

Abstracts

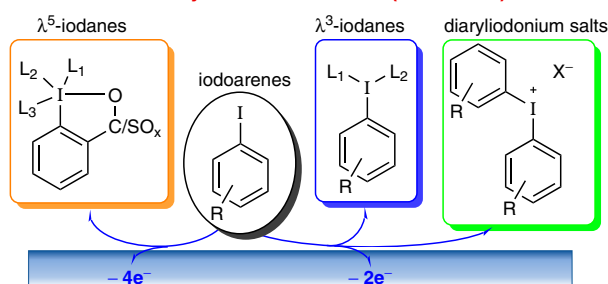
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2 Electrochemical Synthesis of Hypervalent Iodine Compounds

Tomas Bystron^{1b} and Martin Jirasko^{1b}

Hypervalent iodine compounds (or iodonanes) represent an interesting class of chemicals possessing a multivalent iodine atom. They are popular oxidation and ligand-transfer agents that are renowned for their versatility and selectivity, but also for their high cost and in some cases low stability. Compared to classical synthetic procedures, the electrochemical synthesis of these compounds offers significant benefits, such as increased safety, and potentially reduced cost and environmental impact. This review summarizes advances in the electrochemical synthesis of various iodonanes, and briefly mentions their applications for in-cell and ex-cell mediation.

Electrosynthesis of Iodonanes (1967–2024)



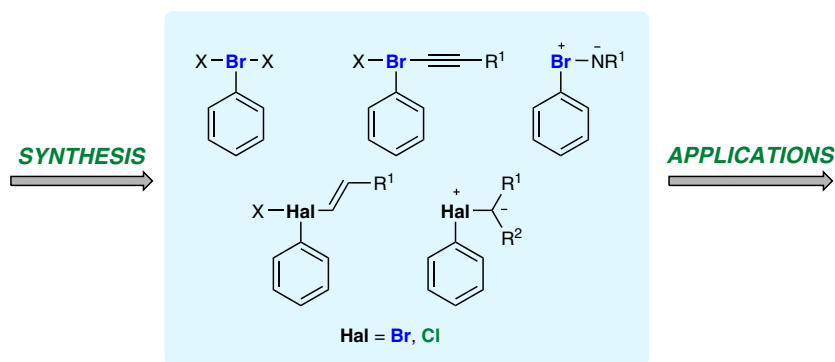
Keywords: hypervalent iodine compounds · electroorganic chemistry · iodonanes · iodoarene oxidation · iodonium salts · iodanyl radicals · benziodoxolone · iodobenzenes · electrochemical synthesis · electrolysis · electrosynthesis · anodic oxidation · mediation · flow reactors

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3 Synthesis and Applications of Aryl- λ^3 -bromanes and Aryl- λ^3 -chloranes

Igors Sokolovs^{1b} and Edgars Suna^{1b}

Hypervalent halogen compounds have emerged as powerful reagents in contemporary organic synthesis. Among these, λ^3 -bromanes and λ^3 -chloranes stand out as the most reactive species, enabling unique and unconventional synthetic transformations that underpin novel bond-forming strategies. This review provides a comprehensive overview of the synthesis and applications of monoaryl- λ^3 -bromanes and monoaryl- λ^3 -chloranes (including bromonium and chloronium ylides) as well as alkenyl(aryl)- and alkynyl(aryl)- λ^3 -bromanes and the corresponding λ^3 -chloranes.



