



Review

Development of new hypervalent iodine reagents with improved properties and reactivity by redirecting secondary bonds at iodine center



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ABSTRACT

Hypervalent iodine reagents have found wide application in organic synthesis as versatile, efficient, and environmentally sustainable reagents. Particularly important hypervalent iodine reagents used as atom and group transfer reagents include: iodosylbenzene, (PhIO)_n, (tosylimino)iodobenzene, (PhINTs)_n, and iodonium ylide, PhI=C(CO₂CH₃)₂. Despite the significant interest in these reagents as primary sources of “O”, “NR” and “CR₂” units in transition metal catalyzed processes, their practical application is hampered. In particular, their tightly aggregated and polymeric structures in the solid state render these polyvalent iodine species insoluble in all nonreactive media and prevent their use in chemical reactions under homogenous conditions, which can be undesirable for many synthetic and mechanistic studies. In this review we describe our work on the rational design and development of new soluble, thermally stable, and highly reactive hypervalent iodine reagents based on structural modifications that lead to redirection of secondary bonding from intermolecular to intramolecular modes. Specifically, the introduction of a coordinating donor in the *ortho*-position of the phenyliodine (III) moiety leads to a significant improvement of solubility of a hypervalent iodine reagent. Based on this approach, we have developed a series of new hypervalent iodine reagents, which can be used as selective oxidants, nitrene or carbene precursors, and atom transfer reagents. Specific examples of these new reagents are represented by iodosylarenes and iminophenyliodanes bearing *tert*-butylsulfonyl group in the *ortho*-position of the phenyl ring and by the *ortho*-alkoxy substituted iodonium imides and ylides. These new pseudocyclic (and cyclic) reagents have excellent solubility in organic solvents and can be used as efficient reagents for catalytic formation of new C–O, C–N and C–C bonds, as well as to enable the generation and detection of highly reactive metal species involved in catalysis and biomimetic reactions.

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Abbreviations: PhIO, iodosylbenzene; PhINTs, (tosylimino)iodobenzene; IBX, 2-iodoxybenzoic acid; EXAFS, extended X-ray absorption fine structure; NMR, nuclear magnetic resonance; porph, porphyrin; TDCPP, tetra-(2,6-Cl₂C₆H₃)porphyrin; TPP, tetraphenylporphyrin; ESI-MS, electrospray ionization mass spectrometry; DMSO, dimethylsulfoxide; IBA, 2-iodosylbenzoic acid.

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1. Introduction

Organic compounds of polyvalent iodine, commonly known as hypervalent iodine reagents, have found broad application in organic synthesis as versatile, efficient, and environmentally sustainable reagents [1–5]. The reactivity pattern of polyvalent iodine in many aspects is similar to the reactivity of transition metals, in that the reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination, and ligand coupling, which are typical terms to describe fundamental reaction steps in transition metal chemistry. One of the most impressive recent achievements in the area of hypervalent iodine chemistry has been the development of numerous catalytic reactions promoted by generated in situ organohypervalent iodine species [1,2,6].

Despite the significant interest in hypervalent iodine chemistry, practical application of several common reagents, such as iodosylbenzene (PhIO)_n, iodylbenzene (PhIO₂), (tosyliminoiodo)benzene (PhINTs)_n, 2-iodoxybenzoic acid (IBX), and iodonium ylides (PhI=CX₂), is hampered by their unfavorable physical properties. Iodosylbenzene is widely used as a common oxygen transfer agent in synthetic and biomimetic studies. Likewise (tosylimino)iodobenzene has found broad synthetic application as a useful nitrene precursor, and iodonium ylides, such as PhI=C(CO₂CH₃)₂, are used as an efficient carbene precursors. Structural studies of these compounds reveal extensive networks of I···O or I···N intermolecular secondary bonds resulting in highly aggregated polymeric structures [7,8]. These derivatives of polyvalent iodine are thus insoluble in all nonreactive media and can only be used under heterogeneous conditions, which can be undesirable for many synthetic applications and mechanistic studies.

In this review, we describe our work on the design and development of new classes of soluble, stable, and highly reactive hypervalent iodine reagents. This goal has been achieved by the introduction of structural modifications that redirect I···X (X=O or N) secondary bonding from intermolecular to intramolecular modes. In particular, we have demonstrated that the introduction of a coordinating substituent in the *ortho*-position of the phenyliodine(III) moiety leads to a significant improvement of solubility and reactivity of a hypervalent iodine reagent. Based on this approach, we have developed a series of new hypervalent iodine reagents, which can be used as selective oxidants, nitrene or carbene precursors, reagents for “atom transfer”, and organocatalysts.

