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Viktor V. Zhdankin

Department of Chemistry and Biochemistry
University of Minnesota Duluth, Minnesota, USA

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Contents

Preface

Iodine is the heaviest non-radioactive element in the Periodic Table that is classified as a nonmetal and it is the largest, the least electronegative and the most polarizable of the halogens. It formally belongs to the main group p-block elements; however, the bonding description, structural features and reactivity of iodine compounds differ from the light main-group elements. The electronic structure of polyvalent iodine is best explained by the hypervalent model of bonding and, therefore, in modern literature organic compounds of trivalent and pentavalent iodine are commonly named as hypervalent iodine compounds. The reactivity pattern of hypervalent iodine in many aspects is similar that of transition metals – the reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination and ligand coupling, which are typical of transition metal chemistry.

Since the beginning of the twenty-first century, the organic chemistry of hypervalent iodine compounds has experienced an unprecedented, explosive development. Hypervalent iodine reagents are now commonly used in organic synthesis as efficient multipurpose reagents whose chemical properties are similar to derivatives of mercury, thallium, lead, osmium, chromium and other metals, but without the toxicity and environmental problems of these heavy metal congeners. One of the most impressive recent achievements in the field of iodine chemistry has been the discovery of hypervalent iodine catalysis.

This book is the first comprehensive monograph covering all main aspects of the chemistry of organic and inorganic polyvalent iodine compounds, including applications in chemical research, medicine and industry. The introductory chapter (Chapter 1) provides a historical background and describes the general classification of iodine compounds, nomenclature, hypervalent bonding, general structural features and general principles of reactivity of polyvalent iodine compounds. Chapter 2 gives a detailed description of the preparative methods and structural features of all known classes of organic and inorganic derivatives of polyvalent iodine. Chapter 3, the central chapter of the book, deals with the applications of hypervalent iodine reagents in organic synthesis. Chapter 4 describes the most recent achievements in hypervalent iodine catalysis. Chapter 5 deals with recyclable polymer-supported and nonpolymeric hypervalent iodine reagents. Chapter 6 covers the "green" reactions of hypervalent iodine reagents, including solvent-free reactions, reactions in water and reactions in ionic liquids. The final chapter (Chapter 7) provides an overview of important practical applications of polyvalent iodine compounds in medicine and in industry.

This book is aimed at all chemists interested in iodine compounds, including academic and industrial researchers in inorganic, organic, physical, medicinal and biological chemistry. It will be particularly useful to synthetic organic and inorganic chemists, including graduate and advanced undergraduate students. The book also covers the green chemistry aspects of hypervalent iodine chemistry, including the use of water as solvent, reactions under solvent-free conditions, recyclable reagents and solvents and catalytic reactions, which makes it especially useful for industrial chemists. The last chapter provides a detailed summary of practical applications of polyvalent iodine compounds, including various industrial applications, biological activity and applications of iodonium salts in PET (positron emission tomography) diagnostics; this chapter should be especially useful for medical and pharmaceutical researchers. Overall, the book is aimed at a broad, multidisciplinary readership and specialists working in different areas of chemistry, pharmaceutical and medical sciences and industry.

1

Introduction and General Overview of Polyvalent Iodine Compounds

1.1 Introduction

Iodine is a very special element. It is the heaviest non-radioactive element in the Periodic Table classified as a non-metal and it is the largest, the least electronegative and the most polarizable of the halogens. It formally belongs to the main group, p-block elements; however, because of the large atom size, the bonding description in iodine compounds differs from the light main group elements. In particular, the interatomic π-bonding, typical of the compounds of light p-block elements with double and triple bonds, is not observed in the compounds of polyvalent iodine. Instead, a different type of bonding occurs due to the overlap of the 5p orbital on the iodine atom with the appropriate orbitals on the two ligands (L) forming a linear L–I–L bond. Such a three-center-four-electron (3c-4e) bond is commonly referred to as a "hypervalent bond" [1]. The hypervalent bond is highly polarized and is longer and weaker than a regular covalent bond and the presence of hypervalent bonding leads to special structural features and reactivity pattern characteristic of polyvalent iodine compounds. In current literature, synthetically useful derivatives of polyvalent iodine are commonly named as hypervalent iodine reagents. The reactivity pattern of hypervalent iodine in many aspects is similar to the reactivity of transition metals and the reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination and ligand coupling, which are typical of transition metal chemistry.

Iodine was first isolated from the ash of seaweed by the industrial chemist B. Courtois in 1811 and was named by J. L. Gay Lussac in 1813 [2, 3]. Its name derives from the Greek word ιώδες (iodes) for violet, reflecting the characteristic lustrous, deep purple color of resublimed crystalline iodine. Various inorganic derivatives of polyvalent iodine in oxidation states of +3, +5 and +7 were prepared as early as the beginning of the nineteenth century. For example, iodine trichloride was first discovered by Gay Lussac as the result of treating warm iodine or iodine monochloride with an excess of chlorine [4]. In the same paper [4], the preparation of potassium iodate by the action of iodine on hot potash lye was described. The inorganic chemistry of polyvalent iodine has been summarized in numerous well-known texts [3, 5–8]. A detailed review on the history of iodine and all aspects of its chemistry and applications commemorating two centuries of iodine research was published in 2011 by Kuepper and coauthors [9].

Most of the world's production of iodine comes from the saltpeter deposits in Chile and natural brines in Japan. In Chile, calcium iodate is found in caliche deposits extracted from open pit mines in the Atacama Desert. Applying an alkaline solution to the caliche yields sodium iodate and iodine is obtained from the sodium iodate by reduction with sulfur dioxide. In Japan, iodine is a by-product of the production of natural gas, which is extracted from brine deposits a mile or two below ground. Iodine is recovered from the brines by one of the following two methods. In the blowout process elemental iodine is liberated as a result of the reaction of chlorine with sodium iodide in the brines. Elemental iodine is blown out of the brine with air and then purified in subsequent reaction steps. The second method, ion exchange, involves recovery of dissolved iodine from oxidized brines using anion-exchange resins packed in columns. In 2010, Chile produced 18 000 metric tons of iodine, compared to Japan's output of 9800 metric tons. Chile has reserves of 9 million metric tons, some 60% of the world's total reserves of iodine [10].

Iodine plays an important role in many biological organisms and is an essential trace element for humans. In the human body, iodine is mainly present in the thyroid gland in the form of thyroxine, a metabolism-regulating hormone. In natural organic compounds, iodine occurs exclusively in the monovalent state. The first polyvalent organic iodine compound, (dichloroiodo)benzene, was prepared by the German chemist C. Willgerodt in 1886 [11]. This was rapidly followed by the preparation of many others, including (diacetoxyiodo)benzene [12] and iodosylbenzene [13] in 1892, 2-iodoxybenzoic acid (IBX) in 1893 [14] and the first examples of diaryliodonium salts reported by C. Hartmann and V. Meyer in 1894 [15]. In 1914 Willgerodt published a comprehensive book describing nearly 500 polyvalent organoiodine compounds known at that time [16].

