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Hypervalent Iodine

Diaryliodonium Salts: A Journey from Obscurity to Fame

Eleanor A. Merritt and Berit Olofsson*

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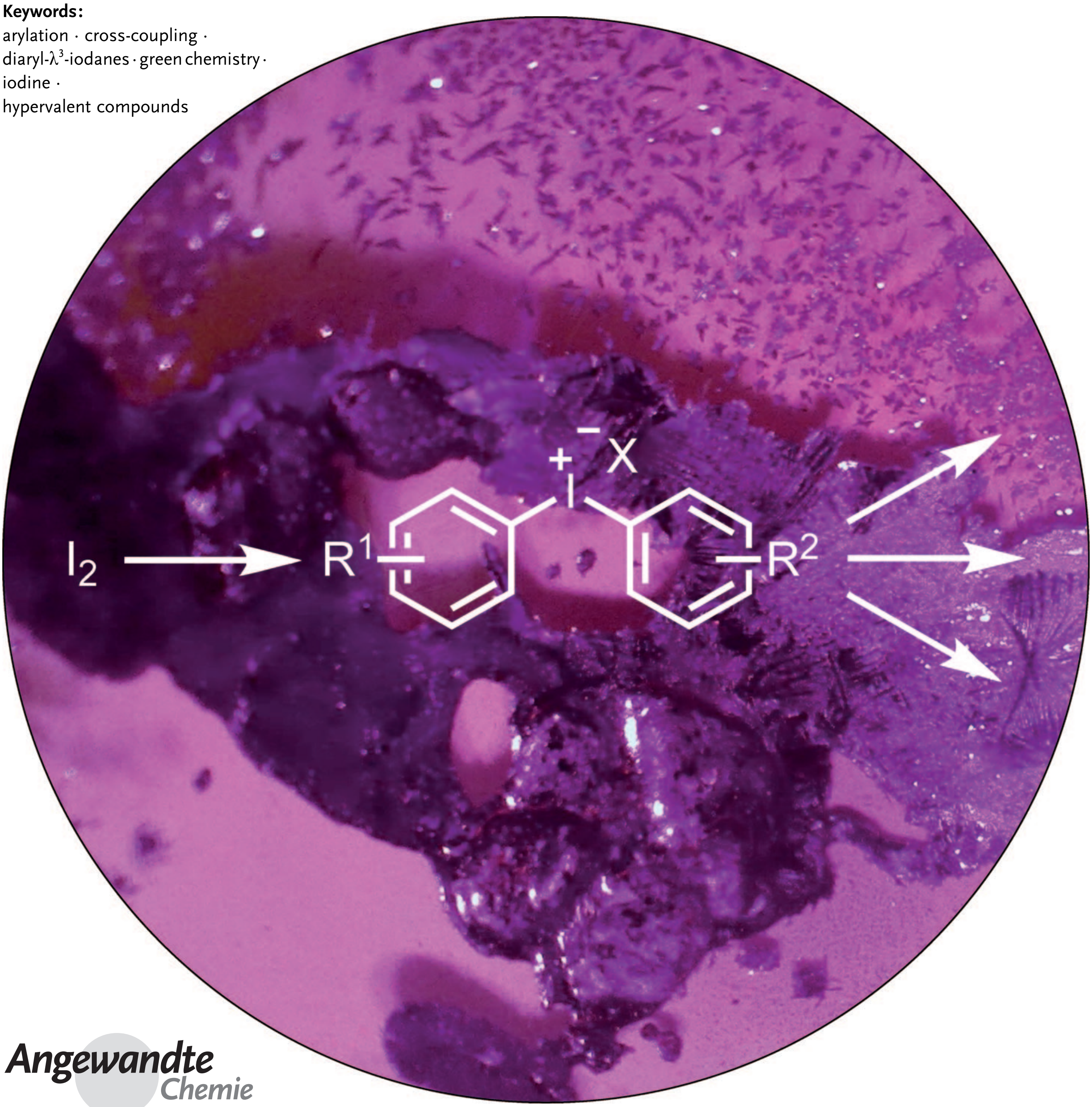

The recent groundbreaking developments in the application of diaryliodonium salts in cross-coupling reactions has brought this class of previously underdeveloped reagents to the forefront of organic chemistry. With the advent of novel, facile, and efficient synthetic routes to these compounds, many more applications can be foreseen. Herein we provide an overview of the historical and recent advances in the synthesis and applications of diaryliodonium salts.

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1. Introduction to Hypervalent Iodine

Hypervalent iodine compounds have recently received considerable attention as mild, nontoxic, and selective reagents in organic synthesis.[1] They are efficient alternatives to toxic heavy-metal-based oxidants and expensive organometallic catalysts for many organic transformations. Iodine(V) reagents, such as Dess–Martin periodinane and IBX (2-iodoxybenzoic acid), are frequently used as mild oxidants of alcohol moieties in total syntheses of natural products. IBX can also effect oxidative transformations of a variety of other functional groups.[2] Iodine(III) compounds with two heteroatom ligands, for example, (diacetoxyiodo)benzene (PIDA) and iodosylbenzene, are employed in oxidations of alcohols and alkenes, as well as in the α-functionalization of carbonyl compounds.[1]

In contrast, iodine(III) reagents with two carbon ligands have properties resembling those of Hg, Pb, and Pd complexes, and can be employed in reaction pathways that are similar to metal-catalyzed reactions.[3] As the use of transition metals in organic synthesis suffers from drawbacks including cost, toxicity, and threshold values in pharmaceutical products, the interest in these iodine(III)-mediated reactions has recently increased considerably.[3] Diaryliodonium salts are the best known compounds in this class. Owing to their highly electron-deficient nature and excellent leaving-group ability, they serve as versatile arylating agents with a variety of nucleophiles.

Several comprehensive reviews[4–6] and books[7] have been published on the topic of hypervalent iodine chemistry. This Review gives a brief historical view, but focuses on recent synthetic developments and applications of diaryliodonium salts in organic chemistry.

1.1. Structure and Reactivity

Diaryliodonium salts are air- and moisture-stable compounds that have been known since 1894.[8] Their structure consists of two aryl moieties and an "anion" X^-, as depicted in Figure 1 a. Diaryliodonium salts with halide anions are generally sparingly soluble in many organic solvents, whereas triflate and tetrafluoroborate salts have better solubility. Another attractive property with the latter anions is their weak or non-existent nucleophilicity, which makes them easily applicable in organic synthesis (see Section 3).

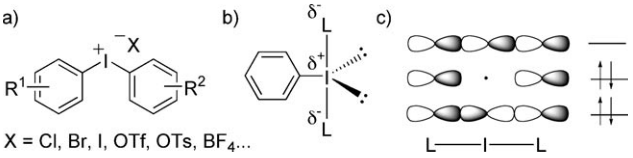
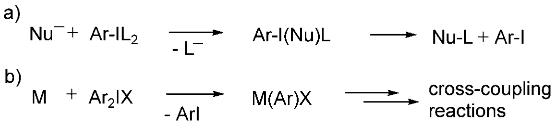


Figure 1. a) General structure of diaryliodonium salts. b) T-shaped form determined by X-ray structure analysis. c) Orbitals in the hypervalent bond.

