

Review article

Iodine catalysis: A green alternative to transition metals in organic chemistry and technology

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Abstract

Iodine and compounds of iodine in higher oxidation states have emerged as versatile and environmentally benign reagents for organic chemistry. One of the most impressive recent achievements in this area has been the discovery of catalytic activity of iodine in numerous oxidative transformations leading to the formation of new C—O, C—N, and C—C bonds in organic compounds. These catalytic transformations in many cases are very similar to the transition metal-catalyzed reactions, but have the advantage of environmental sustainability and efficient utilization of natural resources. Iodine is an environmentally friendly and a relatively inexpensive element, which is currently underutilized in industrial applications. One of the main goals of this review is presenting to industrial researchers the benefits of using catalytic iodine in chemical technology as an environmentally sustainable alternative to transition metals. The present review summarizes catalytic applications of iodine and compounds of iodine in organic synthesis. The material is organized according to the nature of active catalytic species (hypoiodite, trivalent, or pentavalent hypervalent iodine species) generated in these reactions from appropriate pre-catalysts. Numerous synthetic procedures based on iodine(III) or iodine(V) catalytic species in the presence of hydrogen peroxide, Oxone, peroxyacids or other stoichiometric oxidants are summarized. A detailed discussion of catalytic cycles involving hypervalent iodine, hypoiodites, and other active intermediates is presented.

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Keywords: Hypervalent catalysis; Iodine catalysis; Hypoiodite catalysis; Hypervalent iodine

1. Introduction

Iodine is one of the heaviest non-radioactive elements in the Periodic Table classified as a non-metal, and it is the largest, the least electronegative, and the most polarizable of the halogens. Iodine can form inorganic and organic derivatives in various oxidation states (−1, 0, +1, +3, +5, +7) and structural features and reactivity pattern of iodine compounds in many aspects are similar to the derivatives of heavy transition metals. Reactions of iodine compounds are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination, and ligand coupling, which are typical of the transition metal chemistry [1]. In contrast to the heavy metals, iodine is an environmentally friendly and a relatively inexpensive element; iodine bulk price in the last 10 years was within the range of \$20–100 per kg, which

is orders of magnitude cheaper than platinum, palladium, or osmium. Iodine annual production is about 30,000 tons with estimated world's total reserves of 15 million metric tons located mainly in Chile and Japan [2].

Compounds of iodine have found some industrial application. About 16% of iodine world production is utilized in industrial catalysis. Hydroiodic acid is used as a co-catalyst for the production of acetic acid by the Monsanto and Cativa processes. In this technology, which is the main industrial process for the production of acetic acid, hydroiodic acid converts the methanol feedstock into methyl iodide, which then undergoes Rh-catalyzed carbonylation. Hydrolysis of the resulting acetyl iodide regenerates hydroiodic acid and gives acetic acid. Other practical applications of iodine compounds include the use in polymer industry, in liquid-crystal display polarizers, and also numerous applications in food industry, medicine, and pharmaceuticals [3].

In recent years, organic derivatives of polyvalent iodine (which are known under common name of “hypervalent” iodine compounds) have attracted significant research activity as versatile

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and environmentally benign reagents for organic synthesis [1,4,5]. One of the most impressive recent achievements in this area has been the discovery of catalytic activity of iodine in numerous oxidative transformations leading to the formation of new C—O, C—N, and C—C bonds in organic compounds. These catalytic transformations in many cases are very similar to the transition metal-catalyzed reactions, but have the advantage of environmental sustainability and efficient utilization of natural resources.

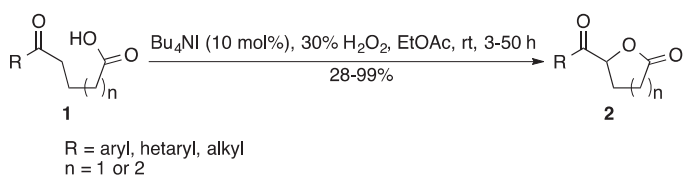
In the present review, we summarize catalytic applications of iodine and compounds of iodine in organic synthesis. The material is organized according to the nature of active catalytic species (hypoiodite, trivalent, or pentavalent iodine species) generated in these reactions from appropriate pre-catalysts. One of the main goals of this review was to attract attention of the industrial researchers to the benefits of using catalytic iodine in chemical technology as an environmentally sustainable alternative to transition metals.