2. Soluble iodosylarenes and iodylarenes: reagents for oxygenations

Iodosylbenzene, (PhIO)_n, has been used as an oxygen transfer agent in numerous synthetic and biomimetic studies [9]. In particular, iodosylbenzene is an efficient source of oxygen atoms for the oxidations catalyzed by cytochrome P-450 and by discrete transition metal complexes [10]. Despite its usefulness as an oxidant, practical applications of iodosylbenzene are restrained by its low solubility in nonreactive media, as well as low thermal stability and explosive properties upon moderate heating [9]. While iodosylbenzene (and other two-coordinate iodine(III) species) are sometimes drawn as having I=X double bonds, the bonds actually have a high degree of polarity, as represented by resonance structure **B**, Fig. 1. The low solubility of iodosylbenzene is thus explained by a zigzag polymeric, asymmetrically bridged structure, in which monomeric dipole units of PhIO are linked by intermolecular I···O secondary bonds of mostly electrostatic nature [7,10]. These secondary bonds may also be thought of as heavier inorganic versions of hydrogen bonds [11]. In particular, the powder diffraction EXAFS analysis of iodosylbenzene revealed the T-shaped geometry around

iodine centers with the primary I–O single bond of 2.04 Å, the secondary, intermolecular, I···O bond of 2.377(12) Å, and an I–O–I angle of 114° (structure **1**, Fig. 1) [7]. The zigzag asymmetrically bridged structure of (PhIO)_n has been confirmed by single crystal X-ray diffraction studies of the oligomeric iodosylsulfate (PhIO)₃·SO₃ (structure **2**, Fig. 1) [12].

In the late 1990s, one of us (JDP) suggested that disruption of intermolecular electrostatic forces in polymeric (PhIO)_n could be achieved by placing strong internal dipoles (e.g., the sulfonyl group) into *ortho* position of the PhIO moiety for introducing intramolecular I···O secondary bonds to replace intermolecular I···O secondary bonds [13–15]. Based on this idea, a new class of soluble, nonpolymeric iodosylarenes and iodylarenes has been engineered.

The *ortho*-substituted iodosylarene **5** bearing *tert*-butylsulfonyl group was prepared as outlined in Scheme 1. Oxidation of aryl iodide **3** with peracetic acid led to the (diacetoxyiodo)arene **4**, which was further converted to iodosylarene **5** in excellent yield [16].

Iodosylarene **5** has high solubility in organic solvents (up to 0.08 M in chloroform) and can be analyzed by NMR spectroscopy in solution [13]. Single crystal X-ray analysis of compound **5** showed a pseudocyclic structure with an intramolecular distance of 2.707(5) Å between one of the sulfone oxygen atoms and the hypervalent iodine center (Fig. 2) [14]. The I–O bond length in the iodosyl group of **5** is 1.848(6) Å and the intramolecular O–I–O bond angle is 167.3(2)°. The iodine centers in **5** have a pseudo square-planar geometry by the presence of intermolecular I···O secondary bond (2.665(6) Å) to a neighboring iodosyl oxygen atom [14]. This structure also revealed hydrogen bonding to chloroform within the crystal.

Because of the excellent solubility in common organic solvents, iodosylarene **5** has powerful oxidizing properties. In particular, it reacts readily with tertiary phosphines and organic sulfides with the formation of the respective phosphine oxides and sulfoxides in high yield [13]. Two dozen papers from other groups have appeared where iodosylarene **5** has been successfully used as an oxygenating reagent under homogeneous conditions (sometimes at very low temperatures) for the generation and detection of new metal-oxo species for mechanistic and catalytic studies [17–40]. In particular, questions continue to be asked about the true nature of high valent metal intermediates generated by iodosylbenzene that effect hydrocarbon oxidations. As an example of the utility of soluble **5**, Collman and coworkers studied the rates of olefin epoxidation catalyzed by a manganese porphyrin complex (Scheme 2, upper pathway, Ar=C₆F₅) [22]. Studies of this cytochrome P450 model showed the reaction to be first order in the catalyst and zero order in **5**, and suggested that an intermediate complex between the Mn complex and **5** could be involved in the reaction. More recent studies by Lei and coworkers examined reactions of related manganese porphyrins (Scheme 2, lower pathway, Ar=2,6-Cl₂C₆H₃ (TDCPP), Ph (TPP), or substituted-Ph) with **5** by UV–vis spectroscopy [34]. In the presence of tri-*tert*-butylphenol as reductant, a [Mn(porph)=O] intermediate was observed. In the presence of *cis*-stilbene a mixture of [MnCl(porph)=O] and [MnCl(porph)·**5**] was produced. In the absence of substrate, [MnCl(TDCPP)·**5**] was rapidly formed which then produced [MnCl(porph)=O]. Furthermore, the adducts [Mn(TPP)·**5**]⁺ and [MnCl(TDCPP)·**5**]⁺ were also detectable by electrospray ionization mass spectrometry (ESI-MS).

Solutions of iodosylarene **5** in dichloromethane slowly disproportionate to give a colorless precipitate of the iodylbenzene **6** (Scheme 3) [14]. The X-ray structural study of crystalline **6**·CH₂Cl₂ demonstrated the presence of numerous intermolecular as well as intramolecular I···O secondary bonds in the solid-state structure [14]. Each iodine atom of **6** uses both intramolecular (2.693(3) Å) and intermolecular (2.777(3) Å and 2.566(2) Å) I···O bonds to adopt a pseudo octahedral geometry and a chain-like structure

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