Some Reactions of Polystyrene Iodosoacetate. *Kogyo Kagaku Zasshi* **64**: 232–235.
91. Huang, X. and Zhu, Q. (2001). The Synthesis of Cross-Linked Poly[styrene(iodosoacetate)] and Application in Preparation of Pyrazoline. *Synthetic Communications* **31**: 111–115.
92. Abe, S., Sakuratani, K., Togo, H. (2001). Synthetic use of Poly[4-hydroxy(tosyloxy)iodo]styrenes. *The Journal of Organic Chemistry* **66**: 6174–6177.
93. Abe, S., Sakuratani, K., Togo, H. (2001). Novel Preparation and Reactivity of Poly[4-hydroxy(tosyloxy)iodo]styrenes. *Synlett* 0022–0024.
94. Ficht, S., Mülbaier, M., Giannis, A. (2001). Development of New and Efficient Polymer-Supported Hypervalent Iodine Reagents. *Tetrahedron* **57**: 4863–4866.
95. Tohma, H., H., Maruyama, A., Maeda, A., Maegawa, T., Dohi, T., Shiro, M., Morita, T., Kita, Y. (2004). Preparation and Reactivity of 1, 3, 5, 7-Tetrakis-[4-(diacetoxyiodo) phenyl]adamantane, A Recyclable Hypervalent Iodine(III) Reagent. *Angewandte Chemie International Edition* **43**: 3595–3598.
96. Dohi, T., Maruyama, A., Yoshimura, M., Morimoto, K., Tohma, H., Shiro, M., Kita, Y. (2005). A Unique Site-Selective Reaction of Ketones with New Recyclable Hypervalent Iodine(III) Reagents Based On A Tetraphenylmethane Structure. *Chemical Communications* 2205–2207.
97. Dohi, T., Fukushima, K.I., Kamitanaka, T., Morimoto, K., Takenaga, N., Kita, Y. (2012). An Excellent Dual Recycling Strategy for the Hypervalent Iodine/Nitroxyl Radical Mediated Selective Oxidation of Alcohols to Aldehydes and Ketones. *Green Chemistry* **14**: 1493–1501.
98. Thorat, P.B., Bhong, B.Y., Karade, N.N. (2013). 2, 4, 6-Tris-[(4-dichloroiodo)phenoxy]-1, 3, 5-triazine as a New Recyclable Hypervalent Iodine(III) Reagent for Chlorination and Oxidation Reactions. *Synlett* **24**: 2061–2066.
99. Liu, Z., Chen, Z.-C., Zheng, Q.-G. (2003). Mild Oxidation of Alcohols with *o*-Iodoxybenzoic Acid (IBX) in Ionic Liquid 1-Butyl-3-methyl-imidazolium Chloride and Water. *Organic Letters* **5**: 3321–3323.
100. More, J.D. and Finney, N.S. (2002). A Simple and Advantageous Protocol for the Oxidation of Alcohols with *o*-Iodoxybenzoic Acid (IBX). *Organic Letters* **4**: 3001–3003.

101. Mülbaier, M. and Giannis, A. (2001). The Synthesis and Oxidative Properties of Polymer-supported IBX. *Angewandte Chemie International Edition* **40**: 4393–4394.
102. Sorg, G., Mengel, A., Jung, G., Rademann, J. (2001). Oxidizing Polymers: A Polymer-supported, Recyclable Hypervalent Iodine (V) Reagent for the Efficient Conversion of Alcohols, Carbonyl Compounds, and Unsaturated Carbamates in Solution. *Angewandte Chemie International Edition* **40**: 4395–4397.
103. Bizzarri, B.M., Abdalghani, I., Botta, L., Taddei, A.R., Nisi, S., Ferrante, M. (2018). Passacantando, M., Crucianelli, M., Saladino, R., Iodoxybenzoic Acid Supported on Multi Walled Carbon Nanotubes as Biomimetic Environmental Friendly Oxidative Systems for the Oxidation of Alcohols to Aldehydes. *Nanomaterials* **8**: 516–529.
104. Ladziata, U., Willging, J., Zhdankin, V.V. (2006). Facile Preparation and Reactivity of Polymer-Supported *N*-(2-Iodol-phenyl)-acylamide, an Efficient Oxidizing System. *Organic Letters* **8**: 167–170.
105. Chung, W.-J., Kim, D.-K., Lee, Y.-S. (2005). Polymer-Supported IBX-Amide Reagents: Significant Role of Spacer and Additive in Alcohol Oxidation. *Synlett* 2175–2178.