2. Catalytic cycles involving elemental iodine or iodide anion as pre-catalysts

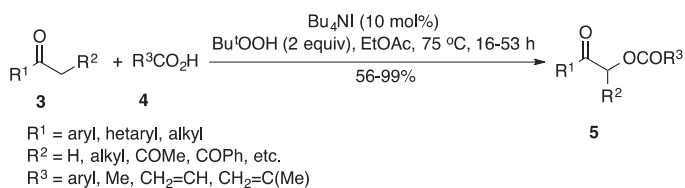
Catalytic reactions, utilizing iodide anion or elemental iodine as the pre-catalysts, usually involve the iodine cation, hypoiodic acid, or inorganic iodine(III) species as active oxidants. There has been significant recent interest in these reactions since 2010, when first examples of such reactions were reported. The oxidative catalytic reactions utilizing iodide anion or elemental iodine as a catalyst or pre-catalyst have been summarized in several reviews [6–9].

In 2010, Ishihara and co-workers have first reported that tetrabutylammonium iodide can be used as a highly effective pre-catalyst for the oxylactonization of oxocarboxylic acids **1** with aqueous hydrogen peroxide at room temperature (Scheme 1) [10]. Importantly, no Baeyer–Villiger products were obtained under these reaction conditions. Both γ -aryl- and γ -heteroarylcarbonyl- γ -butyrolactones **2** (R = aryl or heteroaryl, n = 1) were obtained in excellent yields, and γ -alkylcarbonyl- γ -butyrolactones **2** (R = alkyl, n = 1) and δ -valerolactones **2** (n = 2), in moderate yields. Lactones are important intermediate products in organic synthesis and in the manufacturing of polyesters, therefore, this simple and environmentally friendly procedure represents interest to industrial chemists.

This catalytic procedure has been further applied to the oxidative coupling of carbonyl compounds with carboxylic acids using Bu₄NI as catalyst and *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant [10]. Various ketones **3** as well as 1,3-dicarbonyl compounds as substrates react with carboxylic



Scheme 1. Tetrabutylammonium iodide as a pre-catalyst for the oxylactonization of oxocarboxylic acids.



Scheme 2. Tetrabutylammonium iodide-catalyzed oxidative coupling of carbonyl compounds with carboxylic acids.

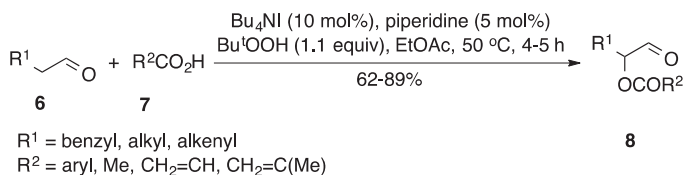
acids **4** under these conditions to give the corresponding α -acyloxy ketones **5** in good to excellent yields (Scheme 2) [10]. A similar TBAI-catalyzed oxidative coupling of β -ketoesters with carboxylic acid has been reported in a more recent work [11].

Aldehydes can be α -oxyacylated under similar conditions in the presence of piperidine [10]. Thus, aldehydes **6** and acids **7** react upon mild heating in the presence of catalytic amounts of Bu₄NI and piperidine and TBHP as the terminal oxidant in ethyl acetate to afford α -acyloxy aldehydes **8** in high yields (Scheme 3). Various functional groups such as terminal or internal alkenyl, benzyloxy, silyloxy, acetal, halogen, and ester are stable under these conditions.

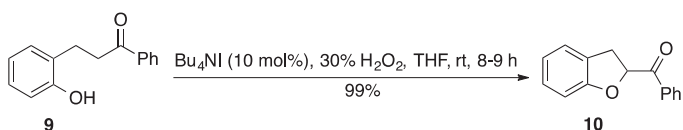
The Bu₄NI/TBHP catalytic system has also been applied toward the α -oxyacylation of ethers with carboxylic acids in ethyl acetate at 80 °C [12], possibly, via a radical mechanism.

During their studies on the oxylactonization of oxocarboxylic acids **1** (Scheme 1), Ishihara and co-workers discovered that the catalytic oxidative system Bu₄NI/H₂O₂ could be used for the oxidative cycloetherification of oxo-substituted phenols [6]. For example, the oxidation of phenolic substrate **9** with two equivalents of 30% aqueous H₂O₂ in the presence of Bu₄NI as a catalyst in THF or ether at room temperature selectively afforded the corresponding 2-acyldihydrobenzofurane **10** in excellent yield and (Scheme 4).

Based on this reaction (Scheme 4), Ishihara and co-workers have developed a highly enantioselective oxidative cycloetherification of substrates **11** using hydrogen peroxide as the oxidant in the presence of the chiral quaternary ammonium iodide catalyst **12** (Scheme 5) [13]. This cycloetherification leads to the chiral 2-acyl-2,3-dihydrobenzofuran skeleton **13**, which is a key structural unit in numerous biologically active compounds, for example, entremirol and entremiridol.



Scheme 3. Catalytic α -acyloxylation of aldehydes.



Scheme 4. Catalytic oxidative cycloetherification of phenolic substrates.

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