Keywords: hypervalent halogens · λ^3 -bromanes · λ^3 -chloranes · bromonium ylides · chloronium ylides · nucleofugality · oxidation · rearrangements · C–H activation

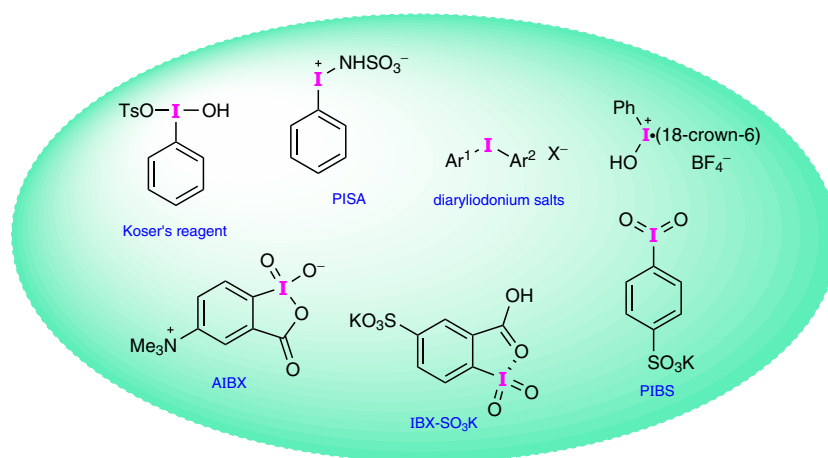
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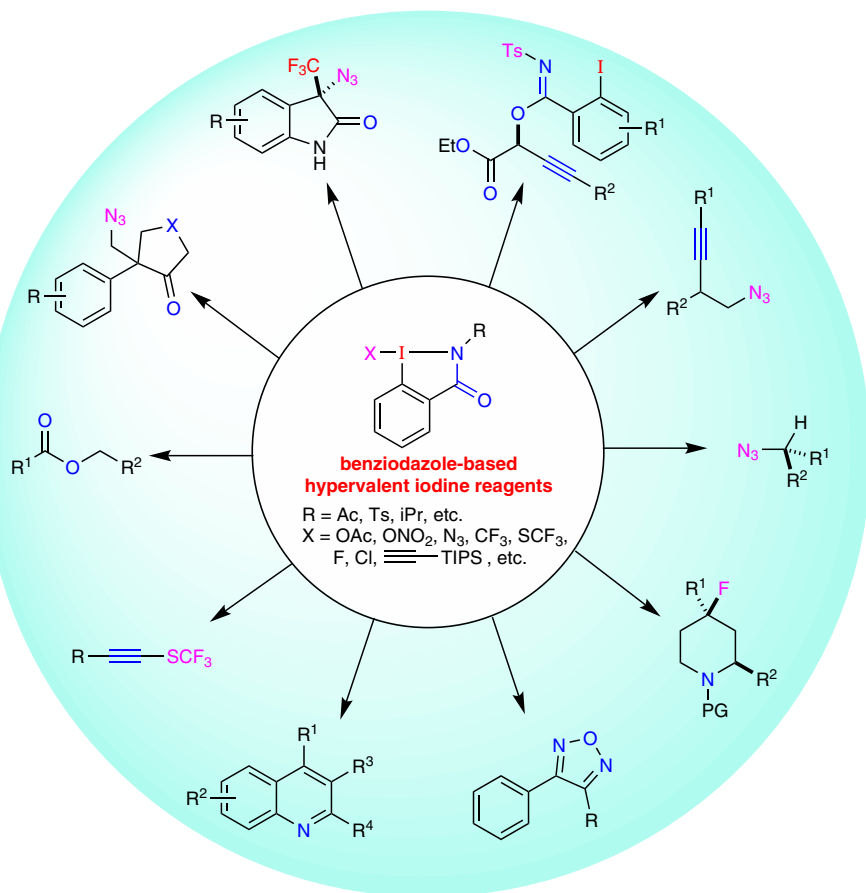
Synthesis and Applications of Water-Soluble Hypervalent Iodine Reagents

Chi Zhang^{1b} and Ya-Nan Duan^{1b}

The development of water-soluble hypervalent iodine reagents represents a significant advancement in green chemistry, addressing the environmental concerns associated with traditional organic solvents. In this review, the synthesis and applications of water-soluble iodine(III) and iodine(V) reagents are comprehensively summarized. By leveraging hydrophilic ligands or functional groups, these reagents achieve high reactivity in water or mixed aqueous solvents, aligning with the principles of sustainable chemistry. This chapter underscores the potential of water-soluble hypervalent iodine reagents to replace conventional methods, offering scalable, more eco-friendly alternatives for diverse organic transformations.