106. Nambu, H., Shimokawa, I., Fujiwara, T., Yakura, T. (2016). Recyclable Magnetic Nanoparticle-Supported Iodoarene Catalysts for Oxidation of 4-Alkoxyphenols to Quinones. *Asian Journal of Organic Chemistry* **5**: 486–489.
107. Ballaschk, F. and Kirsch, S.F. (2019). Oxidation of Secondary Alcohols Using Solid-supported Hypervalent Iodine Catalysts. *Green Chemistry* **21**: 5896–5903.
108. Lyalin, V.V., Orda, V.V., Alekseeva, L.A., Yagupolskii, L.M. (1971). Arylperfluoroalkyliodonium and Arylpentafluorophenylodonium Compounds. *Zhurnal Organicheskoi Khimii* **7**: 1473.
109. Rocaboy, C. and Gladysz, J.A. (2003). Convenient Syntheses of Fluorous Aryl Iodides and Hypervalent Iodine Compounds: $\text{ArI}(\text{L})_n$ Reagents that are Recoverable by Simple Liquid/liquid Biphasic Workups, and Applications in Oxidations of Hydroquinones. *Chemistry—A European Journal* **9**: 88–95.
110. Tesevic, V. and Gladysz, J. (2006). Oxidations of Secondary Alcohols to Ketones Using Easily Recyclable Bis(trifluoroacetate) Adducts of Fluorous Alkyl Iodides, $\text{CF}_3(\text{CF}_2)_n\text{-I}(\text{OCOCF}_3)_2$. *The Journal of Organic Chemistry* **71**: 7433–7440.
111. Schäfer, S. and Wirth, T. (2010). A Versatile and Highly Reactive Polyfluorinated Hypervalent Iodine(III) Compound. *Angewandte Chemie International Edition* **49**: 2786–2789.
112. Zhang, G., Tan, H., Chen, W., Shen, H.C., Lu, Y., Zheng, C., Xu, H. (2020). Synthesis of NH-Sulfoximines Using Recyclable Hypervalent Iodine(III) Reagents under Aqueous Micellar Conditions. *ChemSusChem* **13**: 922–928.
113. Miyamoto, K., Yamashita, J., Narita, S., Sakai, Y., Hirano, K., Saito, T., Wang, C., Ochiai, M., Uchiyama, M. (2017). Iodoarene-Catalyzed Oxidative Transformations Using Molecular Oxygen. *Chemical Communications* **53**: 9781–9784.
114. Miyamoto, K., Sakai, Y., Goda, S., Ochiai, M. (2012). A Catalytic Version of Hypervalent Aryl- λ^3 -Iodane-Induced Hofmann Rearrangement of Primary Carboxamides: Iodobenzene as an Organocatalyst and *m*-Chloroperbenzoic Acid as a Terminal Oxidant. *Chemical Communications* **48**: 982–984.
115. Lucchetti, N., Scalone, M., Fantasia, S., Muñiz, K. (2016). An Improved Catalyst for Iodine(I/III)-Catalysed Intermolecular C–H Amination. *Advanced Synthesis & Catalysis* **358**: 2093–2099.
116. Chauhan, J., Ravva, M.K., Sen, S. (2019). Harnessing Autoxidation of Aldehydes: In Situ Iodoarene Catalyzed Synthesis of Substituted 1,3,4-Oxadiazole, in the Presence of Molecular Oxygen. *Organic Letters* **21**: 6562–6565.
117. Ochiai, M., Takeuchi, Y., Katayama, T., Sueda, T., Miyamoto, K. (2005). Iodobenzene-Catalyzed α -Acetoxylation of Ketones. In Situ Generation of Hypervalent (Diacyloxyiodo)benzenes Using *m*-Chloroperbenzoic Acid. *Journal of the American Chemical Society* **127**: 12244–12245.
118. Sheng, J., Li, X., Tang, M., Gao, B., Huang, G. (2007). An Efficient Method for the α -Acetoxylation of Ketones. *Synthesis* 1165–1168.
119. Yamamoto, Y. and Togo, H. (2006). PhI-Catalyzed α -Tosyloxylation of Ketones with *m*-Chloroperbenzoic Acid and *p*-Toluenesulfonic Acid. *Synlett* 0798–0800.
120. Akiike, J., Yamamoto, Y., Togo, H. (2007). Efficient Conversion of Ketones to α -Tosyloxyketones with *m*-Chloroperbenzoic Acid and *p*-Toluenesulfonic Acid in the Presence of Catalytic Amount of IL-Supported PhI in [emim]OTf. *Synlett* 2168–2172.