The term "salt" is somewhat misleading, as X-ray structures of iodine(III) compounds show a T-shaped molecule, where the iodine and two apical ligands (L) share a hypervalent bond (Figure 1 b).[9] Iodine(III) compounds with two heteroatom ligands are believed to retain this T-shape also in solution, whereas the diaryliodonium salt structure in solution has been debated and could depend both on the X and the solvent.[9] The IUPAC nomenclature for this compound class is "diaryl-λ^3-iodanes", although the old term diaryliodonium salt is still in use.

Iodine(III) compounds are electrophilic at iodine, because of the node in the nonbonding orbital of the hypervalent bond (Figure 1 c). Thus, they react with various nucleophiles by initial Nu–I bond formation and release of one of the ligands (Scheme 1 a). Subsequent nucleophilic substitution by the free ligand anion or reductive elimination yields the product Nu-L and releases ArI. The mechanism of the second step depends on the nucleophile, the nature of the ligand, and the reaction conditions.[7]

Diaryliodonium salts are generally believed to react through the reductive elimination pathway, delivering one of the aryl moieties to the nucleophile. Radical mechanisms



Scheme 1. General reactivity of diaryliodonium salts in a) reactions with nucleophiles, b) metal-catalyzed reactions.

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[*] Dr. E. A. Merritt, Prof. B. Olofsson
Department of Organic Chemistry
Arrhenius Laboratory, Stockholm University
SE-106 91 Stockholm (Sweden)
Fax: (+46) 8-154908
E-mail: berit@organ.su.se
Homepage: http://www.organ.su.se/bo/

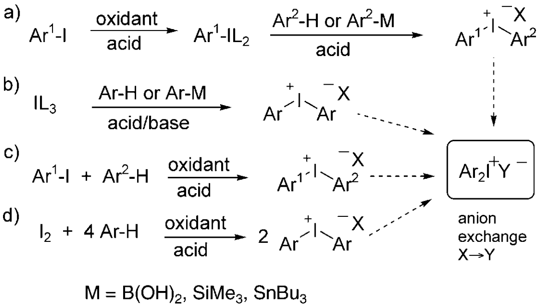
have also been suggested, but product distribution studies and results using radical inhibitors argue against the involvement of radicals in several cases.[7] In metal-catalyzed reactions, diaryliodonium salts behave as more reactive versions of aryl iodides, delivering an aryl moiety and a ligand to the metal center in an oxidative addition (Scheme 1 b). The aryl metal complex then reacts further to give cross-coupling products (Section 3.2).[7]

Symmetric diaryliodonium salts (Figure 1 a, $R^1 = R^2$) are generally preferable to unsymmetric salts, as their use avoids selectivity issues in aryl-transfer reactions. Unsymmetric salts ($R^1 \neq R^2$) are, however, desirable when the starting materials are expensive, as one aryl moiety can be selectively transferred, with the other aryl moiety behaving as a "dummy ligand". The aryl groups can often be differentiated electronically or sterically,[10] and this type of selectivity will be referred to as the chemoselectivity of the reaction. The general trend is that the more electron-deficient aryl moiety is transferred in enolate and heteroatom arylations (Sections 3.1, 3.4) whereas the more electron-rich aryl group is transferred in cross-coupling reactions (Sections 3.2, 3.3). Furthermore, the properties of unsymmetric salts can be varied more easily, which is beneficial in some applications (Section 3.5).

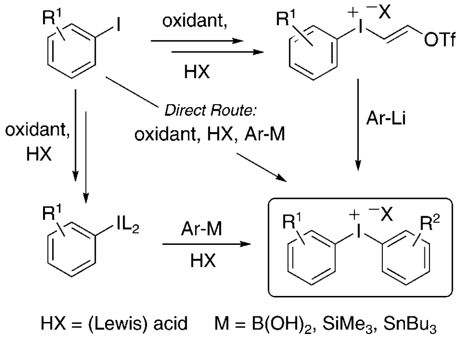
2. Synthetic Strategies to Diaryliodonium Salts

Synthetic routes to diaryliodonium salts typically involve two or three steps, with initial oxidation of an aryl iodide to iodine(III) and then ligand exchange with an arene or an organometallic reagent to obtain the diaryliodonium salt (Scheme 2 a, Section 2.1). In many cases a subsequent anion-exchange step is necessary. To shorten the synthetic route to symmetric iodonium salts, preformed inorganic iodine(III) reagents can be employed (Scheme 2 b, Sections 2.2, 2.3). Recent progress involves one-pot oxidation and ligand-exchange reactions to obtain the diaryliodonium salts directly from arenes and iodoarenes or molecular iodine (Scheme 2 and d, Sections 2.4, 2.5). The vast majority of the reactions are run under acidic conditions, although some neutral or basic methods exist.

A common feature of most synthetic routes is the electrophilic aromatic substitution (EAS) of an arene (Ar-H) onto an iodine(III) intermediate, which limits the number of salts that can be obtained by these methods. High *para*-selectivity is usually obtained with *o*/*p*-directing substituents, whereas *m*-directing substituents often lead to poor yields and byproduct formation. Synthetically useful yields of symmetric salts with *ortho- and meta*-substituents can only be obtained by a limited number of routes, employing lithiated arenes, arylboronic acids, stannanes, or silanes (Scheme 3).



Scheme 2. Synthetic strategies for preparing diaryliodonium salts.



Scheme 3. Regiospecific strategies for preparing diaryliodonium salts.

2.1. Synthesis with Preformed Organic Iodine(III) Compounds

The most common way of synthesizing diaryliodonium salts is a stepwise approach in which an aryl iodide is converted into an aryliodine(III) compound by treatment with an inorganic oxidant under acidic conditions. This aryliodine(III) species is isolated and subsequent ligand exchange with an arene, an arylstannane, or an arylsilane

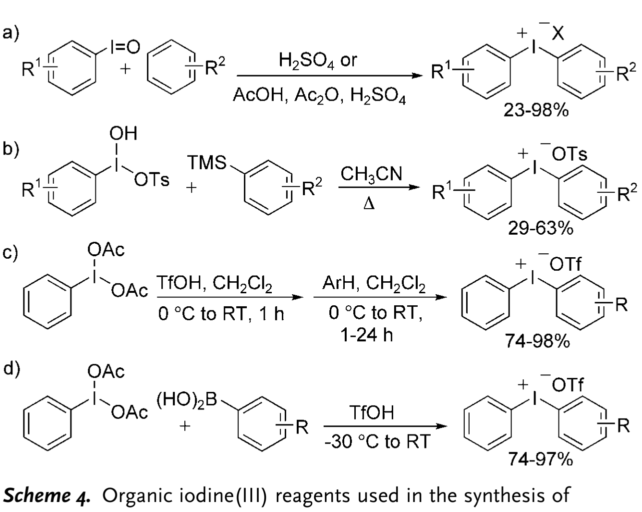
Eleanor A. Merritt, born in the UK in 1982, obtained her MChem degree from Cardiff University in 2004. She completed her PhD in 2008 with Dr. Mark C. Bagley at Cardiff University, on the synthesis of thiopeptide antibiotics. Currently she is undertaking postdoctoral research at Stockholm University under the direction of Berit Olofsson, where she is working on the development of environmentally benign methods within hypervalent iodine chemistry.

