



Digest paper

Synthetic application of water-soluble hypervalent iodine reagents in aqueous media

Yong-Chao Han, Chi Zhang*

State Key Laboratory of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), College of Chemistry, Nankai University, Tianjin 300071, China

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ABSTRACT

Along with the vigorous development of hypervalent iodine chemistry, water-soluble hypervalent iodine reagents have received considerable attentions in recent years. In order to obtain water-soluble hypervalent iodine reagents, two strategies have been employed including introduction of hydrophilic functional groups onto the phenyl ring and formation of complex of iodosylbenzene with crown ether. And, it is observed that four kinds of hypervalent iodine reagents exhibit more or less solubility in water including hypervalent iodine reagents containing hydrophilic ligands, diaryliodonium salts, oligomeric iodosylbenzene sulfate, and iodylbenzene and its derivatives. In this review, we summarize these water-soluble hypervalent iodine reagents and their broad synthetic applications in aqueous media.

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Introduction

Since the preparation of PhICl_2 by Willgerodt in 1886, hypervalent iodine compounds have been known for more than one century [1]. Until now, hypervalent iodine reagents have been widely used in organic synthesis and many hypervalent iodine reagents, including phenyliodine(III) diacetate (PIDA), phenyliodine(III) bis(trifluoroacetate) (PIFA), [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent), 2-iodoxybenzoic acid (IBX), et al. are now commercially available. Hypervalent iodine reagents have been recognized as a useful synthetic tool because they are

nontoxic, environmentally friendly, easy to regenerate and readily available. More importantly, they show reactivities similar to that of heavy metals, such as mercury, chromium, lead and thallium [1]. These beneficial features make them as preferred organo-oxidants in organic synthesis, replacing the highly toxic oxidants that used in the classical organic reactions. A large number of hypervalent iodine reagents have been reported through more than one century of development, however, only a fraction of them are soluble in water. No review that introduces specifically water soluble hypervalent iodine reagents has appeared to date.

Water is a nontoxic, environmentally friendly and inexpensive solvent and satisfies the requirements of green chemistry as a solvent. The properties of water at high temperature (200–350 °C) are similar to those of polar organic solvents at room temperature,

* Corresponding author.

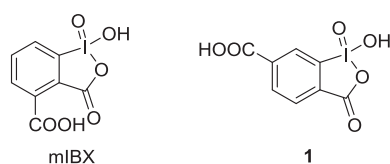
E-mail address: zhangchi@nankai.edu.cn (C. Zhang).

thus facilitating organic reactions such as ionic condensation of alkenes, alcohols, and aldehydes, cleavage of aryl ethers, aryl thioether, and secondary arylamines and hydrolysis of polyesters, polyurethane, glycerol triacetate and so on [2]. The self-ionization of water enhances significantly with the increase of temperature, so hot water (40–100 °C) is believed to act as a Brønsted acid to promote several organic reactions such as *N*-Boc deprotection [3], rearrangement of allylic alcohols [4], epoxide-opening reactions [5] and S_N1 solvolysis reactions of allylic and benzylic alcohols [6]. Water can also accelerate reaction rate and improve reaction selectivity [7] via hydrophobic effect of organic substrates which has been studied by Breslow et al. [8]. In the field of hypervalent iodine chemistry, it is found that water molecule can coordinate to the iodine center of water-soluble hypervalent iodine reagents, which enhances iodine reagents' thermal stability and maintain their oxidizing ability in water; [9] therefore a number of important organic reactions can be mediated by water-soluble hypervalent iodine reagents in aqueous media [9]. Hence, it will be of great significance to develop new water-soluble hypervalent iodine reagents and explore their reactivities in aqueous media.

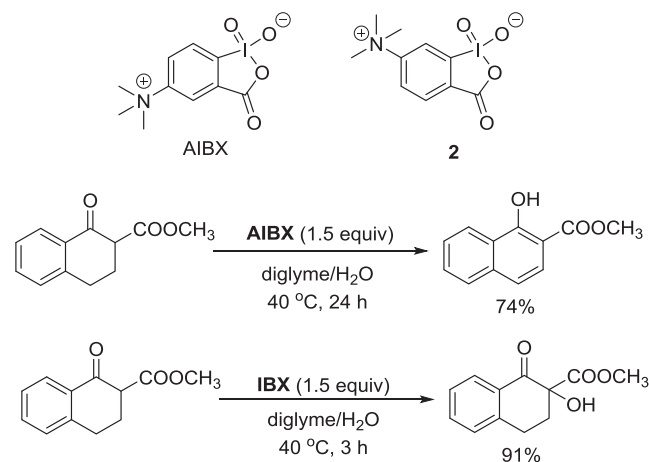
This review summarizes water-soluble hypervalent iodine reagents and their reactivities in aqueous media. Two strategies are used to obtain water-soluble hypervalent iodine reagents including introduction of hydrophilic functional groups onto the phenyl ring of hypervalent iodine reagents and formation of complex of iodosylbenzene with crown ether. Besides the water-soluble hypervalent iodine reagents designed and synthesized following the strategies mentioned above, four kinds of hypervalent iodine reagents themselves have water solubility more and less, including hypervalent iodine reagents containing hydrophilic ligands [hydroxyl group (–OH), sulfonyloxy group (–OTs)], diaryliodonium salts, oligomeric iodosylbenzene sulfate [(PhIO)₃·SO₃], and iodylbenzene (PhIO₂) and its derivatives; synthetic application of these hypervalent reagents are also reviewed. We hope this review will serve as reference and guidance, and enlighten chemists to design new water-soluble hypervalent iodine reagents and explore their unique reactivities in aqueous media.