121. Yamamoto, Y., Kawano, Y., Toy, P.H., Togo, H. (2007). PhI- and Polymer-Supported PhI-Catalyzed Oxidative Conversion of Ketones and Alcohols to α -Tosyloxyketones with *m*-Chloroperbenzoic Acid and *p*-Toluenesulfonic Acid. *Tetrahedron* **63**: 4680–4687.
122. Pu, Y., Gao, L., Liu, H., Yan, J. (2012). An Effective Catalytic α -Phosphoryloxylation of Ketones with Iodobenzene. *Synthesis* **44**: 99–103.
123. Kitamura, T., Muta, K., Kuriki, S. (2013). Catalytic fluorination of 1,3-dicarbonyl compounds using iodoarene catalysts. *Tetrahedron Letters* **54**: 6118–6120.

124. Suzuki, S., Kamo, T., Fukushi, K., Hiramatsu, T., Tokunaga, E., Dohi, T., Kita, Y., Shibata, N. (2014). Iodoarene-Catalyzed Fluorination and Aminofluorination by an Ar-I/HF·pyridine/*m*CPBA System. *Chemical Science* **5**: 2754–2760.
125. Richardson, R.D., Page, T.K., Altermann, S., Paradine, S.M., French, A.N., Wirth, T. (2007). Enantioselective α -Oxytosylation of Ketones Catalysed by Iodoarenes. *Synlett* 0538–0542.
126. Hirt, U.H., Schuster, M.F., French, A.N., Wiest, O.G., Wirth, T. (2001). Chiral Hypervalent Organo-Iodine(III) Compounds. *European Journal of Organic Chemistry* 1569–1579.
127. Abazid, A.H. and Nachtsheim, B.J. (2020). A Triazole-Substituted Aryl Iodide with Omnipotent Reactivity in Enantioselective Oxidations. *Angewandte Chemie International Edition* **59**: 1479–1484.
128. Altermann, S.M., Richardson, R.D., Page, T.K., Schmidt, R.K., Holland, E., Mohammed, U., Paradine, S.M., French, A.N., Richter, C., Bahar, A.M., Witulski, B., Wirth, T. (2008). Catalytic Enantioselective α -Oxysulfonylation of Ketones Mediated by Iodoarenes. *European Journal of Organic Chemistry*: 5315–5328.
129. Guilbault, A.-A. and Legault, C.Y. (2012). Drastic Enhancement of Activity in Iodane-Based α -Tosyloxylolation of Ketones: Iodine(III) Does the Hypervalent Twist. *ACS Catalysis* **2**: 219–222.
130. Guilbault, A.-A., Basdevant, B., Wanie, V., Legault, C.Y. (2012). Catalytic Enantioselective α -Tosyloxylolation of Ketones Using Iodoaryloxazoline Catalysts: Insights on the Stereoinduction Process. *The Journal of Organic Chemistry* **77**: 11283–11295.
131. Brenet, S., Berthiol, F., Einhorn, J. (2013). 3,3'-Diiodo-BINOL-Fused Maleimides as Chiral Hypervalent Iodine(III) Organocatalysts. *European Journal of Organic Chemistry* 8094–8096.
132. Pluta, R., Krach, P.E., Cavallo, L., Falivene, L., Rueping, M. (2018). Metal-Free Catalytic Asymmetric Fluorination of Keto Esters Using a Combination of Hydrogen Fluoride (HF) and Oxidant: Experiment and Computation. *ACS Catalysis* **8**: 2582–2588.
133. Wang, Y., Yuan, H., Lu, H., Zheng, W.-H. (2018). Development of Planar Chiral Iodoarenes Based on [2.2]Paracyclophane and Their Application in Catalytic Enantioselective Fluorination of β -Ketoesters. *Organic Letters* **20**: 2555–2558.
134. Dohi, T., Maruyama, A., Yoshimura, M., Morimoto, K., Tohma, H., Kita, Y. (2005). Versatile Hypervalent-Iodine(III)-Catalyzed Oxidations with *m*-Chloroperbenzoic Acid as a Cooxidant. *Angewandte Chemie International Edition* **44**: 6193–6196.
135. Dohi, T., Takenaga, N., Nakae, T., Toyoda, Y., Yamasaki, M., Shiro, M., Fujioka, H., Maruyama, A., Kita, Y. (2013). Asymmetric Dearomatizing Spirolactonization of Naphthols Catalyzed by Spirobiindane-Based Chiral Hypervalent Iodine Species. *Journal of the American Chemical Society* **135**: 4558–4566.
136. Uyanik, M., Yasui, T., Ishihara, K. (2010). Enantioselective Kita Oxidative Spirolactonization Catalyzed by In Situ Generated Chiral Hypervalent Iodine(III) Species. *Angewandte Chemie International Edition* **49**: 2175–2177.