Berit Olofsson was born in 1972 in Sundsvall, Sweden. She got her MSc in 1998 from Lund University, and finished her PhD on asymmetric synthesis in 2002 at KTH, Stockholm (with P. Somfai). After a postdoctoral position with V. K. Aggarwal at Bristol University, UK, on natural product synthesis, she became assistant supervisor in the group of J.-E. Bäckvall at Stockholm University. In 2006 she was appointed Assistant Professor, and was promoted to Associate Professor in 2008. Her research interests include the synthesis and application of hypervalent iodine compounds in asymmetric synthesis and total synthesis.

delivers the diaryliodonium salt under acidic or neutral conditions. The anion usually originates from the acid used, and an anion exchange is often performed to give a more easily isolated and/or applicable salt. Structurally diverse diaryliodonium salts can be obtained by employing different reagents depending on the electronic properties of the aryl moieties, although choosing the correct method can be difficult for non-specialists in the field. The strategy is rather lengthy, but can be shortened by the use of commercially available aryliodine(III) compounds. The synthesis of the iodine(III) intermediates discussed below has been thoroughly reviewed[4,5,7] and is beyond the scope of this Review.

The first synthesis of diaryliodonium salts was reported in 1894 by Hartmann and Meyer.[8] Early syntheses involved the condensation of preformed hypervalent iodine compounds, such as iodosylarenes (ArI=O) and iodoxyarenes ($ArIO_2$).[11] These reactions were time-consuming, atom-inefficient, and often low-yielding, which resulted in diaryliodonium salts being considered obscure reagents for several decades.[12]

Considerable contributions to the field were made by Beringer and co-workers, who published a large number of synthetic routes in the 1950s. Their method focused on treating arenes with a range of hypervalent iodine compounds, such as iodosylarenes, (diacetoxyiodo)arenes, and iodoxyarenes, in the presence of various acids to yield symmetric and unsymmetric diaryliodonium salts (Scheme 4a).[13,14] The electronic properties of the arene influenced the reactivity and yields considerably, as expected in EAS reactions. The reagent combination acetic anhydride/trifluoroacetic acid was found to be efficient for electron-rich arenes and heteroarenes, such as thiophene,[15,16] whereas sulfuric acid was needed for electron-deficient substrates.[14] Polymer-supported diaryliodonium salts have recently been prepared from the corresponding (diacetoxyiodo)arenes in this manner.[17,18]



Scheme 4. Organic iodine(III) reagents used in the synthesis of diaryliodonium salts.

The first regiospecific synthesis of diaryliodonium tosylates was discovered by Koser and co-workers in 1980. The reaction of hydroxy(tosyloxy)iodobenzene (PhI(OH)OTs, Koser's reagent) with arylsilanes under neutral conditions occurred at the *ipso*-position regardless of substituents (Scheme 4b).[19] Substituted versions of Koser's reagent could also be employed, delivering both symmetric and unsymmetric salts in moderate yields. Electron-rich arenes, such as thiophene, react with ArI(OH)OTs without need for the trimethylsilyl (TMS) activating group.[20] It was subsequently reported that phenylsilane also reacted with BF_3-activated iodosylbenzene, yielding diphenyliodonium tetrafluoroborate after anion exchange.[21,22]

The use of triflic acid (TfOH; trifluoromethane sulfonic acid) in organic solvents was found to be an efficient alternative to the inorganic acids previously used, both for reasons of reactivity and because the products could be easily isolated as triflate salts without anion exchange. In 1992, Kitamura et al. reported that triflic acid activates iodosylbenzene towards ligand exchange reactions with arenes.[23] The method was later improved by using (diacetoxyiodo)benzene (DIB, PIDA) instead of iodosylbenzene, thus forming [$PhI(OAc)_2\cdot 2\,TfOH$] in situ, and subsequent addition of electron-rich arenes to give diaryliodonium triflates (Scheme 4c).[24] Substituted (diacetoxyiodo)arenes have also been used, which allows for a larger product scope.[25] This route has been used in the synthesis of uracil-based diaryliodonium salts[26] and TMS-substituted salts that are used as precursors for benzyne (see Section 3.5.2).[27]

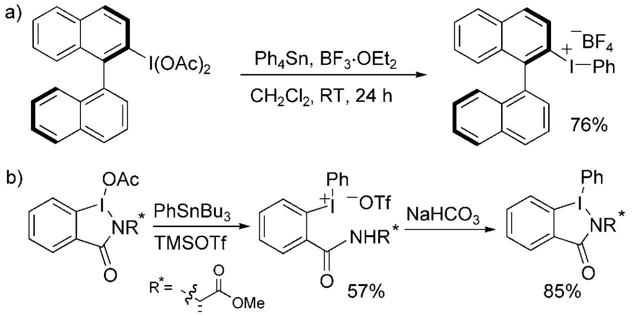
Arylstannanes are more reactive than the corresponding aryl silanes in reactions with iodine(III) compounds. They have been employed with aryl(cyano)iodonium triflates, which are prepared from aryl iodides in two steps, yielding diaryliodonium triflates.[28] Koser's reagent can also be utilized with arylstannanes, delivering diaryliodonium tosylates in moderate yields under mild reaction conditions.[29] Heteroaromatic iodonium salts were formed in excellent yields using this method.[30]

Phenyliodine(III) sulfate, which is obtained by treatment of iodosylbenzene with sulfur trioxide, reacts with both electron-deficient and electron-rich arenes to give unsymmetric diaryliodonium hydrosulfates.[31] Various fluorinated aryliodine(III) reagents[32] and other specialized reagents[33] have been employed in the synthesis of polyfluorinated diaryliodonium salts.

Ochiai et al. developed a high-yielding synthesis of diaryliodonium tetraarylborates, which are used as photoinitiators (see Section 3.5.4). The reaction employed (diacetoxyiodo)arenes and alkali-metal tetraarylborates, and the corresponding tetrafluoroborate salts could be obtained after anion exchange.[34] The use of arylboronic acids was subsequently investigated, and delivered both symmetric and unsymmetric diaryliodonium tetrafluoroborates regiospecifically upon reaction with (diacetoxyiodo)arenes and boron trifluoride.[35]

This method was further developed by Widdowson and co-workers, who treated arylboronic acids with PIDA in the presence of triflic acid, giving diaryliodonium triflates in high yields (Scheme 4d).[36] Heteroaryl boronic acids performed better in couplings with Koser's salt than with PIDA, and gave the corresponding tosylate salts without addition of acid. In a similar fashion, aryltrifluoroborates react with aryliodine difluorides to give diaryliodonium tetrafluoroborates.[37]

The first synthesis of chiral diaryliodonium salts was published by Ochiai and co-workers in 1999.[38] They treated 2-(diacetoxyiodo)-1,1′-binaphthyl[39] with tetraphenylstannane in the presence of boron trifluoride etherate, and obtained the chiral tetrafluoroborate salt in good yield (Scheme 5 a). Some substituted versions were also synthesized (see section 3.1.2). In a similar fashion, Zhdankin et al. prepared chiral benziodazole structures in which the N-functionalized amide moiety served as an internal anion (Scheme 5 b)[40]



Scheme 5. Synthesis of chiral diaryliodonium salts.