Keywords: hypervalent iodine · iodine(III) reagents · iodine(V) reagents · Koser's reagent · PISA · diaryliodonium salts · AIBX · dehydrogenation · oxidative functionalization · water · aqueous media · sustainable chemistry · recyclable reagents

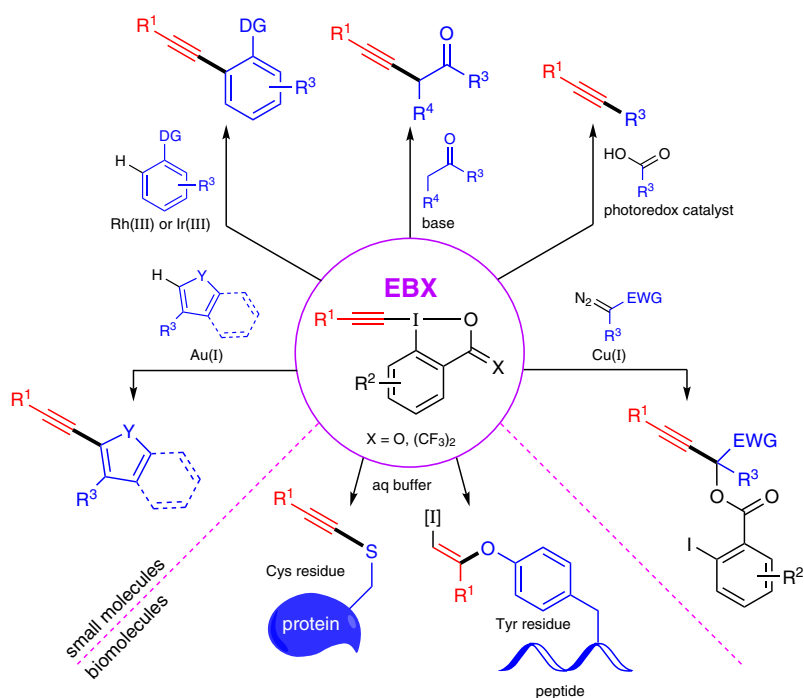
Dan Xiao and Yunfei Du 

Keywords: hypervalent iodine reagents · benziodazoles · cyclic hypervalent iodine compounds · metal-free conditions · bond formation

6 Synthesis and Applications of Alkynylbenziodoxol(on)es

Stefano Nicolai^{id} and Jérôme Waser^{id}

The synthetic value of the C≡C bond has prompted assiduous efforts to develop effective methods for the synthesis of acetylenes. First introduced in the 1990s and then rediscovered twenty years later, alkynylbenziodoxol(on)es (EBXs) have rapidly emerged as one of the most powerful class of alkynylating reagents. Easily accessed, bench stable and nontoxic, these compounds were initially employed for acetylene transfer onto nucleophilic substrates under a variety of conditions. However, they have later shown their great utility in the alkynylation of radicals. Key to their success is their cyclic structure, which provides them with enhanced stability and permits the fine-tuning of their reactivity through structural adjustments of the benziodoxol(on)yl core. After presenting the principal procedures for the preparation of EBXs, this review will summarize the most important synthetic applications of these reagents. The functionalization of small molecules is discussed first; following that, the more recently established methods for the labeling of biomolecules with EBXs are described.