137. Murray, S.J. and Ibrahim, H. (2015). Asymmetric Kita Spirolactonisation Catalysed by anti-Dimethanoanthracene-based Iodoarenes. *Chemical Communications* **51**: 2376–2379.
138. Ogasawara, M., Sasa, H., Hu, H., Amano, Y., Nakajima, H., Takenaga, N., Nakajima, K., Kita, Y., Takahashi, T., Dohi, T. (2017). Atropisomeric Chiral Diiododienes (*Z,Z*)-2,3-Di(1-iodoalkylidene)tetralins: Synthesis, Enantiomeric Resolution, and Application in Asymmetric Catalysis. *Organic Letters* **19**: 4102–4105.
139. Dohi, T., Sasa, H., Miyazaki, K., Fujitake, M., Takenaga, N., Kita, Y. (2017). Chiral Atropisomeric 8,8'-Diiodobinaphthalene for Asymmetric Dearomatizing Spirolactonizations in Hypervalent Iodine Oxidations. *The Journal of Organic Chemistry* **82**: 11954–11960.
140. Uyanik, M., Sasakura, N., Mizuno, M., Ishihara, K. (2017). Enantioselective Synthesis of Masked Benzoquinones Using Designer Chiral Hypervalent Organoiodine(III) Catalysis. *ACS Catalysis* **7**: 872–876.
141. Uyanik, M., Yasui, T., Ishihara, K. (2017). Chiral Hypervalent Organoiodine-Catalyzed Enantioselective Oxidative Spirolactonization of Naphthol Derivatives. *The Journal of Organic Chemistry* **82**: 1946–1953.
142. Hempel, C., Maichle-Mössmer, C., Pericàs, M.A., Nachtsheim, B.J. (2017). Modular Synthesis of Triazole-Based Chiral Iodoarenes for Enantioselective Spirocyclizations. *Advanced Synthesis & Catalysis* **359**: 2931–2941.
143. Zheng, H., Sang, Y., Houk, K.N., Xue, X.-S., Cheng, J.-P. (2019). Mechanism and Origins of Enantioselectivities in Spirobiindane-Based Hypervalent Iodine(III)-Induced Asymmetric Dearomatizing Spirolactonizations. *Journal of the American Chemical Society* **141**: 16046–16056.
144. Wang, Y., Zhao, C.-Y., Wang, Y.-P., Zheng, W.-H. (2019). Enantioselective Intramolecular Dearomative Lactonization of Naphthols Catalyzed by Planar Chiral Iodoarene. *Synthesis* **51**: 3675–3682.

145. Jain, N., Hein, J.E., Ciufolini, M.A. (2019). Oxidative Cyclization of Naphtholic Sulfonamides Mediated by a Chiral Hypervalent Iodine Reagent: Asymmetric Synthesis versus Resolution. *Synlett* **30**: 1222–1227.
146. Jain, N., Xu, S., Ciufolini, M.A. (2017). Asymmetric Oxidative Cycloetherification of Naphtholic Alcohols. *Chemistry – A European Journal* **23**: 4542–4546.
147. Cao, Y., Zhang, X., Lin, G., Zhang-Negrierie, D., Du, Y. (2016). Chiral Aryliodine-Mediated Enantioselective Organocatalytic Spirocyclization: Synthesis of Spirofurooxindoles via Cascade Oxidative C–O and C–C Bond Formation. *Organic Letters* **18**: 5580–5583.
148. Sreenithya, A., Patel, C., Hadad, C.M., Sunoj, R.B. (2017). Hypercoordinate Iodine Catalysts in Enantioselective Transformation: The Role of Catalyst Folding in Stereoselectivity. *ACS Catalysis* **7**: 4189–4196.
149. Ito, M., Kubo, H., Itani, I., Morimoto, K., Dohi, T., Kita, Y. (2013). Organocatalytic C–H/C–H' Cross-Biaryl Coupling: C-Selective Arylation of Sulfonanilides with Aromatic Hydrocarbons. *Journal of the American Chemical Society* **135**: 14078–14081.
150. Wu, H., He, Y.-P., Xu, L., Zhang, D.-Y., Gong, L.-Z. (2014). Asymmetric Organocatalytic Direct C(sp²)–H/C(sp³)–H Oxidative Cross-Coupling by Chiral Iodine Reagents. *Angewandte Chemie International Edition* **53**: 3466–3469.
151. Wang, X., Gallardo-Donaire, J., Martin, R. (2014). Mild ArI-Catalyzed C(sp²)–H or C(sp³)–H Functionalization/C–O Formation: An Intriguing Catalyst-Controlled Selectivity Switch. *Angewandte Chemie International Edition* **53**: 11084–11087.