Research activity in the area of polyvalent organoiodine compounds during the period between 1914 and 1970s was relatively low and represented mainly by valuable contributions from the laboratories of I. Masson, R. B. Sandin, F. M. Beringer, K. H. Pausacker, A. N. Nesmeyanov and O. Neilands. Only three significant reviews were published during this period, most notably the reviews by Sandin [17] and Banks [18] published in *Chemical Reviews* in 1943 and 1966, respectively and a comprehensive tabulation of the physical properties of polyvalent iodine compounds published in 1956 by Beringer [19].

Since the early 1980s interest in polyvalent organoiodine compounds has experienced a renaissance. This resurgence of interest in multivalent organic iodine has been caused by the discovery of several new classes of polyvalent organoiodine compounds and, most notably, by the development of useful synthetic applications of some of these compounds, which are now regarded as valuable organic reagents known under the general name of hypervalent iodine reagents. The foundation of modern hypervalent iodine chemistry was laid in the 1980s by the groundbreaking works of G. F. Koser, J. C. Martin, R. M. Moriarty, P. J. Stang, A. Varvoglis and N. S. Zefirov.

Important contributions to the development of hypervalent iodine chemistry in the 1990s were made by the research groups of A. Varvoglis, N. S. Zefirov, L. M. Yagupolskii, A. R. Katritzky, R. A. Moss, J. C. Martin, D. H. R. Barton, R. M. Moriarty, G. F. Koser, P. J. Stang, H.-J. Frohn, T. Umemoto, M. Yokoyama, Y. Kita, M. Ochiai, T. Okuyama, T. Kitamura, H. Togo, E. Dominguez, I. Tellitu, J. D. Protasiewicz, A. Kirschning, K. S. Feldman, T. Wirth, S. Quideau, S. Hara, N. Yoneda, L. Skulski, S. Spyroudis, V. V. Grushin, V. W. Pike, D. A. Widdowson and others. During the 1980s–1990s, hypervalent iodine research was summarized in several reviews and books. Most notable were the two books published in 1992 and 1997 by A. Varvoglis: the comprehensive monograph *The Organic Chemistry of Polycoordinated Iodine* [20] and a book on the application of hypervalent iodine compounds in organic synthesis [21]. Several general reviews [22–28], numerous book chapters [29–34] and specialized reviews on phenyliodine(III) carboxylates [35, 36], [hydroxy(tosyloxy)iodo]benzene [37], the chemistry of iodonium salts [38], electrophilic perfluoroalkylations [39], application of hypervalent iodine in the carbohydrate chemistry [40], hypervalent iodine oxidations [41–43], fluorinations using hypervalent iodine fluorides [44], hypervalent iodine compounds as free radical precursors [45], synthesis of heterocyclic compounds using organohypervalent iodine reagents [46] and the chemistry of benziodoxoles [47] were also published during 1980s and 1990s.

Since the beginning of the twenty-first century, the chemistry of organohypervalent iodine compounds has experienced explosive development. This surge in interest in iodine compounds is mainly due to the very useful oxidizing properties of hypervalent iodine reagents, combined with their benign environmental character and commercial availability. Iodine(III) and iodine(V) derivatives are now routinely used in organic synthesis as reagents for various selective oxidative transformations of complex organic molecules. Numerous reviews and book chapters summarizing various aspects of hypervalent iodine chemistry have been published since 2000 [48–122]. A book edited by T. Wirth on the application of hypervalent iodine in organic synthesis was published in 2003 [123]. Starting in 2001, the International Conference on Hypervalent Iodine Chemistry has regularly been convened in Europe, the Society of Iodine Science (SIS) holds annual meetings in Japan and the American Chemical Society presents the National Award for Creative Research and Applications of Iodine Chemistry sponsored by SQM S.A. biennially in odd-numbered years. The most impressive modern achievements in the field of organoiodine chemistry include the development of numerous new hypervalent iodine reagents and the discovery of catalytic applications of organoiodine compounds. The discovery of similarities between transition metal chemistry and hypervalent iodine chemistry and, in particular, the development of highly efficient and enantioselective catalytic systems based on the iodine redox chemistry have added a new dimension to the field of hypervalent iodine chemistry and initiated a major increase in research activity, which is expected to continue in the future.

1.2   Classification and Nomenclature of Polyvalent Iodine Compounds

Iodine can form chemical compounds in oxidation states of $+3$, $+5$ and $+7$. The six most common structural types of polyvalent iodine species are represented by structures **1**–**7** (Figure 1.1). Species **2**–**7** can be generally classified using the Martin–Arduengo *N-X-L* designation for hypervalent molecules [124, 125], where *N* is the number of valence electrons formally assignable to the valence shell of the central atom, *X*, either as unshared pairs of electrons or as pairs of electrons in the sigma bonds joining a number, *L*, of ligands to the atom *X*. Structure **1,** the iodonium ion, formally does not belong to hypervalent species since it has only eight valence electrons on the iodine atom; however, in the modern literature iodonium salts are commonly treated as ten-electron hypervalent compounds by taking into account the closely associated anionic part of the molecule. The first three species, structures **1**–**3,** are conventionally considered as derivatives of trivalent iodine, while **4** and **5** represent the most typical structural types of pentavalent iodine. Structural types **6** and **7** are typical of heptavalent iodine; only inorganic compounds of iodine(VII), such as iodine(VII) fluoride (IF_7), iodine(VII) oxyfluorides and the derivatives of periodic acid (HIO_4) are known.

In the older literature, derivatives of iodine(III) were known under the general name of iodinanes, while compounds of pentavalent iodine were called periodinanes. According to the 1983 IUPAC recommendations "Treatment of variable valence in organic nomenclature (lambda convention)" [126], these old names were replaced by λ^3-iodanes for iodine(III) and λ^5-iodanes for iodine(V) compounds. In the lambda nomenclature,

10-I-3	*12-I-4*	*10-I-4*	*12-I-5*	*14-I-6*	*14-I-7*
1	**2**	**3**	**4**	**5**	**6**	**7**
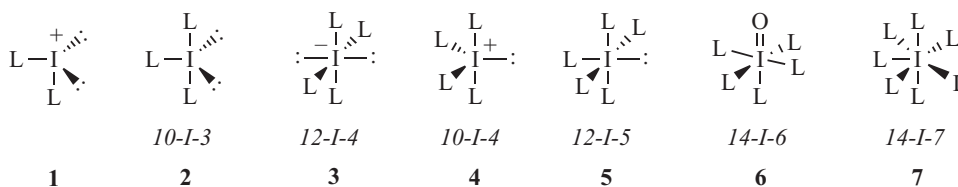
Figure 1.1   *Typical structural types of polyvalent iodine compounds.*

the symbol λ^n is used to indicate any heteroatom in nonstandard valence states (n) in a formally neutral compound; for iodine the standard valence state is 1. The names λ^3-iodanes and λ^5-iodanes have found broad application in modern literature to indicate the general type of hypervalent iodine compounds and to specify the number of primary bonds at the iodine atom. The λ^3-iodane designation is particularly useful for naming iodonium salts, for example, Ph_2ICl, because it better reflects the actual structure of these compounds with a tricoordinated iodine atom [127].