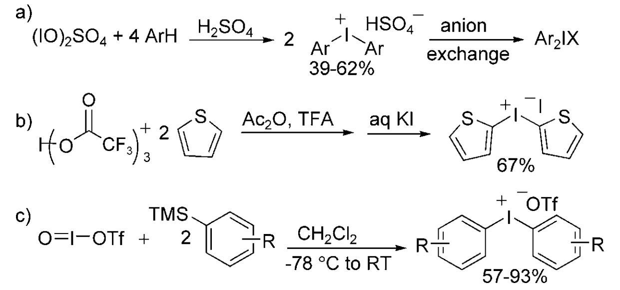
Recent progress in the development of reactions employing iodine(III) reagents involves the beneficial effect of using 2,2,2-trifluoroethanol (TFE) as the solvent in reactions with Koser's reagent (see Section 2.5).[41]

2.2. Synthesis with Preformed Inorganic Hypervalent Iodine Reagents

The synthesis of iodonium salts can be shortened by employing inorganic hypervalent iodine reagents. This strategy is generally efficient in the synthesis of symmetric diaryliodonium salts, the drawback of the process being that the inorganic iodine reagents must be prepared beforehand, and that some of them are not stable enough to be stored.

Early work in this field was done by Masson and co-workers, who discovered that arenes could be treated with iodic acid or iodosyl sulfate to form diaryliodonium salts.[42] This theme was further developed by Beringer, who also performed anion exchanges to generate the corresponding diaryliodonium halides (Scheme 6 a).[13,14] A modified procedure has recently been published (see Section 2.5).[43] The use of electron-rich arenes and heteroarenes was subsequently investigated, and bis(2-thienyl)iodonium salts could be formed in good yields from thiophene and iodine(III) trifluoroacetate (Scheme 6 b).[15,44]

More recently, several reagents that can be employed with activated arenes to give diaryliodonium salts in a regiospecific fashion have been reported by Stang, Zhdankin and co-workers. Iodosyl triflate, which is available by the reaction of iodine and iodine pentoxide in triflic acid (TfOH), reacts with arylsilanes at low temperatures (Scheme 6 c).[45] (Dicyano)iodonium triflate, which in turn is derived from iodosyl triflate, is an unstable compound that reacts with electron-rich arylstannanes to give diaryliodonium salts in moderate yields.[46] This approach has been applied to the synthesis of bis(heteroaryl)iodonium salts.[47] Iodosyl fluorosulfate ($O{=}IOSO_2F$) gives diaryliodonium hydrosulfates upon reaction with arenes.[48]



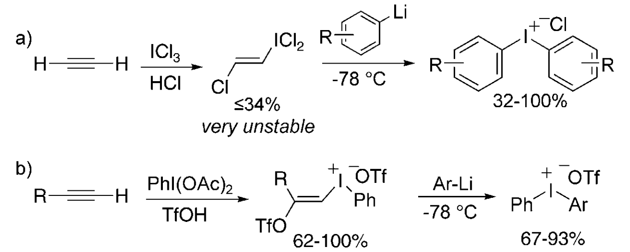
Scheme 6. Inorganic hypervalent iodine(III) reagents used in the synthesis of diaryliodonium salts.

2.3. Synthesis with Vinyl Iodine(III) Reagents under Basic Conditions

The reactions described in Sections 2.1–2.2 are either performed under acidic conditions or use reagents that are synthesized in acidic media. Substrates containing acid-sensitive substituents or heteroatoms that are prone to oxidation or protonation, thereby deactivating the heteroarene, often cannot be employed under these conditions.

Alternative routes employing very reactive iodine(III) reagents, have been developed to circumvent this problem. These reagents can be used under strongly basic conditions, such as in reactions with metallated arenes. Both symmetric and unsymmetric diaryliodonium salts can be obtained in a regiospecific manner, which is an advantage. Drawbacks include the synthesis of the unstable iodine(III) reagents, which are not commercially available, and the need for strong bases and low temperatures.

Beringer and Nathan reported the use of *trans*-chlorovinyliodoso dichloride, a highly unstable compound synthesized from ethyne and iodine trichloride, in 1969 (Scheme 7 a).[49,50] This compound reacts with lithiated arenes at low temperatures to give symmetric diaryliodonium salts in moderate to good yields.[49,51] This approach is especially useful in the



Scheme 7. Reactions of metallated arenes with iodine(III) reagents.

synthesis of nitrogen-containing bis(heteroaryl)iodonium salts, which are difficult to obtain under acidic conditions.[52,53]

More recently, a variety of aryl(vinyl)iodonium triflates have been prepared by the reaction of (diacetoxy)iodoarenes with alkynes.[54] These reagents are treated with lithiated arenes to give unsymmetric diaryliodonium salts in good yields (Scheme 7b).[55] The reaction of aryliodine(III) compounds directly with metallated arenes has also been reported, although this type of transformation is poor yielding.[56,57]

The groups of Beringer[58] and Koser[59] have reported that ligand-exchange reactions occur also on other iodine(III) species. Treatment of diaryliodonium or aryl(alkynyl)iodonium salts, respectively, with aryl lithium reagents caused formation of diaryliodonium salts with expulsion of an aryl or alkynyl moiety, respectively. Owing to the exotic starting materials, this transformation is of more academic than synthetic interest.

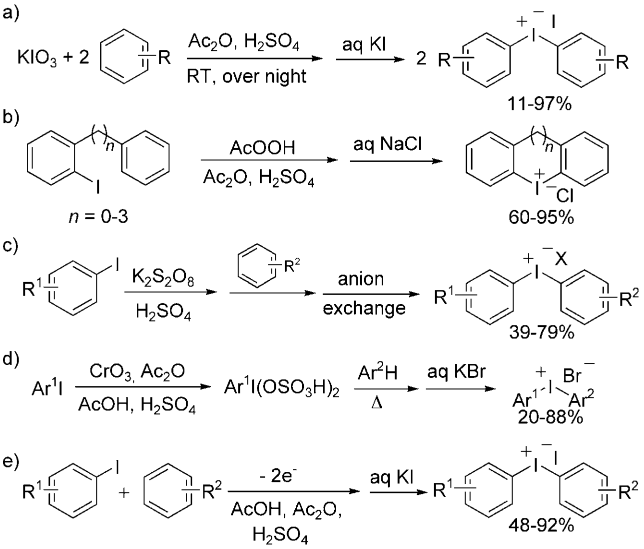
2.4. One-Pot Syntheses

The development of synthetic routes to diaryliodonium salts directly from iodoarenes, without isolation of an iodine (III) intermediate, is attractive for many reasons. Advantages include reduced reaction time and increased substrate scope, as many intermediates are unstable towards isolation. Furthermore, the applicability is improved when diversely substituted diaryliodonium salts can be obtained by the same method.

For a one-pot reaction to be successful, the reaction conditions and the electronic properties of the aryl iodide and the arene must often be carefully selected. The arene cannot be too electron deficient, so as to avoid byproduct formation caused by the aryl iodide reacting as the arene in the EAS. The temperature and reaction time are often varied to match fast or slow oxidation and EAS steps.