Introduction of hydrophilic groups onto the phenyl ring of hypervalent iodine reagents

Introduction of hydrophilic groups, such as carboxyl (–COOH), trimethylammonium (–⁺NMe₃), and sulfonate (–SO₃[–]), onto the phenyl ring of hypervalent iodine reagents is the most frequently used method to give water-soluble hypervalent iodine reagents. 2-Iodoxybenzoic acid (IBX) [10] is the preferred organo-oxidant to oxidize alcohols to the corresponding carbonyl compounds. However, IBX is insoluble in most common organic solvents as well as in water, which restricts its broad application in organic synthesis. To overcome this limitation, water-soluble derivative of IBX, including mIBX [11] and **1** [12] in which a carboxyl group was introduced onto the phenyl ring of IBX, were synthesized by Vinod et al. (Scheme 1). These two reagents have been successfully used to oxidize benzylic and allylic alcohols to carbonyl compounds in water [11,12].

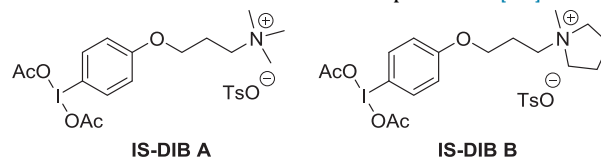


Scheme 1. Water-soluble derivatives of IBX containing a carboxyl group.



Scheme 2. Water-soluble derivatives of IBX containing a trimethylammonium group.

Togo et al. prepared two derivatives of (diacetoxyiodo)benzene, IS-DIB A and IS-DIB B, in which a trimethylammonium group (–⁺NMe₃) was introduced into the iodine(III) reagent through a ether carbon chain. IS-DIB A or B can promote several important organic transformations in organic solvent including oxidation of alcohols and *N,N*-diisopropylbenzylamines, Hofmann rearrangement and so on. However, the information about their solubility and chemical reactions in water are not presented [13].



In 2011, Zhang et al. designed and synthesized two new recyclable water-soluble IBX derivatives AIBX (0.38 M at rt) and its isomer **2** (0.3 M at rt), in which a trimethylammonium group was installed directly onto the phenyl ring [14]. Zhang et al. also reported the first reactivity of AIBX, that is, the dehydrogenation of various β -keto esters in mixed solvent of water and diglyme. On the contrary, the hydroxylated product was obtained when using IBX as the oxidant under the otherwise same reaction conditions (Scheme 2).

In 2015, Zhang et al. discovered the AIBX-mediated dehydrogenative α,β' -bifunctionalization of β -keto esters for the construction of benzo-fused 2,3-dihydrofurans [15]. A protected aglycone of a natural product isolated from *Kaempferia parviflora* [16] was synthesized successfully, which proved the utility of this method (Scheme 3). The proposed mechanism for this interesting transformation involved dehydrogenation of β -keto esters, Michael addition, and intramolecular oxidative cyclisation (Scheme 4).

Based on the comprehension to AIBX-mediated dehydrogenative α,β' -bifunctionalization of β -keto esters, a method for the synthesis of cyclopropanes from the C(sp²)-C(sp³) single bonds of β -keto esters was developed by Zhang et al. as well [17]. Compared with previous work, the nucleophilic reagent β -diketone was replaced by malononitrile in this work. A similar mechanism involving the sequence of dehydrogenation, Michael addition, and ring-closure has been proposed (Scheme 5).

Recently, Zhang et al. reported a new method for the direct formation of epoxide groups from carbon(sp²)-carbon(sp³) single bonds of β -keto esters using AIBX [18]. A mechanism involving dehydrogenation of the substrate β -keto esters and epoxidation of the resulting enone intermediates was proposed (Scheme 6).

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