Notably, however, the lambda nomenclature is not used for naming common hypervalent iodine reagents such as $PhICl_2$, $PhI(OAc)_2$, $ArIO$, $ArIO_2$ and others. According to the 1979 IUPAC rules [128], "compounds containing the group $–I(OH)_2$ or derivatives of this group are named by adding the prefixes "dihydroxyiodo-", "dichloroiodo-", "diacetoxyiodo-", etc. to the name of the parent compound" (IUPAC Rule C-106.3). Likewise, "compounds containing the group $–IO$ or $–IO_2$, are named by adding the prefix "iodosyl-" or "iodyl-" (IUPAC Rule C–106.1) [128], which replaces prefixes "iodoso-" and "iodoxy-" used in the older literature. According to IUPAC Rule C-107.1 "cations of the type $R^1R^2I^+$ are given names derived from the iodonium ion H_2I^+ by substitution" [128]. In addition to the IUPAC recommended names, numerous common names and abbreviations are used for polyvalent iodine compounds; for example, about 15 different names have been used in the literature for $PhI(OAc)_2$ [20]. Table 1.1 summarizes commonly used names and abbreviations for several important organic and inorganic polyvalent iodine compounds.
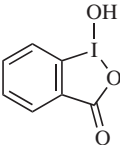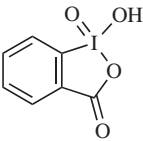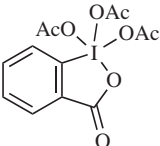
Organoiodine(III) compounds are commonly classified by the type of ligands attached to the iodine atom. The following general classes of iodine(III) compounds have found broad application as reagents in organic synthesis: (difluoroiodo)arenes **8**, (dichloroiodo)arenes **9**, iodosylarenes **10**, [bis(acyloxy)iodo]arenes **11**, aryliodine(III) organosulfonates **12**, five-membered iodine heterocycles (benziodoxoles **13** and benziodazoles **14**), iodonium salts **15**, iodonium ylides **16** and iodonium imides **17** (Figure 1.2). The most important and commercially available representatives of aryliodine(III) carboxylates are (diacetoxyiodo)benzene $PhI(OAc)_2$, which has several commonly used abbreviations, such as DIB, PID, PIDA (phenyliodine diacetate), IBD, or IBDA (iodosobenzene diacetate) and [bis(trifluoroacetoxy)iodo]benzene $PhI(OCOCF_3)_2$, which is abbreviated as BTI or PIFA [(phenyliodine bis(trifluoroacetate)] (Table 1.1). The most important representative of aryliodine(III) organosulfonates, the commercially available [hydroxy(tosyloxy)iodo]benzene $PhI(OH)OTs$, is abbreviated as HTIB and is also known as Koser's reagent.

Organoiodine(V) compounds are represented by several common classes shown in Figure 1.3; all these compounds have found application as efficient oxidizing reagents. Particularly important in organic synthesis are noncyclic iodylarenes **18**, numerous five-membered heterocyclic benziodoxole derivatives **19** and **20**, including IBX and DMP (Table 1.1), pseudocyclic iodylarenes **21–23** and cyclic or pseudocyclic derivatives of 2-iodylbenzenesulfonic acid, **24–26**.

1.3 Hypervalent Bonding

The definition of "hypervalent" species as ions or molecules of the elements of Groups 15–18 bearing more than eight electrons within a valence shell was established by J. I. Musher in 1969 [129]. General aspects of bonding in hypervalent organic compounds were summarized by K.-y. Akiba in the book *Chemistry of Hypervalent Compounds* [1]. In principle, there are two possible explanations for the ability of main-group elements to hold more than the octet of electrons within a valence shell: (i) by the involvement of the higher-lying d orbitals resulting in dsp^3 or d^2sp^3 hybridization or (ii) by the formation of a new type of highly ionic orbital without involvement of d orbitals. In modern literature, it is generally agreed that the contribution of d orbitals is not essential to form hypervalent compounds and that hypervalent bonding is best explained by a molecular orbital description involving a three-center-four-electron bond.

Table 1.1 *Names and abbreviations of important derivatives of polyvalent iodine.*

Compound	IUPAC names [126, 128]	Common names	Common abbreviations
ICl_3	Iodine trichloride or trichloro-λ^3-iodane	Iodine(III) chloride	None
$PhICl_2$	(Dichloroiodo)benzene	Iodobenzene dichloride Iodosobenzene dichloride Phenyliodo dichloride Phenyliodine(III) dichloride	IBD
$PhI(OAc)_2$	(Diacetoxyiodo)benzene	Iodobenzene diacetate Phenyliodo diacetate Iodosobenzene diacetate Phenyliodine(III) diacetate	DIB, IBD PIDA IBDA
$PhI(OCOCF_3)_2$	[Bis(trifluoroacetoxy) iodo]benzene	Iodobenzene bis(trifluoroacetate) Phenyliodo bis(trifluoroacetate) Phenyliodine(III) bis(trifluoroacetate)	BTI PIFA
PhI(OH)OTs	[Hydroxy(4-methylphenyl sulfonyloxy)iodo]benzene	[Hydroxy(tolsyloxy)iodo] benzene Koser's reagent	HTIB, HTI
PhIO	Iodosylbenzene	Iodosobenzene	IDB
	1-Hydroxy-1H-1λ^3-benzo[d][1,2]iodoxol-3-one	2-Iodosobenzoic acid 2-Iodosylbenzoic acid o-Iodosobenzoic acid 1-Hydroxy-1,2-benziodoxol-3-(1H)-one	IBA
Ph_2ICl	Diphenyliodonium chloride or chloro(diphenyl)-λ^3-iodane	Chlorodiphenyliodonium	DPI
PhINTs	[N-(4-Methylphenylsulfonyl) imino]phenyl-λ^3-iodane	(N-Tosylimino)phenyliodinane	None
IF_5	Iodine pentafluoride or pentafluoro-λ^5-iodane	Iodine(V) fluoride Iodic fluoride	None
HIO_3	Iodic acid	Iodic(V) acid	None
$PhIO_2$	Iodylbenzene	Iodoxybenzene	None
	1-Hydroxy-1-oxo-1H-1λ^5-benzo[d][1,2]iodoxol-3-one	2-Iodoxybenzoic acid 2-Iodylbenzoic acid o-Iodoxybenzoic acid	IBX
	1,1,1-Triacetoxy-1H-1λ^5-benzo[d][1,2]iodoxol-3-one	Dess–Martin periodinane	DMP
IF_7	Iodine heptafluoride or heptafluoro-λ^7-iodane	Iodine(VII) fluoride Heptafluoroiodine	None
HIO_4	Periodic acid	Iodic(VII) acid	None

$$\text{Ar—I} \begin{matrix} \text{F} \\ | \\ \text{F} \end{matrix} \qquad \text{Ar—I} \begin{matrix} \text{Cl} \\ | \\ \text{Cl} \end{matrix} \qquad (\text{ArIO})_n$$

8   9   10   11   12
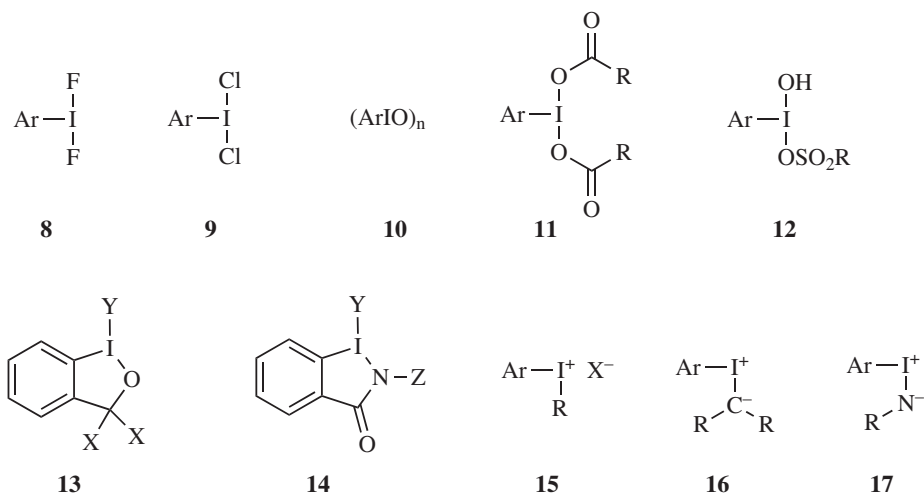
X = Me, CF$_3$ or 2X = O;
Y = OH, OAc, N$_3$, CN, etc.; Z = H, Ac, etc.