152. Novák, P., Correa, A., Gallardo-Donaire, J., Martin, R. (2011). Synergistic Palladium-Catalyzed C(sp³)–H Activation/C(sp³)–O Bond Formation: A Direct, Step-Economical Route to Benzolactones. *Angewandte Chemie International Edition* **50**: 12236–12239.
153. Cheng, X.-F., Li, Y., Su, Y.-M., Yin, F., Wang, J.-Y., Sheng, J., Vora, H.U., Wang, X.-S., Yu, J.-Q. (2013). Pd(II)-Catalyzed Enantioselective C–H Activation/C–O Bond Formation: Synthesis of Chiral Benzofuranones. *Journal of the American Chemical Society* **135**: 1236–1239.
154. Yang, M., Jiang, X., Shi, W.-J., Zhu, Q.-L., Shi, Z.-J. (2013). Direct Lactonization of 2-Arylacetic Acids through Pd(II)-Catalyzed C–H Activation/C–O Formation. *Organic Letters* **15**: 690–693.
155. Li, Y., Ding, Y.-J., Wang, J.-Y., Su, Y.-M., Wang, X.-S. (2013). Pd-catalyzed C–H Lactonization for Expedient Synthesis of Biaryl Lactones and Total Synthesis of Cannabinol. *Organic Letters* **15**: 2574–2577.
156. Lee, J.M. and Chang, S. (2006). Pt-Catalyzed sp³ C–H bond activation of *o*-Alkyl Substituted Aromatic Carboxylic Acid Derivatives for the Formation of Aryl Lactones. *Tetrahedron Letters* **47**: 1375–1379.
157. Gallardo-Donaire, J. and Martin, R. (2013). Cu-Catalyzed Mild C(sp²)–H Functionalization Assisted by Carboxylic Acids en Route to Hydroxylated Arenes. *Journal of the American Chemical Society* **135**: 9350–9353.
158. Wang, Y., Gulevich, A.V., Gevorgyan, V. (2013). General and Practical Carboxyl-Group-Directed Remote C–H Oxygenation Reactions of Arenes. *Chemistry–A European Journal* **19**: 15836–15840.
159. Liang, D., Yu, W., Nguyen, N., Deschamps, J.R., Imler, G.H., Li, Y., MacKerell, A.D., Jiang, C., Xue, F. (2017). Iodobenzene-Catalyzed Synthesis of Phenanthridinones via Oxidative C–H Amidation. *The Journal of Organic Chemistry* **82**: 3589–3596.
160. Bal, A., Maiti, S., Mal, P. (2018). Iodine(III)-Enabled Distal C–H Functionalization of Biarylsulfonanilides. *The Journal of Organic Chemistry* **83**: 11278–11287.
161. Ding, Q., He, H., Cai, Q. (2018). Chiral Aryliodine-Catalyzed Asymmetric Oxidative C–N Bond Formation via Desymmetrization Strategy. *Organic Letters* **20**: 4554–4557.
162. Zhu, C., Liang, Y., Hong, X., Sun, H., Sun, W.-Y., Houk, K.N., Shi, Z. (2015). Iodoarene-Catalyzed Stereospecific Intramolecular sp³ C–H Amination: Reaction Development and Mechanistic Insights. *Journal of the American Chemical Society* **137**: 7564–7567.
163. Bose, A., Maiti, S., Sau, S., Mal, P. (2019). An Intramolecular C(sp³)–H Imination Using PhI–mCPBA. *Chemical Communications* **55**: 2066–2069.
164. Dohi, T., Sasa, H., Dochi, M., Yasui, C., Kita, Y. (2019). Oxidative Coupling of *N*-Methoxyamides and Related Compounds toward Aromatic Hydrocarbons by Designer μ -Oxo Hypervalent Iodine Catalyst. *Synthesis* **51**: 1185–1195.
165. Li, X., Chen, P., Liu, G. (2018). Recent Advances in Hypervalent Iodine(III)-Catalyzed Functionalization of Alkenes. *Beilstein Journal of Organic Chemistry* **14**: 1813–1825.
166. Zhong, W., Liu, S., Yang, J., Meng, X., Li, Z. (2012). Metal-Free, Organocatalytic Syn-Diacetoxylation of Alkenes. *Organic Letters* **14**: 3336–3339.
167. Kolb, H.C., VanNieuwenhze, M.S., Sharpless, K.B. (1994). Catalytic Asymmetric Dihydroxylation. *Chemical Reviews* **94**: 2483–2547.