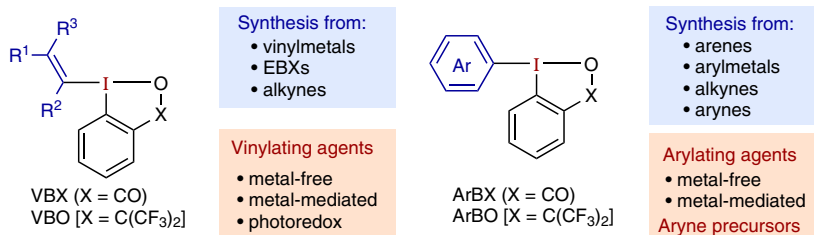


Keywords: hypervalent iodine · ethynyl benziodoxolones · ethynyl benziodoxoles · alkynes · electrophilic alkynylation · somophilic alkynylation · transition-metal catalysis · photoredox catalysis · bioconjugation

7 Synthesis and Applications of Vinyl- and Arylbenziodoxol(on)es

Naohiko Yoshikai 

This chapter reviews the synthesis and applications of vinyl- and arylbenziodoxol(on)es as a distinct class of stable organoiodanes. Recent advancements have enabled their efficient preparation via multiple synthetic approaches, expanding their utility in vinylation and arylation reactions. These compounds have demonstrated unique versatility in metal-free, metal-mediated, and photoassisted transformations, underscoring their growing importance as group-transfer reagents in modern organic synthesis.

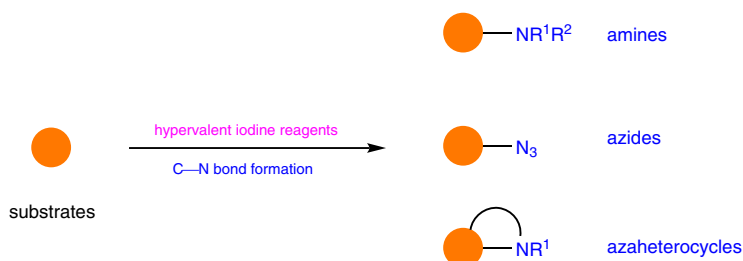


Keywords: hypervalent iodine · vinylation · arylation · metal-free reactions · cross coupling · C—H activation · photoredox catalysis · arynes · organoboron compounds · nucleophilic addition · alkynes · difunctionalization · cyclopropenes

8 C—N Bond Forming Reactions with Hypervalent Iodine Reagents

Kensuke Kiyokawa 

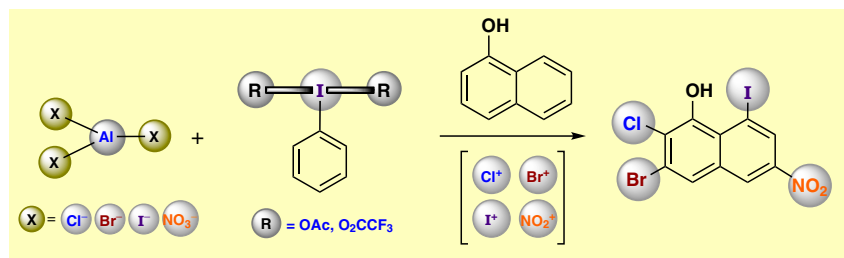
Hypervalent iodine reagents containing transferable nitrogen functional groups, or the combined use of hypervalent iodine oxidants with aminating reagents, have proven to be powerful tools for oxidative amination, an umpolung strategy for introducing nitrogen functional groups into organic molecules. The discovery of new reactivities of hypervalent iodine reagents has expanded the scope of C—N bond formation reactions, and these advancements provide an efficient approach to synthesizing nitrogen-containing organic molecules, which serve as promising building blocks for the preparation of biologically active and medically significant compounds. This review highlights recent advances in C—N bond forming reactions using hypervalent iodine reagents.