In 1953, Beringer et al. reported that certain diaryliodonium salts could be prepared directly from alkyl-substituted arenes with the commercial oxidant potassium iodate (Scheme 8a).[13,14,60] Cyclic diaryliodonium salts are generally easier to form than the corresponding acyclic structures.[61] Thus, it is not surprising that one of the first one-pot procedures involved cyclic structures. In 1956, Sandin and co-workers reported that treatment of 2-iodobiphenyl and similar compounds with peracetic acid, followed by addition of sulfuric acid brought about ring closure (Scheme 8b).[62] Similarly, cyclization of the diazonium salt prepared from 2-amino-2′-iodobiphenyl was high-yielding.[63] Hydrogen peroxide in acetic anhydride/sulfuric acid could be used in the formation of certain heterocyclic diaryliodonium salts, for example, from 2-iodophenyl(phenyl) ether.[64]

The next synthesis of acyclic diaryliodonium salts was reported in 1959, when aryl iodides were oxidized in situ with potassium persulfate or barium peroxide, followed by condensation with an arene (Scheme 8c).[14,65] Diaryliodonium salts with internal carboxylate anions have also been prepared in this way.[66]



Scheme 8. One-pot syntheses of diaryliodonium salts from aryl iodides.

Kaźmierczak and Skulski reported a sequential one-pot reaction from electron-deficient aryl iodides that employs chromium trioxide with the reagent combination acetic anhydride, acetic acid, and sulfuric acid under anhydrous conditions. Subsequent heating with an electron-rich arene followed by anion exchange delivered diaryliodonium bromides (Scheme 8d).[67] The reaction is fast but requires toxic reagents and tedious purification steps. An oxidative anion-exchange process was also developed, where hydrogen peroxide was used to replace the bromide ion with various other anions.[67] It was later described that sodium perborate could be employed with the same reagent combination in the synthesis of iodonium salts from electron-rich aryl iodides, however longer reaction times and reagents in excess are required.[68]

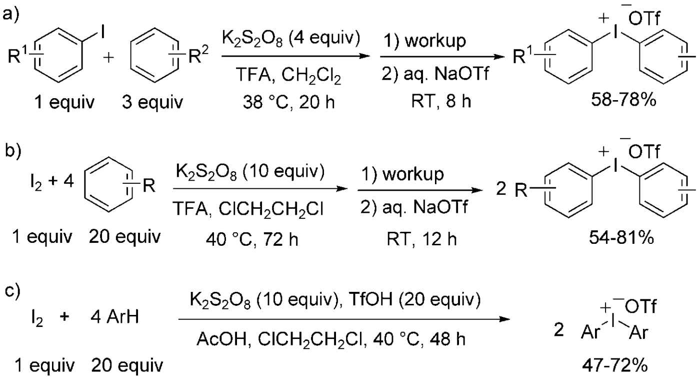
An elegant electrosynthesis of diaryliodonium salts was reported by Peacock and Pletcher in 2000.[69] The anodic oxidation of aryl iodides in acidic media in the presence of arenes delivered diaryliodonium iodides in good yields (Scheme 8e). The scope was limited to alkyl-substituted diaryliodonium salts, as electron-rich substrates gave byproducts and electron-deficient ones were too unreactive.[69,70]

2.5. Recent Progress

Several advances have been made in the last few years, including the finding of 2,2,2-trifluoroethanol (TFE) as a very efficient solvent and the development of one-pot routes to easily applicable triflate and tetrafluoroborate salts. Herein, these methods are described in more detail, to demonstrate the scope, limitations, reaction times, ease of handling, and atom efficiency of the reactions.

The most recent progress involves one-pot reactions of arenes with iodine in the presence of an oxidant. The need for expensive aryl iodides is thereby circumvented, and the yields are often excellent, especially considering that iodination, oxidation to iodine(III), and ligand exchange are performed in one pot. The substrate scope of this reaction type is inherently limited to arenes that do not give a regioisomeric mixture upon iodination.

The research groups of Olofsson and Kitamura have independently developed several one-pot routes to diaryliodonium salts in the last few years. Hossain and Kitamura treated aryl iodides and arenes with potassium persulfate (compare with Scheme 8c) and TFA, which upon anion exchange gave diaryliodonium triflates (Scheme 9a).[71] The reaction required excess reagents and was limited to electron-deficient aryl iodides and alkylarenes.



Scheme 9. Kitamura's one-pot syntheses of diaryliodonium salts. Number of examples reported: a) 14, b) 5, c) 7.

A similar oxidation system was employed in the synthesis of (diacetoxyiodo)arenes directly from arenes and iodine,[72] and a combination of the two reactions resulted in a direct synthesis of diaryliodonium triflates from iodine and arenes (Scheme 9b).[73] Although the scope of this method is limited to benzene, *tert*-butylbenzene, and halobenzenes, it circumvents the need for expensive aryl iodides. The anion-exchange step was later avoided by adding triflic acid to the reaction, which also resulted in slightly shorter reaction times (Scheme 9c).[74] By exchanging triflic acid for a combination of *p*-toluenesulfonic acid (tosic acid) and sulfuric acid, diaryliodonium tosylates could be obtained with a similar product pallet.[74]

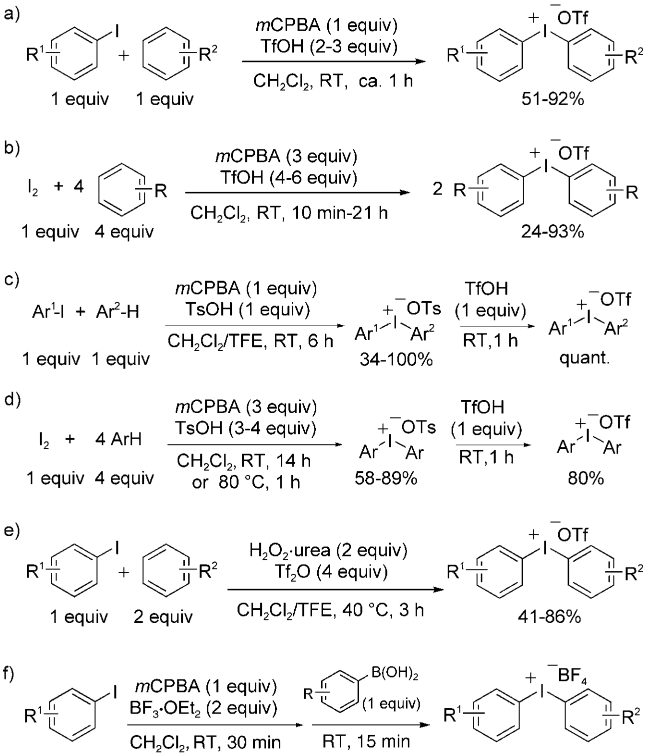
Olofsson and co-workers recently developed an atom-efficient, simple, and general one-pot synthesis of diaryliodonium triflates from aryl iodides and arenes. *m*-Chloroperbenzoic acid (*m*CPBA) was selected as the oxidant, as it had been reported as an efficient oxidant of aryl iodides to (diacyloxy)iodoarenes.[75] Furthermore, both *m*CPBA and the reduced form, *m*-chlorobenzoic acid (*m*CBA), are readily soluble in organic solvents, which was envisioned to simplify product purification. Triflic acid was employed to activate the oxidant and simultaneously deliver the triflate anion to the salt. In this manner, diaryliodonium triflates were obtained in high yields, short reaction times, and without need for excess reagents (Scheme 10a).[76] A large set of symmetric and unsymmetric salts with varying electronic properties could be synthesized by variation of the reaction conditions from 0 °C, 10 min to 80 °C, 15 h. The limitations were symmetric salts with very electron-rich or electron-deficient aryl groups.

It should be noted that this method also allowed the synthesis of pyridyl(aryl)iodonium salts, which had previously only been obtainable by routes employing basic conditions (see Section 2.3). Product isolation was indeed facile, and consisted of concentration, addition of diethyl ether, and collection of the precipitated, pure product.