Figure 1.2   *Common classes of organoiodine(III) compounds.*

$$\text{ArIO}_2$$

18

13   14   15   16   17

19   20

21   22   23

24   25   26
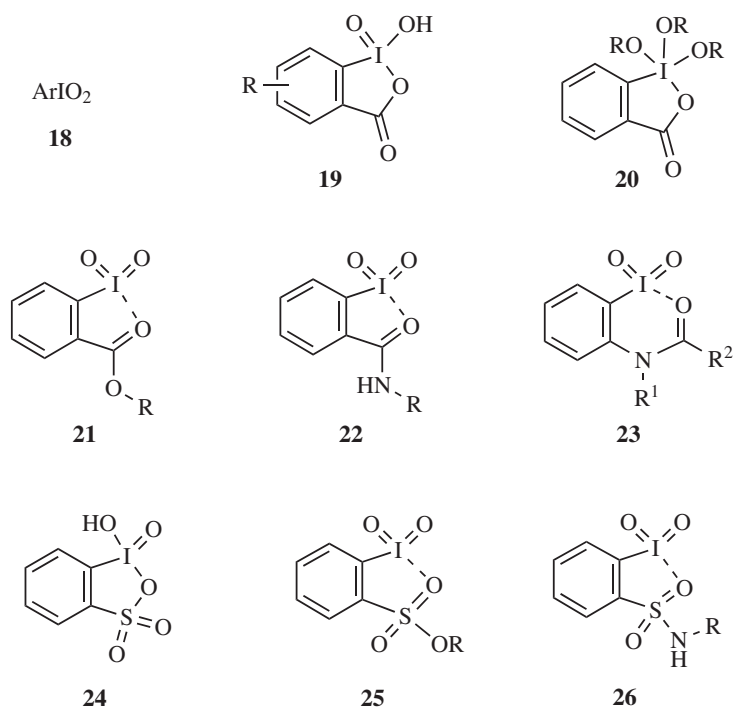
Figure 1.3   *Common classes of organoiodine(V) compounds.*
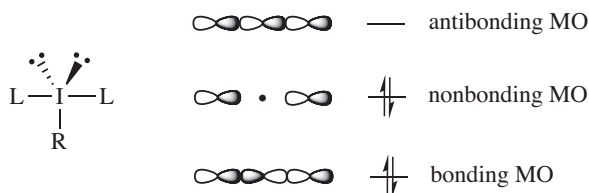
Figure 1.4 *Molecular orbital description of the three-center-four-electron bond in hypervalent iodine(III) molecules RIL$_2$.*

The idea of a three-center-four-electron (3c-4e) bond was independently proposed by G. C. Pimentel [130] and R. E. Rundle [131] in 1951 on the basis of molecular orbital theory. According to the fundamental description of the 3c-4e bond for L–X–L, one pair of bonding electrons is delocalized to the two ligands L, resulting in the charge distribution of almost –0.5 on each ligand and +1.0 on the central atom X. In iodine(III) molecules RIL$_2$, the interaction of the filled 5p orbital of the central iodine atom and the half-filled orbitals of the two ligands L *trans* to each other leads to formation of three molecular orbitals: bonding, nonbonding and antibonding (Figure 1.4). Because the highest occupied molecular orbital (HOMO) contains a node at the central iodine, the hypervalent bonds show a highly polarized nature; hence, more electronegative atoms tend to occupy the axial positions formed by the interaction of the orbitals of three collinear atoms. The carbon substituent R is bound by a normal covalent bond and the overall geometry of molecule RIL$_2$ is a distorted trigonal bipyramid with two heteroatom ligands L occupying the apical positions and the least electronegative carbon ligand R and both electron pairs reside in equatorial positions.

The bonding in iodine(V) compounds, RIL$_4$, with a square bipyramidal structure may be described in terms of a normal covalent bond between iodine and the organic group R in an apical position and two orthogonal, hypervalent 3c-4e bonds, accommodating four ligands L. The carbon substituent R and unshared electron pair in this case should occupy the apical positions with the electronegative ligands L residing at equatorial positions (Figure 1.5).

Several theoretical computational studies concerning bonding, structure and reactivity of hypervalent iodine compounds were published in the 1990s and 2000s [132–137]. In particular, Reed and Schleyer provided a general theoretical description of chemical bonding in hypervalent molecules in terms of the dominance of ionic bonding and negative hyperconjugation over d-orbital participation [132]. The simple, qualitative bonding concepts for hypervalent molecules developed in this work supersede the inaccurate and misleading dsp^3 and d^{2}sp^3 models. It has been recognized that there are fundamental similarities in bonding, structure and reactivity of hypervalent λ^3- and λ^5-iodanes with organometallic compounds. In fact, it has been stated in some theoretical studies that, similar to the heavy main group elements, hypervalent bonding commonly occurs in transition metal complexes and the 3c-4e bond is particularly important in the structure of transition metal hydrides [138–142]. The important and well known in transition metal complexes, effect of *trans*
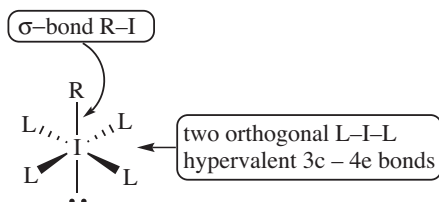
Figure 1.5 *Bonding in hypervalent iodine(V) molecules.*

influence [136] is also typical of hypervalent iodine(III) compounds (Section 1.4.2) [135, 136, 143]. The reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, reductive elimination, ligand exchange and ligand coupling, which are typical of transition metal chemistry (Section 1.5).

Typical structures of iodine(VII) involve a distorted octahedral configuration **6** about iodine in most periodates [144] and the oxyfluoride, IOF_5 [145] and the heptacoordinated, pentagonal bipyramidal species **7** for IF_7 and the IOF_6^- anion (Figure 1.1) [146, 147]. The pentagonal bipyramidal structure **7** has been described as two covalent, collinear, axial bonds between iodine and the ligands in the apical positions and a coplanar, hypervalent 6c-10e bond system for the five equatorial bonds [146].