Keywords: amination · amines · anilines · azaheterocycles · azides · C—N bond formation · cyclization · iodine · hypervalent iodine · nitrogen-containing organic molecules · oxidation

9 Aromatic Halogenation and Nitration with Hypervalent Iodine Reagents*César R. Solorio-Alvarado* 

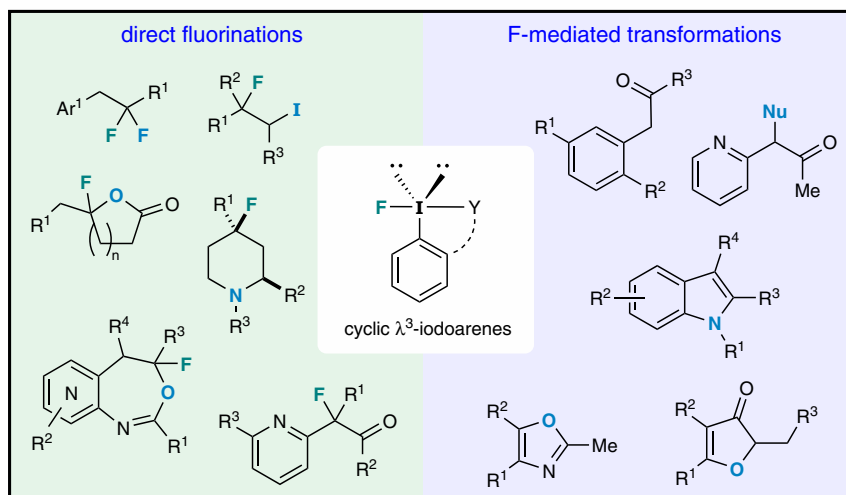
Iodine(III) compounds have gained increasing prominence in organic synthesis due to their use as nontoxic and easy to handle reagents and more environmentally friendly nature. Their versatility as oxidants has been applied in the development of various methodologies for the functionalization of aromatic systems, allowing the introduction of various inorganic groups, including halogens and nitro groups. In this review, the most representative procedures for the halogenation of arene and hetarene systems using different iodine(III) reagents in combination with halide sources are described.



Keywords: hypervalent iodine · iodine(III) reagents · oxidative aromatic halogenation · arenes · aryl halides · nitroarenes · fluorination · chlorination · bromination · iodination · nitration

10 Reactions with Fluorinated Cyclic Hypervalent Iodine Reagents*Jan Balzer* , *Markus Tost* , and *Tanja Gulder* 

Fluorinated cyclic hypervalent iodine reagents (fluoro- λ^3 -iodanes) have emerged as versatile fluorinating agents in organic synthesis. Their characteristic three-center-four-electron (3c–4e) bond imparts unusual stability and reactivity, enabling selective fluorination under mild conditions. In comparison, cyclic λ^3 -iodanes are more stable toward oxygen, moisture, and heat, but also less reactive than their linear analogues. An increased reactivity can be achieved by activation with Lewis acids and bases, Brønsted acids, or hydrogen bonding. Mechanistic studies have revealed iodine coordination, σ -metathesis, and aryl migration pathways that generate highly functionalized products. This review highlights their diverse applications in direct fluorination reactions of alkenes, oxyfluorinations, aminofluorinations, and cascade reactions toward fluorinated heterocycles and α -fluoro carbonyl compounds. Moreover, fluorine can also act as a traceless directing group, enabling the formation of heterocycles, Umpolung reactions, and oxidation processes through fluorinated reactive intermediates. The combination of high reactivity, tunable selectivity, and compatibility with catalytic activation makes cyclic hypervalent iodine reagents powerful tools for constructing C–F, C–O, C–N, and C–C bonds in complex molecules.