The oxidation system could be extended to the direct formation of diaryliodonium triflates from iodine and arenes by increasing the amount of reagents (Scheme 10b).[77] Although more limited in substrate scope, this method is efficient with alkyl- and halobenzenes,[76] as demonstrated by the large-scale synthesis of bis(4-*tert*-butylphenyl)iodonium triflate in 78 % yield in 45 min.[78]

A one-pot reaction yielding symmetric, electron-rich diaryliodonium salts was subsequently developed. Triflic acid was replaced by the less-reactive tosic acid, which resulted in formation of diaryliodonium tosylates in good yields (Scheme 10c).[79] An efficient in situ anion exchange to triflate was obtained by addition of triflic acid to the reaction mixture after completion of the reaction. This oxidation system could also be applied to the direct synthesis from arenes and iodine (Scheme 10d).[79]

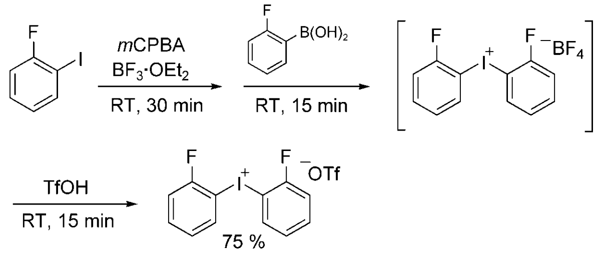
The use of environmentally benign oxidizing agents instead of *m*CPBA is advantageous for industrial use. Urea-hydrogen peroxide[80] in combination with triflic anhydride formed an efficient oxidation



Scheme 10. Olofsson's one-pot syntheses of diaryliodonium salts. Number of examples reported: a) 32, b) 9, c) 9, d) 5, e) 16, f) 24.

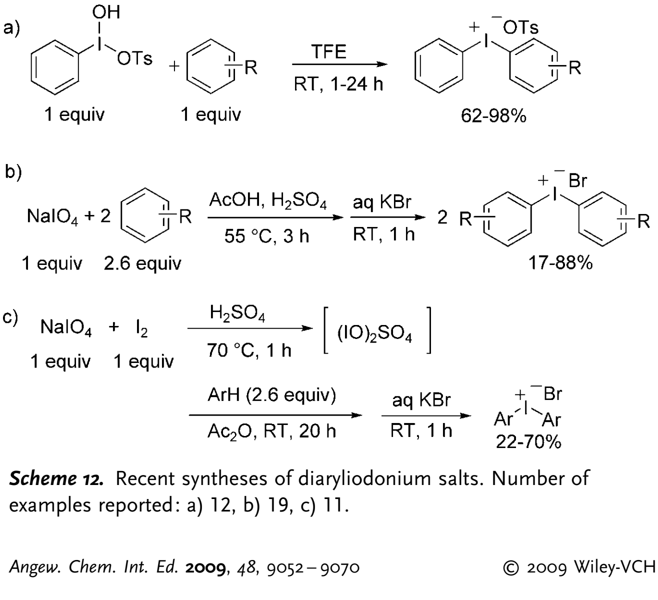
system, delivering a range of diaryliodonium triflates in good yields (Scheme 10e).[81]

To further widen the scope of easily accessible diaryliodonium salts, a regiospecific one-pot reaction starting from iodoarenes and a suitably activated arene source was envisioned. Arylboronic acids were selected because of their high reactivity and low toxicity compared to silanes and stannanes, respectively. A fast and efficient sequential one-pot reaction employing *m*CPBA and boron trifluoride etherate was developed, giving diaryliodonium tetrafluoroborates in high yields without need for an extra anion-exchange step (Scheme 10 f).[82] Both symmetric and unsymmetric, electron-deficient and electron-rich salts can be synthesized in a regiospecific manner, and the substitution pattern can easily be varied. An in situ anion exchange with triflic acid gives access to diaryliodonium triflates that cannot be obtained by the triflic acid method described above. An example being the synthesis of bis(2-fluorophenyl)iodonium triflate (Scheme 11).[82]



Scheme 11. Regiospecific one-pot synthesis with in situ anion exchange.

Kita and co-workers recently described a versatile synthesis of diaryliodonium salts by the reaction of arenes and Koser's reagent using TFE as solvent (Scheme 12a).[41] TFE greatly enhanced the efficiency of the condensation, leading to a larger product scope than previously described (see Section 2.1). The reaction employs unsubstituted to electron-rich arenes and is performed at room temperature under neutral conditions. The anion can be modified by exchanging Koser's reagent for iodosylbenzene and triflic acid or TFA.[41] The use of TFE as the solvent has since been applied in other synthetic routes (Scheme 10c,e).[79,81]



Scheme 12. Recent syntheses of diaryliodonium salts. Number of examples reported: a) 12, b) 19, c) 11.

In 2008, the use of sodium metaperiodate as oxidized iodine source was reported (compare with Scheme 8a). The reaction of arenes and $NaIO_4$ under strongly acidic conditions resulted in formation of diaryliodonium hydrogensulfates. After workup and subsequent anion exchange, the corresponding bromides were isolated (Scheme 12b).[43] Electron-deficient arenes were better suited than alkyl-substituted arenes, while more electron-rich substrates were inefficient. Oxidative anion exchange of the isolated bromides to the more applicable tetrafluoroborates took place in moderate yields.[43] A modified version of Beringer's procedure (see Scheme 6a) with in situ formation of iodosyl sulfate was also reported (Scheme 12c).[43]

Gaunt and co-workers modified the one-pot *m*CPBA-method developed by Olofsson and co-workers (see Scheme 10a) by using tetrafluoroboric acid instead of triflic acid. The diaryliodonium tetrafluoroborates obtained were converted into the corresponding triflates by treatment with TMSOTf.[83]

With the recent development of facile, reliable, and high-yielding routes to diaryliodonium salts with varying substitution patterns, it is no longer considered challenging to prepare these environmentally benign arylating agents.

3. Applications of Diaryliodonium Salts in Organic Synthesis

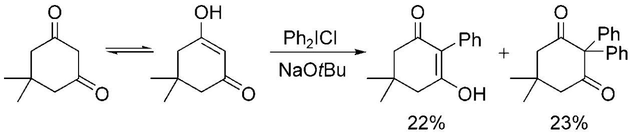
Many applications of diaryliodonium salts in organic synthesis have emerged over the past decade and the field now encompasses such diverse elements as metal-catalyzed cross-couplings through C−H activation, α-arylation of carbonyl compounds, arylation of a wide range of heteroatom nucleophiles, benzyne generation, and dearomatization of phenols. Encouragingly, advances also are being made in asymmetric synthesis although this area remains in its infancy, providing a challenging target for future research. In addition, these versatile compounds are industrially applied as cationic photoinitiators in polymerization processes.

3.1. α-Arylation of Carbonyl Compounds

The introduction of aryl moieties to the α-position of carbonyl compounds, particularly in an asymmetric fashion, is an ongoing challenge in organic synthesis. Diaryliodonium salts provide a means by which this goal can be achieved without the use of heavy metals, such as palladium.