1.4 General Structural Features

The structural aspects of polyvalent iodine compounds were previously summarized in several books and reviews [20, 30, 32, 127]. In general, the molecular structure of λ^3- and λ^5-iodanes is predetermined by the nature of hypervalent bonding discussed in Section 1.3. The key structural features of the hypervalent organoiodine compounds available from numerous X-ray data may be summarized as follows:

1. λ^3-Iodanes RIX_2 (R = C-ligand, X = heteroatom ligands) have an approximately T-shaped structure with a collinear arrangement of the most electronegative ligands X. Including the nonbonding electron pairs, the geometry about iodine is a distorted trigonal bipyramid with the most electronegative groups occupying the apical positions, while the least electronegative C-ligand R and both electron pairs reside in an equatorial position.
2. The I–C bond lengths in iodonium salts $R_2I^+ X^-$ and λ^3-iodanes RIX_2 are approximately equal to the sum of the covalent radii of iodine and carbon, ranging generally from 2.00 to 2.10 Å.
3. Iodonium salts $R_2I^+ X^-$ generally have a typical distance between iodine and the nearest anion X^- of 2.6–2.8 Å and in principle can be considered as ionic compounds with pseudo-tetrahedral geometry about the central iodine atom. However, with consideration of the anionic part of the molecule, the overall experimentally determined geometry is distorted T-shaped structure similar to the λ^3-iodanes RIX_2.
4. For λ^3-iodanes $RI(X)Y$ with two heteroatom ligands X and Y of the same electronegativity, both I–X and I–Y bonds are longer than the sum of the appropriate covalent radii, but shorter than purely ionic bonds. For example, the I–Cl bond lengths in $PhICl_2$ are 2.45 Å [148] and the I–O bond lengths in $PhI(OAc)_2$ are 2.15–2.16 Å [149], while the sum of the covalent radii of I and O is 1.99 Å. When heteroatom ligands X and Y have different electronegativities, the *trans* influence of ligands has a strong effect on the structure, stability and reactivity of λ^3-iodanes $RI(X)Y$ (Section 1.4.2) [135].
5. Various coordination types have been reported for the organoiodine(V) compounds. Depending on the ligands and taking into account secondary bonding, the overall observed geometry for the structural types **4** and **5** (Figure 1.1) can be pseudo-trigonal–bipyramidal, square bipyramidal and pseudooctahedral.
6. Intramolecular positional isomerization (Berry pseudorotation) resulting in an exchange between the apical and the equatorial ligands occurs rapidly in both λ^3- and λ^5-iodanes. This process is important in explaining the mechanisms of hypervalent iodine reactions (Section 1.5).
7. Only inorganic compounds with O- or F-ligands are known for iodine(VII) structural types **6** and **7** (Figure 1.1). Typical iodine(VII) coordination types involve a distorted octahedral configuration and pentagonal bipyramidal species.

Owing to a highly polarized character of hypervalent bond, noncovalent attractive interactions of a predominantly electrostatic nature are extremely important in the structural chemistry of hypervalent iodine

compounds. Such attractive interactions are commonly called secondary bonds. Similarly to hydrogen bonds, secondary bonds involving heavier atoms have strong electrostatic components and show directional preferences [150, 151]. Intermolecular secondary bonding in hypervalent iodine compounds is responsible for crystal packing in the solid state and for the self-assembly of individual molecules into complex supramolecular structures in the solid state and in solution [152, 153]. Intramolecular secondary bonding is commonly observed in the λ^3- and λ^5-aryliodanes, which have a sulfonyl or a carbonyl structural fragment in the *ortho*-position of the phenyl ring [154–159]. The redirection of secondary bonding from intermolecular to intramolecular mode due to the presence of an appropriate *ortho*-substituent leads to a partial disruption of the polymeric network and enhances solubility of a hypervalent iodine compound [154, 155].

1.4.1   Experimental Structural Studies

Numerous X-ray crystal structures have been reported for all main classes of organic polyvalent iodine compounds and the results of these studies are overviewed in the appropriate sections of Chapter 2. Typical coordination patterns in various organic derivatives of iodine(III) in the solid state with consideration of primary and secondary bonding were summarized in 1986 by Sawyer and coworkers [160] and have been updated in several more recent publications [153, 161–165]. Structural features of organic iodine(V) compounds have been discussed in the older papers of Martin and coauthors [166, 167] and in numerous recent publications on IBX and related λ^5-iodanes [155–159, 168–174]. Several general areas of structural research on hypervalent organoiodine compounds have attracted especially active interest. These areas, in particular, include the preparation and structural study of complexes of hypervalent iodine compounds with crown ethers [175–179] or nitrogen ligands [180–182], self-assembly of hypervalent iodine compounds into various supramolecular structures [152, 153, 164, 183, 184] and the intramolecular secondary bonding in *ortho*-substituted aryliodine(V) and aryliodine(III) derivatives [154–159, 168–171, 173, 174, 185–188].

Several important spectroscopic structural studies of polyvalent iodine compounds in solution have been published [108–112, 189]. Reich and Cooperman reported low-temperature NMR study of triaryl-λ^3-iodanes **27** (Scheme 1.1), which demonstrated that these compounds have a nonsymmetrical planar orientation of iodine–carbon bonds and that the barrier to unimolecular degenerate isomerization between **27** and **27′** is greater than 15 kcal mol^{-1}. The exact mechanism of this degenerate isomerization is unknown; both pseudorotation on iodine(III) and intermolecular ligand exchange may account for the isomerization of these compounds [189].
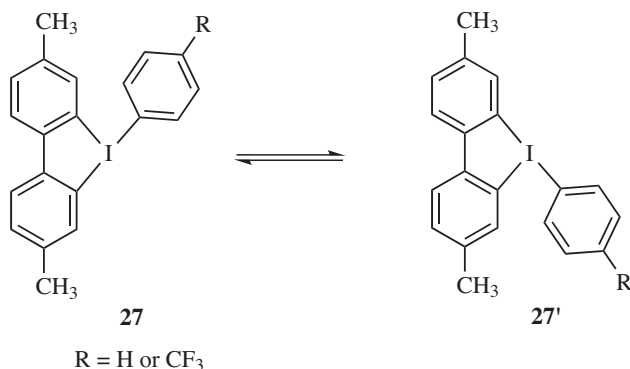
Scheme 1.1   *Degenerate isomerization of triaryl-λ^3-iodanes **27** in solution.*
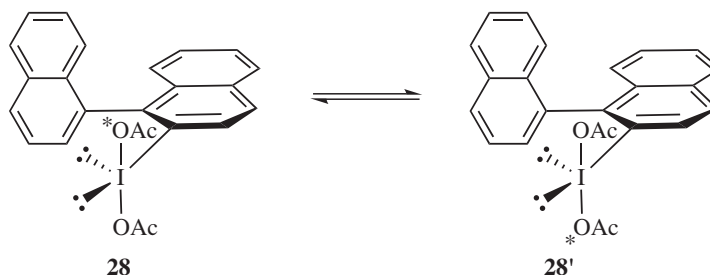
Scheme 1.2   *Degenerate isomerization of (diacetoxyiodo)binaphthyl **28** due to rapid pseudorotation on iodine.*

Ochiai and coworkers observed rapid pseudorotation on iodine(III) for chiral (diacetoxyiodo)binaphthyl **28** (Scheme 1.2) [190]. The two acetoxy groups of compound **28** are anisochronous in CDCl$_3$ at −10 °C and appear as two sharp singlets in ^{1}H NMR spectra. These two singlets coalesce at 34 °C to one singlet with a free activation energy of 15.1 kcal mol^{-1}. Similar temperature dependence was observed in the ^{13}C NMR spectrum. The authors attributed this degenerate isomerization to rapid pseudorotation on iodine [190].