168. Ho, C.M., Yu, W.Y., Che, C.M. (2004). Ruthenium Nanoparticles Supported on Hydroxyapatite as an Efficient and Recyclable Catalyst for Cis-Dihydroxylation and Oxidative Cleavage of Alkenes. *Angewandte Chemie International Edition* **43**: 3303–3307.

169. Yip, W.-P., Yu, W.-Y., Zhu, N., Che, C.-M. (2005). Alkene Cis-Dihydroxylation by $[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{VI}}\text{O}_2]\text{ClO}_4$ (Me_3tacn =1,4,7-trimethyl-1,4,7-triazacyclononane): Structural Characterization of [3+2] Cycloadducts and Kinetic Studies. *Journal of the American Chemical Society* **127**: 14239–14249.
170. de Boer, J.W., Brinksma, J., Browne, W.R., Meetsma, A., Alsters, P.L., Hage, R., Feringa, B.L. (2005). Cis-Dihydroxylation and Epoxidation of Alkenes by $[\text{Mn}_2\text{O}(\text{RCO}_2)_2(\text{tmtacn})_2]$: Tailoring the Selectivity of a Highly H_2O_2 -Efficient Catalyst. *Journal of the American Chemical Society* **127**: 7990–7991.
171. Chow, T.W.-S., Liu, Y., Che, C.-M. (2011). Practical Manganese-Catalysed Highly Enantioselective Cis-Dihydroxylation of Electron-Deficient Alkenes and Detection of a Cis-Dioxomanganese(v) Intermediate by High Resolution ESI-MS Analysis. *Chemical Communications* **47**: 11204–11206.
172. Oldenburg, P.D., Feng, Y., Pryjomska-Ray, I., Ness, D., Que Jr, L. (2010). Olefin Cis-Dihydroxylation with Bio-Inspired Iron Catalysts. Evidence for an $\text{Fe}^{\text{II}}/\text{Fe}^{\text{IV}}$ Catalytic Cycle. *Journal of the American Chemical Society* **132**: 17713–17723.
173. Suzuki, K., Oldenburg, P.D., Que Jr, L. (2008). Iron-Catalyzed Asymmetric Olefin Cis-Dihydroxylation with 97% Enantiomeric Excess. *Angewandte Chemie International Edition* **47**: 1887–1889.
174. Bautz, J., Comba, P., Lopez de Laorden, C., Menzel, M., Rajaraman, G. (2007). Biomimetic High-Valent Non-Heme Iron Oxidants for the *cis*-Dihydroxylation and Epoxidation of Olefins. *Angewandte Chemie International Edition* **46**: 8067–8070.
175. Li, Y., Song, D., Dong, V.M. (2008). Palladium-Catalyzed Olefin Dioxygenation. *Journal of the American Chemical Society* **130**: 2962–2964.
176. Zhu, M.-K., Zhao, J.-F., Loh, T.-P. (2010). Palladium-Catalyzed Oxime Assisted Intramolecular Dioxygenation of Alkenes with 1 atm of Air as the Sole Oxidant. *Journal of the American Chemical Society* **132**: 6284–6285.
177. Haubenreisser, S., Wöste, T.H., Martínez, C., Ishihara, K., Muñoz, K. (2016). Structurally Defined Molecular Hypervalent Iodine Catalysts for Intermolecular Enantioselective Reactions. *Angewandte Chemie International Edition* **55**: 413–417.
178. Aertker, K., Rama, R.J., Opalach, J., Muñoz, K. (2017). Vicinal Difunctionalization of Alkenes under Iodine(III) Catalysis involving Lewis Base Adducts. *Advanced Synthesis & Catalysis* **359**: 1290–1294.
179. Barluenga, J., Trincado, M., Rubio, E., Gonzalez, J.M. (2006). Direct Intramolecular Arylation of Aldehydes Promoted by Reaction with $\text{IPy}_2\text{BF}_4/\text{HBF}_4$: Synthesis of Benzocyclic Ketones. *Angewandte Chemie International Edition* **45**: 3140–3143.
180. Barluenga, J., Vázquez-Villa, H., Ballesteros, A., González, J.M. (2005). Synthesis of Indoles upon Sequential Reaction of 3-Alkynylpyrrole-2-carboxaldehydes with Iodonium Ions and Alkenes. Preparation of Related Benzofuran and Benzothiophene Derivatives. *Advanced Synthesis & Catalysis* **347**: 526–530.
181. Carlsson, A.-C.C., Mehmeti, K., Uhrbom, M., Karim, A., Bedin, M., Puttreddy, R., Kleinmaier, R., Neverov, A.A., Nekoueishahraki, B., Gräfenstein, J.R. (2016). Substituent Effects on the $[\text{N}-\text{I}-\text{N}]^+$ Halogen Bond. *Journal of the American Chemical Society* **138**: 9853–9863.