3.1.1. General α-Arylation Strategies

α-Arylation of carbonyl compounds using diaryliodonium salts has been known for many decades. Indeed, the first report of such a reaction came from Beringer and co-workers in 1960.[84] Phenylation of 5,5-dimethylcyclohexane-1,3-dione was achieved in 22 % yield, together with 23 % of the

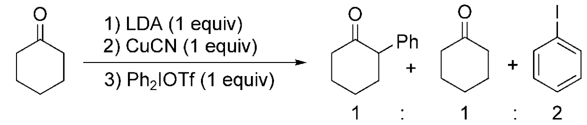


Scheme 13. The first reported α-arylation of a diketone using diphenyliodonium chloride.

bisphenylated product (Scheme 13). The same reaction was conducted using (2-nitrophenyl)phenyliodonium bromide, and only transfer of the substituted phenyl group (i.e. the most electron-deficient arene) was observed.

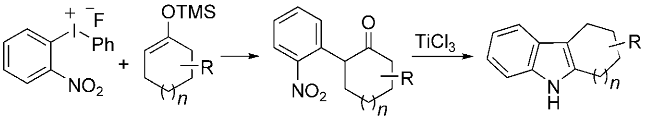
Beringer et al. proceeded to report further successful, albeit moderate-yielding arylations of 1,3-indandiones,[85] malonates,[86] esters and β-ketoesters,[87] and 1-indanones.[88] *tert*-Butanol was used as the solvent and sodium or potassium *tert*-butoxide as base throughout these investigations. A radical mechanism for the arylation was proposed,[85,89] although later studies have disputed this.[90] Similar conditions were employed by Chen and co-workers in the arylation of Meldrum's acid.[91] An alternative method for the arylation of diones was published by Hampton and co-workers, in which phenyl-2,4-pentanedione was prepared using sodamide in liquid ammonia.[92] It was possible to conduct this reaction on a multigram scale, furnishing the product in up to 64% yield.[93]

Ryan and Stang investigated the arylation of ketones, using lithium diisopropylamide (LDA) to generate the lithium enolate of cyclohexanone.[94] Treatment of the enolate with diphenyliodonium triflate was found to yield less than 5% of the desired product, but this could be improved to 50% on addition of one equivalent of copper(I) cyanide. A mixture containing a 1:1:2 ratio of product, cyclohexanone, and iodobenzene was obtained (Scheme 14). It was also noted that five-membered cyclic ketones furnished diarylated products whereas larger ring sizes were only monoarylated.



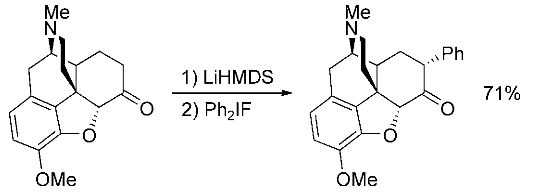
Scheme 14. Copper-mediated arylation of cyclohexanone.

In 1991, Chen and Koser first demonstrated the arylation of silyl enol ethers using diphenyliodonium fluoride. Either α-phenyl or α,α-diphenyl ketones were produced in 20–88% yield; cyclic substrates were in general more suitable than acyclic substrates.[95] Rawal and co-workers were able to arylate TMS-enol ethers using (2-nitrophenyl)phenyliodonium fluoride (Scheme 15).[96] In line with the findings of Beringer, only the electron deficient 2-nitrophenyl group was transferred.[84] Reduction of the nitro group using titanium trichloride followed by spontaneous condensation of the aniline with the ketone furnished the desired indole products. This method was applied in the total synthesis of tabersonine, an *Aspidosperma* alkaloid.[97]



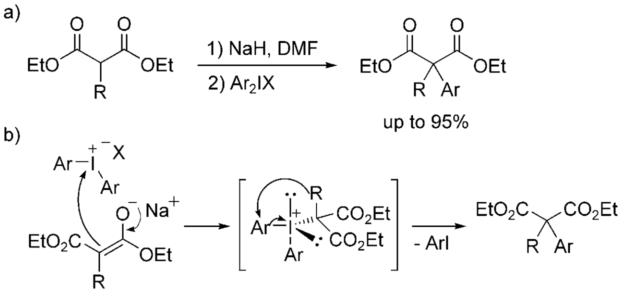
Scheme 15. Arylation of TMS-enol ethers and synthesis of indoles.

Gao and Portoghese were able to arylate ketones using diphenyliodonium iodide and lithium hexamethyldisilazane (LiHMDS) as the base. The monophenylated product was obtained in 71% yield, with only 4% diphenylated byproduct (Scheme 16).[98] This reaction was used as a key step in the synthesis of a series of 7-arylmorphinans to be tested for opioid agonist and antagonist activity.[99]



Scheme 16. Diastereoselective phenylation of morphinan-6-ones.

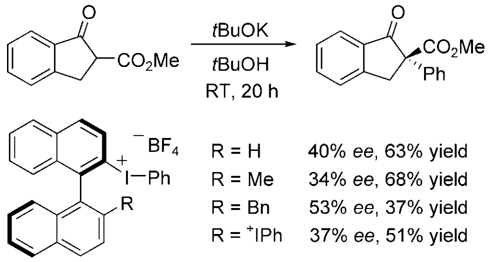
A highly efficient arylation of malonates was reported by Oh et al. in 1999 (Scheme 17 a).[100] In this extensive study, it was determined that addition of a palladium catalyst does not improve the reaction outcome, and that iodoarenes cannot be used. Furthermore, the preference for transfer of the electron-deficient aryl moiety of an unsymmetrical diaryliodonium salt was reaffirmed. An addition–elimination mechanism was proposed to operate in this arylation reaction, as no radical byproducts could be detected (Scheme 17 b).



Scheme 17. Proposed mechanism for the arylation of malonates.

3.1.2. *Asymmetric α-Arylation Strategies*

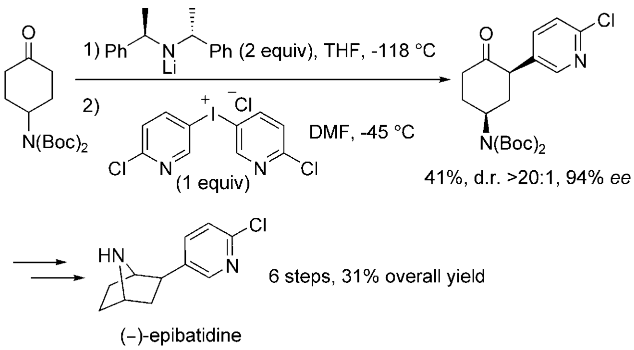
Whilst reports of α-arylation of carbonyl compounds using diaryliodonium salts are numerous, asymmetric variants are conspicuous by their almost complete absence. To date, only two asymmetric α-arylations of this type have been reported. The first of these, published in 1999 by Ochiai et al. utilized chiral diaryliodonium salts based on binap derivatives.[38] Use of the standard *tert*-butoxide/*tert*-butanol system enabled the arylation of β-ketoesters in up to 53% *ee* (Scheme 18). Although the enantiomeric purity of the



Scheme 18. Asymmetric arylation using binap-based iodonium salts.

products is moderate, this remains the only example of an asymmetric α-arylation where the diaryliodonium salt is the source of asymmetric induction.

The second example employs a chiral base to desymmetrize the substrate prior to arylation. This strategy was successfully used by Aggarwal and Olofsson in a short and elegant total synthesis of (−)-epibatidine. (Scheme 19).[53]



Scheme 19. Asymmetric arylation using Simpkins' base.