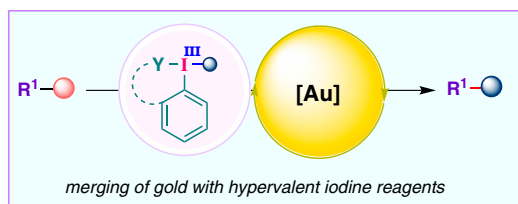
Keywords: hypervalent iodine · fluoro- λ^3 -iodanes · electrophilic fluorination · cyclic iodine reagents · C—F bond formation · C—C bond formation · C—O bond formation · C—N bond formation · aryl migration · Lewis acid activation · Lewis base activation

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11 Hypervalent Iodine Reagents in Gold Catalysis

Nitin T. Patil^{ID}, Prafulla Bera^{ID}, and Bidisha Paroi^{ID}

In the past two decades, hypervalent iodine(III) reagents in partnership with gold catalysts have found extensive application in achieving electrophilic functional-group-transfer reactions. A variety of transformations including alkynylation, arylation, acetoxylation, and cross-coupling reactions have been accomplished by leveraging different reactivity modes of gold catalysis. Presented in this review is an overview of these reactions, categorized based on the employed hypervalent iodine(III) reagents such as ethynylbenziodoxol(on)es (EBXs), (diacetoxyiodo)benzene, 1-(trifluoromethanesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one, diaryliodonium salts, and cyclopropenyl benziodoxoles.

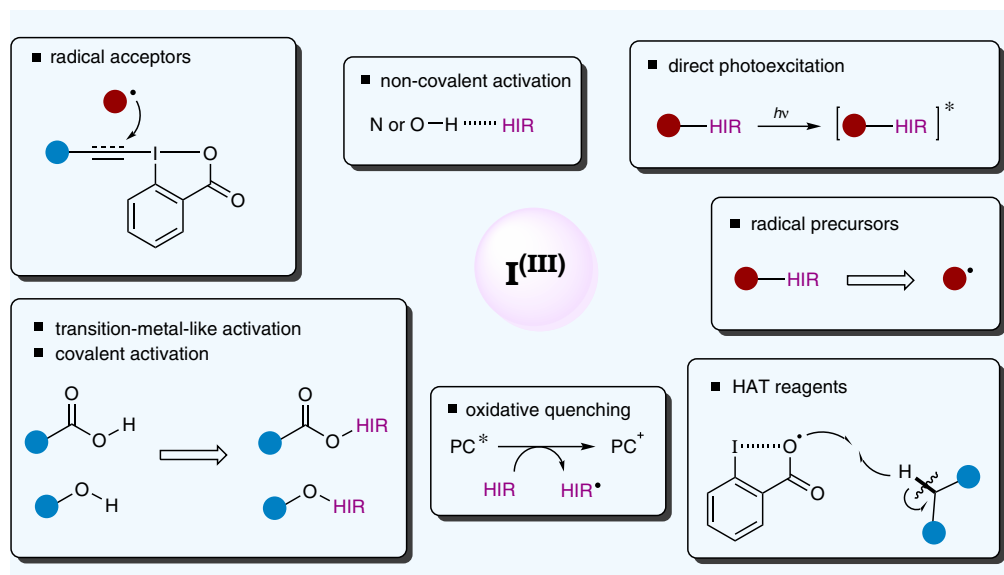


Keywords: hypervalent iodine reagents · ethynylbenziodoxoles · ethynylbenziodoxolones · (diacetoxyiodo)benzene · phenyliodonium diacetate · iodosylbenzoic acid triflate · diaryliodonium salts · cyclopropenyl benziodoxoles · gold catalysis · alkynylation · arylation · acetoxylation · cross coupling

12 Hypervalent Iodine Reagents in Photochemistry

Xiaojuan Dong , Hanzhang Qin , and Yiyun Chen 

Harnessing their unique three-center, four-electron bonding motif, hypervalent iodine compounds have emerged as powerful and versatile reagents in modern organic synthesis, with particularly significant applications in photochemical transformations. This review provides a systematic overview of recent advances that exploit these reagents in diverse photoredox roles, including direct photoexcitation, and their use as radical precursors, radical acceptors, hydrogen-atom-transfer (HAT) reagents, and redox-active agents. Furthermore, it explores their capacity to mimic transition-metal behavior through distinct covalent and non-covalent activation modes. By consolidating these multifaceted reactivities, the integral role of hypervalent iodine reagents in advancing the frontier of sustainable photochemical synthesis is underscored.