Amey and Martin have found that cyclic dialkoxy-λ^3-iodanes undergo rapid degenerate ligand exchange on the NMR time scale occurring via an associative mechanism [191]. Cerioni, Mocci and coworkers investigated the structure of bis(acyloxyiodo)arenes and benziodoxolones in chloroform solution by ^{17}O NMR spectroscopy and also by DFT (density functional theory) calculations [192–194]. This investigation provided substantial evidence that the T-shaped structure of iodine(III) compounds observed in the solid state is also adopted in solution. Furthermore, the "free" carboxylic groups of bis(acyloxyiodo)arenes show a dynamic behavior, observable only in the ^{17}O NMR. This behavior is ascribed to a [1,3]-sigmatropic shift of the iodine atom between the two oxygen atoms of the carboxylic groups and the energy involved in this process varies significantly between bis(acyloxyiodo)arenes and benziodoxolones [193].

Hiller and coworkers reported an NMR and LC-MS study on the structure and stability of 1-iodosyl-4-methoxybenzene and 1-iodosyl-4-nitrobenzene in methanol solution [195]. Interestingly, LC-MS analyzes provided evidence that unlike the parent iodosylbenzene, which has a polymeric structure (Section 2.1.4), the 4-substituted iodosylarenes exist in the monomeric form. Both iodosylarenes are soluble in methanol and provide acceptable ^{1}H and ^{13}C NMR spectra; however, gradual oxidation of the solvent was observed after several hours. Unlike iodosylbenzene, the two compounds did not react with methanol to give the dimethoxy derivative ArI(OMe)$_2$ [195].

Silva and Lopes analyzed solutions of iodobenzene dicarboxylates in acetonitrile, acetic acid, aqueous methanol and anhydrous methanol by electrospray ionization mass spectrometry (ESI-MS) and tandem mass spectrometry (ESI-MS/MS) [196]. The major species found in the solutions of PhI(OAc)$_2$ in acetonitrile, acetic acid and aqueous methanol were [PhI(OAc)$_2$Na]$^+$, [PhI(OAc)$_2$K]$^+$, [PhI]$^+$, [PhIOAc]$^+$, [PhIOH]$^+$, [PhIO$_2$Ac]$^+$, [PhIO$_2$H]$^+$ and the dimer [Ph$_2$I$_2$O$_2$Ac]$^+$. On the other hand, the anhydrous methanol solutions showed [PhIOMe]$^+$ as the most abundant species. In contrast to the data obtained for PhI(OAc)$_2$, the ESI-MS spectral data of PhI(O$_2$CCF$_3$)$_2$ in acetonitrile suggests that the main species in solutions is iodosylbenzene [196]. A similar ESI-MS and ESI-MS/MS study of solutions of [hydroxy(tosyloxy)iodo]benzene has been performed under different conditions and, based on these data, mechanisms were proposed for the disproportionation of the iodine(III) compounds into iodine(V) and iodine(I) species [197].

Richter, Koser and coworkers investigated the nature of species present in aqueous solutions of phenyliodine(III) organosulfonates [198]. It was shown by spectroscopic measurements and potentiometric titrations that PhI(OH)OTs and PhI(OH)OMs upon dissolution in water undergo complete ionization to give the hydroxy(phenyl)iodonium ion (PhI$^+$OH in hydrated form) and the corresponding sulfonate ions. The

hydroxy(phenyl)iodonium ion can combine with [oxo(aquo)iodo]benzene $PhI^+(OH_2)O^-$, a hydrated form of iodosylbenzene that is also observed in the solution, to produce the dimeric μ-oxodiiodine cation $Ph(HO)I-O-I^+(OH_2)Ph$ and dication $Ph(H_2O)I^+-O-I^+(OH_2)Ph$ [198]. Likewise, an ESI-MS study of an aqueous solution of oligomeric iodosylbenzene sulfate, $(PhIO)_3SO_3$, indicated mainly the presence of hydroxy(phenyl)iodonium ion (PhI^+OH) along with dimeric and trimeric protonated iodosylbenzene units [101].

1.4.2   Computational Studies

Relatively few theoretical computational studies concerning the structure and reactivity of hypervalent iodine compounds have appeared. Hoffmann and coworkers analyzed the nature of hypervalent bonding in tri-halide anions X_3^- (X = F, Cl, Br, I) and related halogen species by applying ideas from qualitative MO theory to computational results from density-functional calculations [133]. This systematic, unified investigation showed that the bonding in all of these systems could be explained in terms of the Rundle–Pimentel scheme for electron-rich three-center bonding (Section 1.3). The same authors reported an analysis of intermolecular interaction between hypervalent molecules, including diaryliodonium halides Ar_2IX, using a combination of density-functional calculations and qualitative arguments [150]. Based on fragment molecular orbital interaction diagrams, the authors concluded that the secondary bonding in these species can be understood using the language of donor–acceptor interactions: mixing between occupied states on one fragment and unoccupied states on the other. There is also a strong electrostatic contribution to the secondary bonding. The calculated strengths of these halogen–halogen secondary interactions are all less than 10 kcal mol^{-1} [150].

The self-assembly of hypervalent iodine compounds to form macrocyclic trimers was studied using MO calculations. The principal driving force for the self-assembly of iodonium units is the formation of secondary bonding interactions between iodonium units as well as a rearrangement of primary and secondary bonding around iodine to place the least electronegative substituent in the equatorial position for every iodine in the trimer [199].

Kiprof has analyzed the iodine–oxygen bonds of hypervalent λ^3-iodanes with T-shaped geometry using the Cambridge Crystallographic Database and *ab initio* MO calculations. Statistical analysis of the I–O bond lengths in $PhI(OR)_2$ revealed an average of 2.14 Å and a strong correlation between the two bond lengths [143]. Further theoretical investigation of the mutual ligand interaction in the hypervalent L–I–L′ system has demonstrated that the ligands' *trans* influences play an important role in the stability of hypervalent molecules [135]. In particular, combinations of ligands with large and small *trans* influences, as in $PhI(OH)OTs$, or of two moderately *trans* influencing ligands, as in $PhI(OAc)_2$, are favored and lead to higher stability of the molecule. The *trans* influences also seem to explain why iodosylbenzene, $(PhIO)_n$, adopts an oxo-bridged zigzag polymer structure (Section 2.1.4) in contrast to $PhI(OH)_2$, which is monomeric [135].

A theoretical computational study on quantitative measurement of the *trans* influence in hypervalent iodine complexes has been published by Sajith and Suresh [136]. The *trans* influence of various X ligands in hypervalent iodine(III) complexes of the type $CF_3I(X)Cl$ has been quantified using the *trans* I−Cl bond length (d_X), the electron density $\rho(r)$ at the (3, −1) bond critical point of the *trans* I−Cl bond and topological features of the molecular electrostatic potential (MESP). The MESP minimum at the Cl lone pair region (V_{min}) has been found to be a sensitive measure of the *trans* influence. The *trans* influence of X ligands in hypervalent iodine(V) compounds is smaller than that in iodine(III) complexes, while the relative order of this influence is the same in both species. The quantified values of the *trans* influence parameters may find use in assessing the stability of hypervalent iodine compounds as well as in the design of new stable hypervalent complexes [136].