182. Banik, S.M., Medley, J.W., Jacobsen, E.N. (2016). Catalytic, Diastereoselective 1,2-Difluorination of Alkenes. *Journal of the American Chemical Society* **138**: 5000–5003.
183. Banik, S.M., Medley, J.W., Jacobsen, E.N. (2016). Catalytic, Asymmetric Difluorination of Alkenes to Generate Difluoromethylated Stereocenters. *Science* **353**: 51–54.
184. Muñoz, K., Barreiro, L., Romero, R.M., Martínez, C. (2017). Catalytic Asymmetric Diamination of Styrenes. *Journal of the American Chemical Society* **139**: 4354–4357.
185. Miyamoto, K., Sei, Y., Yamaguchi, K., Ochiai, M. (2009). Iodomesitylene-Catalyzed Oxidative Cleavage of Carbon–Carbon Double and Triple Bonds Using *m*-Chloroperbenzoic Acid as a Terminal Oxidant. *Journal of the American Chemical Society* **131**: 1382–1383.
186. Travis, B.R., Sivakumar, M., Hollist, G.O., Borhan, B. (2003). Facile Oxidation of Aldehydes to Acids and Esters with Oxone. *Organic Letters* **5**: 1031–1034.
187. Hussain, H., Green, I.R., Ahmed, I. (2013). Journey Describing Applications of Oxone in Synthetic Chemistry. *Chemical Reviews* **113**: 3329–3371.
188. Yakura, T. and Konishi, T. (2007). A Novel Catalytic Hypervalent Iodine Oxidation of *p*-Alkoxyphenols to *p*-Quinones Using 4-Iodophenoxyacetic Acid and Oxone. *Synlett* 0765–0768.
189. Yakura, T., Tian, Y., Yamauchi, Y., Omoto, M., Konishi, T. (2009). Catalytic Hypervalent Iodine Oxidation Using 4-Iodophenoxyacetic Acid and Oxone: Oxidation of *p*-Alkoxyphenols to *p*-Benzoquinones. *Chemical and Pharmaceutical Bulletin* **57**: 252–256.
190. Yakura, T., Yamauchi, Y., Tian, Y., Omoto, M. (2008). Catalytic Hypervalent Iodine Oxidation of *p*-Dialkoxybenzenes to *p*-Quinones Using 4-Iodophenoxyacetic Acid and Oxone. *Chemical and Pharmaceutical Bulletin* **56**: 1632–1634.
191. Yakura, T., Omoto, M., Yamauchi, Y., Tian, Y., Ozono, A. (2010). Hypervalent Iodine Oxidation of Phenol Derivatives Using a Catalytic Amount of 4-Iodophenoxyacetic Acid and Oxone as a Co-Oxidant. *Tetrahedron* **66**: 5833–5840.

192. Yakura, T. and Omoto, M. (2009). Efficient Synthesis of p-Quinols Using Catalytic Hypervalent Iodine Oxidation of 4-Arylphenols with 4-Iodophenoxyacetic Acid and Oxone. *Chemical and Pharmaceutical Bulletin* **57**: 643–645.
193. Yoshimura, A., Middleton, K.R., Luedtke, M.W., Zhu, C., Zhdankin, V.V. (2012). Hypervalent Iodine Catalyzed Hofmann Rearrangement of Carboxamides Using Oxone as Terminal Oxidant. *The Journal of Organic Chemistry* **77**: 11399–11404.
194. Yoshimura, A., Middleton, K.R., Todora, A.D., Kastern, B.J., Koski, S.R., Maskae, A.V., Zhdankin, V.V. (2013). Hypervalent Iodine Catalyzed Generation of Nitrile Oxides from Oximes and their Cycloaddition with Alkenes or Alkynes. *Organic Letters* **15**: 4010–4013.
195. Okamura, Y., Sato, D., Yoshimura, A., Zhdankin, V.V., Saito, A. (2017). Iodine(III)-Mediated/Catalyzed Cycloisomerization–Amination Sequence of N-Propargyl Carboxamides. *Advanced Synthesis & Catalysis* **359**: 3243–3247.
196. Thottumkara, A.P., Bowsher, M.S., Vinod, T.K. (2005). In Situ Generation of o-Iodoxybenzoic Acid (IBX) and the Catalytic Use of It in Oxidation Reactions in the Presence of Oxone as a Co-oxidant. *Organic Letters* **7**: 2933–2936.