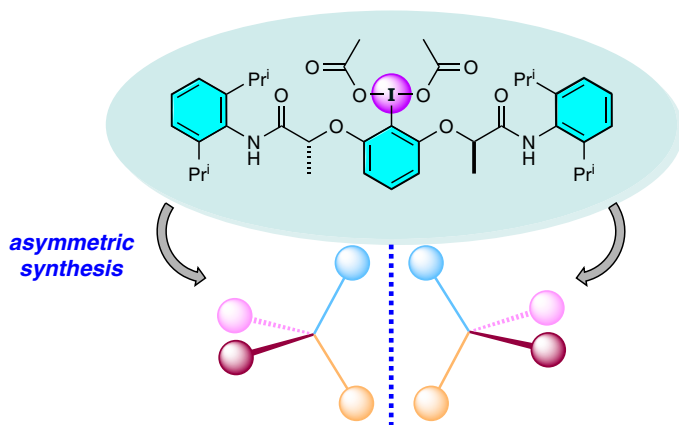


Keywords: hypervalent iodine · photochemistry · photoredox · homolysis · activation · catalysis · hydrogen-atom transfer (HAT) · radical processes

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Hypervalent Iodine in Asymmetric Synthesis*José C. Cunha^{ID}, Beatriz Dedeiras^{ID}, Ana Cláudia R. Negrão^{ID}, and Maria Manuel B. Marques^{ID}*

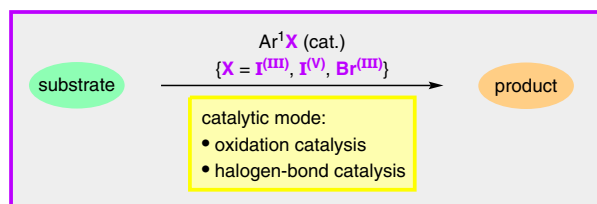
Hypervalent iodine compounds, particularly iodine(III) and iodine(V) species, have emerged as powerful, environmentally friendly reagents in asymmetric synthesis, combining strong oxidative ability with good functional-group tolerance and sustainability. Recent developments in chiral iodine-mediated asymmetric reactions have expanded the scope of oxidative rearrangements, phenol dearomatizations, and α -functionalizations of carbonyl compounds. Special emphasis is placed on C–C bond forming processes such as asymmetric [4 + 2] cycloadditions and nucleophilic additions to C=N bonds, which benefit from tunable C_2 -symmetric chiral iodine(III) scaffolds. This review highlights advances in the structural design, reactivity, and mechanistic understanding of chiral hypervalent iodine reagents, underscoring their growing role in enantioselective oxidative transformations and their potential in sustainable asymmetric catalysis.



Keywords: hypervalent iodine · asymmetric synthesis · chiral iodoarenes · iodine(III) · iodine(V) · oxidative coupling · enantioselective catalysis · sustainable synthesis · oxidative dearomatization · oxidative rearrangement · alkene functionalization · carbonyl α -functionalization · nucleophilic addition

14 Recent Advances in Hypervalent Halogen Catalysis*Hiroataka Sasa^{1b}, Yasuyuki Kita^{1b}, and Toshifumi Dohi^{1b}*

Over the past three decades, hypervalent halogen catalysis has demonstrated significant versatility in facilitating various organic transformations. This review categorizes these catalytic reactions into two main classifications: oxidation catalysis and halogen-bond catalysis. Oxidation catalysis involves the utilization of hypervalent iodine compounds with co-oxidants to promote catalytic oxidation processes. Conversely, halogen-bond catalysis encompasses reactions promoted by the Lewis acidity of iodonium or bromonium salts. The chapter presents selected examples from each category, elucidating the applicable substrates, reaction limitations, and detailed experimental protocols.



Keywords: hypervalent iodine · oxidation catalysis · organocatalysis · halogen-bond catalysis · hypervalent bromine · Lewis acids