The structure and reactivity of several specific classes of hypervalent iodine compounds have been investigated theoretically. Varvoglis, Tsipis and coauthors have studied the geometry and electronic structure of some hypervalent iodine compounds PhIX$_2$ by means of extended Hückel and CNDO/2 quantum chemical approaches [200]. The bonding was analyzed in terms of both the model of delocalized MOs on the basis of interactions between fragment MOs derived from EHMO–SCCC calculations and that of localized MOs derived by the CNDO/2 method. The ability of these compounds to afford *cis*-addition products with alkenes via a synchronous molecular addition mechanism was found to be theoretically feasible [200].

Okuyama and Yamataka investigated the reactivity of vinyliodonium ions with nucleophiles by *ab initio* MO (MP2) calculations at the double-zeta (DZ) + d level [201]. It was proposed that interaction of methyl(vinyl)iodonium ion with chlorine anion leads to chloro-λ^3-iodane CH$_2$=CHI(Me)Cl. Transition states for the S_N2, ligand-coupling substitution and β-elimination were found for reactions at the vinyl group. The barrier to ligand-coupling substitution is usually the lowest in the gas phase, but relative barriers to S_N2 and to β-elimination change with the substituents. Effects of solvent on this reaction were evaluated by a dielectric continuum model and found to be large on S_N2 but small on ligand coupling [201].

Widdowson, Rzepa and coworkers reported *ab initio* and MNDO-d SCF-MO computational studies of the extrusion reactions of diaryliodonium fluorides [202–204]. The results of these studies, in particular, predicted that the intermediates and transition states in these reactions might involve dimeric, trimeric and tetrameric structures. The regioselectivity of nucleophilic substitution in these reactions was investigated theoretically and supported by some experimental observations.

Goddard and Su have investigated theoretically the mechanism of alcohol oxidation with 2-iodoxybenzoic acid (IBX) on the basis of density functional quantum mechanics calculations [134]. It has been found that the rearrangement of hypervalent bonds, so-called hypervalent twisting, is the rate-determining step in this reaction. Based on this mechanism, the authors explain why IBX oxidizes large alcohols faster than small ones and propose a modification to the reagent that is predicted to make it more active [134].

Bakalbassis, Spyroudis and Tsiotra reported a DFT study on the intramolecular thermal phenyl migration in iodonium ylides [205]. The results of this study support a single-step mechanism involving a five-membered ring transition state. The frontier-orbital-controlled migration also confirms the different thermal behavior experimentally observed for two different ylides [205].

Quideau and coworkers presented DFT calculations of spiroheterocyclic iodine(III) intermediates to validate their participation in the PhI(OAc)$_2$-mediated spiroketalization of phenolic alcohols [206]. Molecular orbital computational studies of (arylsulfonylimino)iodoarenes (ArINSO$_2$Ar′) [185], benziodazol-3-ones [207] and a series of *ortho*-substituted chiral organoiodine(III) compounds [208] have been reported in the literature. Results of these calculations were found to be in good agreement with X-ray structural data for these compounds.

1.5   General Principles of Reactivity

Hypervalent iodine reagents are used extensively in organic synthesis as efficient and environmentally benign oxidizing reagents whose chemical properties in many aspects are similar to the derivatives of heavy metals. The following general classes of iodine(III) compounds (Figure 1.2) have found broad application in organic synthesis: (difluoroiodo)arenes **8** and (dichloroiodo)arenes **9** are effective fluorinating and chlorinating reagents, respectively, iodosylarenes **10**, aryliodine(III) carboxylates **11** and organosulfonates **12** in general are strong oxidizing agents and have found widespread application as reagents for oxygenation and oxidative functionalization of organic substrates, benziodoxoles **13** and benziodazoles **14** have found synthetic application as efficient group Y transfer reagents, iodonium salts **15** and ylides **16** are used in numerous C–C bond-forming reactions, while iodonium imides **17** are useful reagents for the aziridination of alkenes and

the amidation of various organic substrates. Organoiodine(V) compounds (Figure 1.3), especially IBX and DMP, have found application as efficient oxidizing reagents, for example, for the oxidation of alcohols to the respective carbonyl compounds. Inorganic derivatives of iodine(VII), such as periodic acid and periodates, are powerful oxidants useful for glycol cleavage and some other applications.

From the simplified point of view of a synthetic organic chemist, the rich chemistry of hypervalent iodine is explained mainly by its strongly electrophilic character combined with the excellent leaving group ability of the phenyliodonio group. At a more advanced level, the reactions of hypervalent iodine reagents are commonly discussed in terms of ligand exchange, reductive elimination and ligand coupling, which are typical of transition metal chemistry. Homolytic and single-electron transfer (SET) pathways are also frequently observed in the reactions of several classes of hypervalent iodine compounds under appropriate conditions. An excellent, comprehensive survey of hypervalent iodine reactivity patterns has been provided by Ochiai (2003) in *Hypervalent Iodine Chemistry* [127]. The general reactivity features of hypervalent iodine reagents are summarized in the following sections.

1.5.1   Ligand Exchange and Reductive Elimination

Most reactions of λ^3-iodanes $PhIL_2$ involve the initial exchange of ligands on the iodine atom with external nucleophiles (Nu:) followed by reductive elimination of iodobenzene (Scheme 1.3). The second step in this simplified scheme can also proceed as "ligand coupling" [1], if it occurs as a concerted process. A similar general mechanistic description can also be applied to the reactions of λ^5-iodanes.

A detailed mechanism of the process shown in Scheme 1.3 is unknown. Two general mechanistic pathways, dissociative and associative, have been proposed for the ligand exchange reactions of λ^3-iodanes (Scheme 1.4) [26, 127]. The dissociative pathway seems to be less likely to occur, because of the low stability of the dico-ordinated iodonium ion $[PhIL]^+$ involved in this mechanism [127]. Such iodonium *8-I-2* species, however, have been frequently observed in the gas phase, for example, in mass spectrometry studies of protonated iodosylbenzene, $[PhIOH]^+$ [101], or in the mass spectra of all known iodonium salts, $[ArIR]^+$. The presence of cationic iodonium species in aqueous solution has been confirmed by spectroscopic measurements and potentiometric titrations of PhI(OH)OTs and PhI(OH)OMs [198]; however, all available experimental data show that the iodonium species in solution are coordinated with solvent molecules or with available counteranions. X-Ray diffraction analysis of the protonated iodosylbenzene aqua complexes $[PhI(H_2O)OH]^+$ isolated from aqueous solutions revealed a T-shaped structure, ligated with one water molecule at the apical site of the iodine(III) atom of hydroxy(phenyl)iodonium ion, with a near-linear O–I–O triad (173.96°), which is in agreement with a regular λ^3-iodane structure [178].
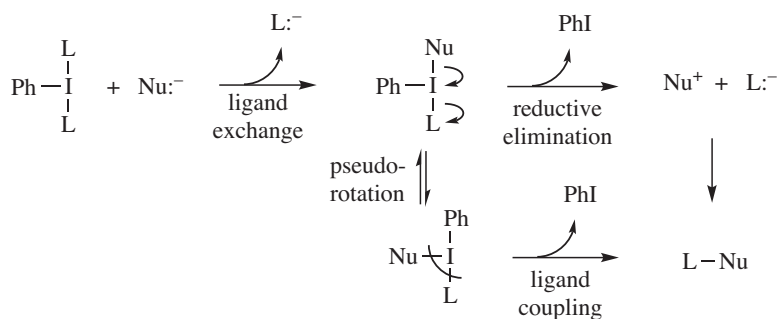
Scheme 1.3   *Simplified description of the reactions of λ^3-iodanes with nucleophiles Nu.*