197. Uyanik, M., Akakura, M., Ishihara, K. (2009). 2-Iodoxybenzenesulfonic Acid as an Extremely Active Catalyst for the Selective Oxidation of Alcohols to Aldehydes, Ketones, Carboxylic Acids, and Enones with Oxone. *Journal of the American Chemical Society* **131**: 251–262.
198. Uyanik, M., Fukatsu, R., Ishihara, K. (2009). IBS-Catalyzed Oxidative Rearrangement of Tertiary Allylic Alcohols to Enones with Oxone. *Organic Letters* **11**: 3470–3473.
199. Uyanik, M., Mutsuga, T., Ishihara, K. (2012). IBS-Catalyzed Regioselective Oxidation of Phenols to 1, 2-Quinones with Oxone®. *Molecules* **17**: 8604–8616.
200. Uyanik, M., Mutsuga, T., Ishihara, K. (2017). 4,5-Dimethyl-2-Iodoxybenzenesulfonic Acid Catalyzed Site-Selective Oxidation of 2-Substituted Phenols to 1,2-Quinols. *Angewandte Chemie International Edition* **56**: 3956–3960.
201. Ye, C., Twamley, B., Shreeve, J.N.M. (2005). Straightforward Syntheses of Hypervalent Iodine(III) Reagents Mediated by Selectfluor. *Organic Letters* **7**: 3961–3964.
202. Braddock, D.C., Cansell, G., Hermitage, S.A. (2006). Ortho-Substituted Iodobenzenes as Novel Organocatalysts for Bromination of Alkenes. *Chemical Communications* 2483–2485.
203. Alhalib, A., Kamouka, S., Moran, W.J. (2015). Iodoarene-Catalyzed Cyclizations of Unsaturated Amides. *Organic Letters* **17**: 1453–1456.
204. Asari, N., Takemoto, Y., Shinomoto, Y., Yagyu, T., Yoshimura, A., Zhdankin, V.V., Saito, A. (2016). Catalytic Cycloisomerization–Fluorination Sequence of N-Propargyl Amides by Iodoarene/HF·Pyridine/Selectfluor Systems. *Asian Journal of Organic Chemistry* **5**: 1314–1317.
205. Wöste, T.H. and Muñoz, K. (2016). Enantioselective Vicinal Diacetoxylation of Alkenes under Chiral Iodine(III) Catalysis. *Synthesis* **48**: 816–827.
206. Sarie, J.C., Neufeld, J., Daniliuc, C.G., Gilmour, R. (2019). Catalytic Vicinal Dichlorination of Unactivated Alkenes. *ACS Catalysis* **9**: 7232–7237.
207. Stodulski, M., Goetzinger, A., Kohlhepp, S.V., Gulder, T. (2014). Halocarbocyclization versus Dihaloxygenation: Substituent Directed Iodine(III) Catalyzed Halogenations. *Chemical Communications* **50**: 3435–3438.
208. Fabry, D.C., Stodulski, M., Hoerner, S., Gulder, T. (2012). Metal-Free Synthesis of 3,3-Disubstituted Oxindoles by Iodine(III)-Catalyzed Bromocarbocyclizations. *Chemistry–A European Journal* **18**: 10834–10838.
209. Ulmer, A., Stodulski, M., Kohlhepp, S.V., Patzelt, C., Pöthig, A., Bettray, W., Gulder, T. (2015). Iodine(III)-Catalyzed Rearrangements of Imides: A Versatile Route to α,α -Dialkylated α -Hydroxy Carboxylamides. *Chemistry – A European Journal* **21**: 1444–1448.
210. Patzelt, C., Pöthig, A., Gulder, T. (2016). Iodine(III)-Catalyzed Cascade Reactions Enabling a Direct Access to β -Lactams and α -Hydroxy- β -amino Acids. *Organic Letters* **18**: 3466–3469.
211. Massignan, L., Tan, X., Meyer, T.H., Kuniyil, R., Messinis, A.M., Ackermann, L. (2020). C–H Oxygenation Reactions Enabled by Dual Catalysis with Electrogenated Hypervalent Iodine Species and Ruthenium Complexes. *Angewandte Chemie International Edition* **59**: 3184–3189.
212. Roth, H.G., Romero, N.A., Nicewicz, D.A. (2016). Experimental and Calculated Electrochemical Potentials of Common Organic Molecules for Applications to Single-Electron Redox Chemistry. *Synlett* **27**: 714–723.
213. Maity, A., Frey, B.L., Hoskinson, N.D., Powers, D.C. (2020). Electrocatalytic C–N Coupling via Anodically Generated Hypervalent Iodine Intermediates. *Journal of the American Chemical Society* **142**: 4990–4995.