Dissociative pathway:

8-I-2

Associative pathway:

12-I-4 (trans)   *12-I-4 (cis)*
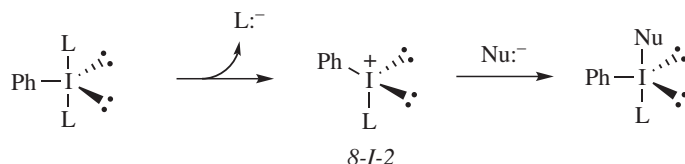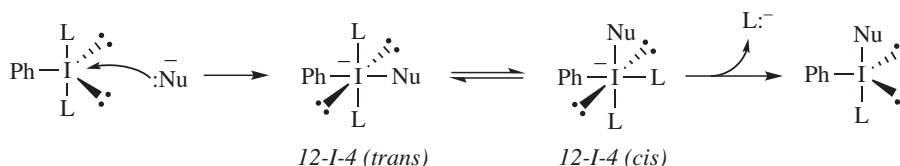
Scheme 1.4 *Dissociative and associative pathways for the ligand exchange reactions of λ^3-iodanes with nucleophiles Nu.*

The associative pathway of ligand exchange starts from the addition of a nucleophile to the positively charged iodine atom of a λ^3-iodane with the initial formation of a *trans* hypervalent *12-I-4* square-planar species. This intermediate species isomerizes to the *cis 12-I-4* square-planar intermediate and eliminates the ligand L to afford the final product (Scheme 1.4). Such a mechanism has been validated by the isolation and X-ray structural identification of several stable *12-I-4* species. For example, the interaction of ICl_3 with chloride anion affords tetrachloroiodate anion, ICl_4^-, which has a distorted square-planar structure as established by X-ray analysis of the trichlorosulfonium salt, $Cl_3S^+ ICl_4^-$ [209].

The second step of reactions of λ^3-iodanes with nucleophiles (Scheme 1.3) includes elimination of iodobenzene or other reduced iodine species. This is a facile and energetically favorable process. The leaving group in this reaction, PhI, is an excellent leaving group, about million times better than the triflate [210] and Ochiai has suggested calling this group a "hypernucleofuge" [127], which reflects the initial hypervalent character and the exceptional leaving group ability of the phenyliodonio group. Elimination of PhI can occur as reductive elimination or as ligand coupling as shown in Scheme 1.3. Reductive elimination leading to formal umpolung of reactivity of the nucleophile, Nu:$^-$ to Nu$^+$ (Scheme 1.3), is a common process in various reactions of hypervalent iodine reagents; it can result in the formation of products of nucleophilic substitution, α-elimination, β-elimination, rearrangement, or fragmentation.

The ligand coupling pathway requires initial pseudorotation to bring ligands L and Nu to apical and equatorial positions favorable for coupling (Scheme 1.3). Experimental studies on the mechanism of ligand coupling reaction are very limited. Ligand coupling usually occurs in the reactions of iodonium salts as a concerted process, proceeding with retention of configuration of the ligands. The ligand-coupling mechanism for the thermolysis of iodonium salts was discussed and generalized by Grushin and coauthors [48, 211].

1.5.2 Radical Reactions

Processes involving free-radical intermediates are relatively common in the reactions of λ^3-iodanes bearing chloro-, oxygen-, or nitrogen-ligands, usually under photochemical or thermal conditions. Bond dissociation energies in iodine compounds are relatively small, which favors homolytic reactions. Typical examples of radical reactions of λ^3-iodanes include chlorination of organic substrates using (dichloroiodo)benzene (Section 3.1.2), azidation of C–H bonds with hypervalent iodine azides (Section 3.1.15) and various radical
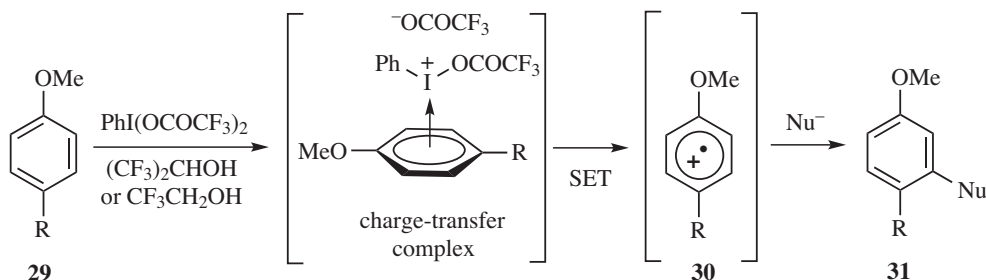
Scheme 1.5 *Simplified single-electron transfer (SET) mechanism for the reaction of* p-*substituted phenol ethers with [bis(trifluoroacetoxy)iodo]benzene.*

fragmentation reactions of alcohols or carboxylic acids with [bis(acyloxy)iodo]arenes in the presence of iodine under photochemical or thermal conditions (Section 3.1.18). These and other homolytic reactions of λ^3-iodanes will be discussed in Chapter 3.

1.5.3 Single-Electron Transfer (SET) Reactions

Processes involving a single-electron transfer (SET) step and cation–radical intermediates can occur in the reactions of λ^3- or λ^5-iodanes with electron-rich organic substrates in polar, non-nucleophilic solvents. Kita and coworkers first found that the reactions of *p*-substituted phenol ethers **29** with [bis(trifluoroacetoxy)iodo]benzene in the presence of some nucleophiles in fluoroalcohol solvents afford products of nucleophilic aromatic substitution **31** via a SET mechanism (Scheme 1.5) [212, 213]. On the basis of detailed UV and ESR spectroscopic measurements, it was confirmed that this process involves the generation of cation-radicals **30** produced by SET oxidation through the charge-transfer complex of phenyl ethers with the hypervalent iodine reagent [213, 214].

A similar SET mechanism involving cation–radical intermediates **30** has also been confirmed for the reactions of phenolic ethers with diaryliodonium salts in hexafluoroisopropanol [215]. The use of fluoroalcohols as solvents in these reactions is explained by their unique ability to stabilize the aromatic cation–radicals [107].

The SET mechanism was also proposed for some oxidations involving λ^5-iodanes. In particular, mechanistic studies involving isotope labeling, kinetic studies, cyclic voltammetry measurements and NMR spectroscopic analysis confirm that SET is a rate-determining step in the IBX-promoted oxidative cyclization of unsaturated anilides in THF–DMSO solutions [216]. The analogous mechanism was proposed for the oxidation of alkylbenzenes at the benzylic position under similar conditions [217].

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