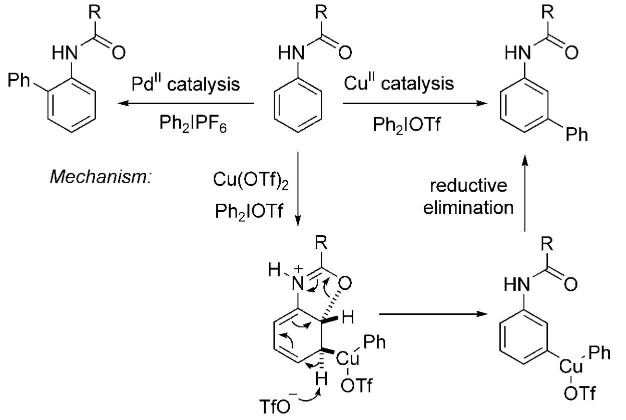
With the recent improvements in preparative methods of diaryliodonium salts, it can be anticipated that new asymmetric arylation routes will follow.

3.2. Metal-Catalyzed Cross-coupling Reactions

Owing to the excellent leaving-group ability of the PhI moiety, diaryliodonium salts are more reactive than aryl halides.[101] Thus, metal-catalyzed cross-coupling reactions involving diaryliodonium salts are becoming more prevalent. In this Section, we present a review of the synthetic applications of these reagents in cross-coupling reactions. The mechanistic aspects of these reactions have been investigated and reviewed in detail[102] and will only be briefly alluded to herein.

3.2.1. *Arylation of Arenes*

The synthesis of biaryls using diaryliodonium salts as one of the coupling partners has become increasingly widespread over the past decade, most recently in cross-coupling reactions involving C–H activation. The ground-breaking *meta*-selective copper-catalyzed C–H bond arylation published by Phipps and Gaunt in 2009 provides a striking example of the utility of diaryliodonium salts in modern organic chemistry.[103] Using 10 mol% $Cu(OTf)_2$ in dichloroethane (DCE), a wide range of *meta*-substituted biaryls could be prepared. The proposed mechanism for this unusual selectivity is illustrated in Scheme 20. It is interesting to note that palladium(II) catalysis leads to the usual *ortho*-substituted product.[104]



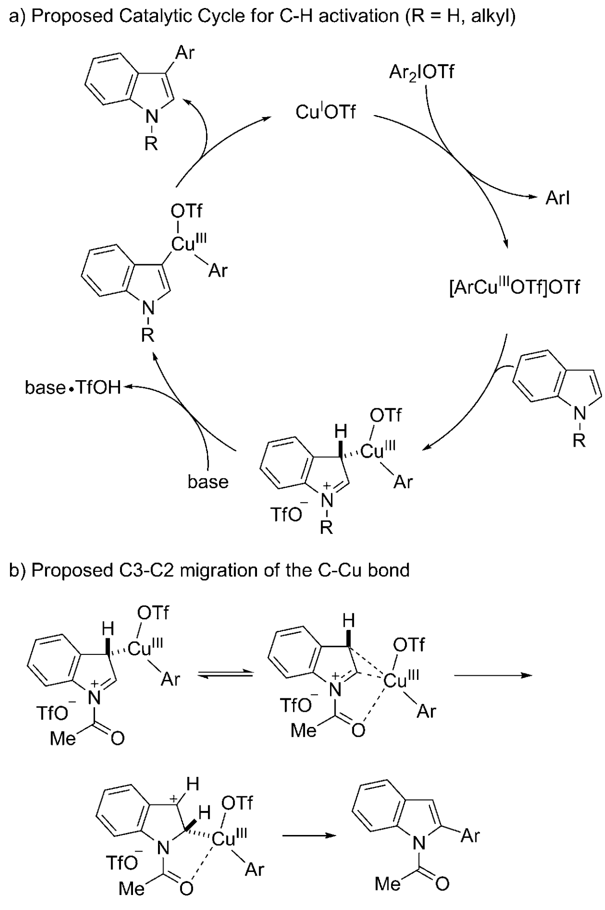
Scheme 20. *meta*-Selective C–H activation/arylation.

Prior to the discovery of this *meta*-selective arylation reaction, Gaunt published a site-selective copper-catalyzed indole arylation in which the regioselectivity could be varied by altering the nature of the substituent on the indole nitrogen. Free *N*-H and *N*-alkyl indoles delivered the 3-arylated product, whereas *N*-acetylindoles afforded the 2-arylated product.[83] The proposed mechanism of the reaction involves a Cu^{III} intermediate which permits a C3→C2 migration of the C–Cu bond when an *N*-acetyl group is present (Scheme 21).

Palladium-catalyzed C–H activation has also been investigated. In 2005, Sanford published a method for the C–H activation/arylation of a range of functionalized arenes and heterocycles (Scheme 22 a).[105] A Pd^{II}/Pd^{IV} catalytic cycle was proposed for this reaction. In the same year, Daugulis and Zaitsev reported the *ortho*-arylation of anilides using aryl iodides or diphenyliodonium hexafluorophosphate (Scheme 22 b).[104] Reactions employing the iodonium salt only needed palladium acetate as the catalyst, whereas aryl iodides required the addition of stoichiometric quantities of silver acetate. The C–H activation/arylation method using diaryliodonium salts has also been applied to the arylation of benzodiazepines[106] and in the synthesis of 3-(1-arylmethylene)oxindoles.[107]

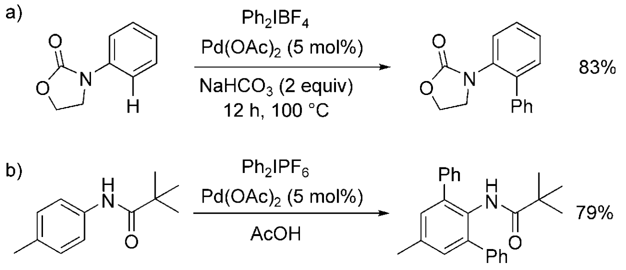
Sanford and co-workers developed a palladium-catalyzed 2-arylation of indoles using diaryliodonium salts (Scheme 23).[108] This mild and facile procedure proved compatible with free *N*-H indoles, with no competing N-arylation reaction. The suggested mechanism invoked Pd^{II}/Pd^{IV} catalysis, and rapid migration from C3→C2 ensured that the 3-arylated indole was not formed. It was also possible to generate the key diaryliodonium species in situ from the corresponding (diacetoxyiodo)arene and an arylboronic acid.

A vast array of metal catalysts and organometallic coupling partners has been used in the cross-coupling of diaryliodonium salts to form biaryl products. The addition of

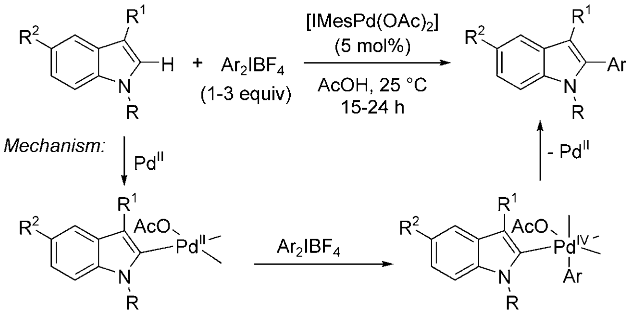

a) Proposed Catalytic Cycle for C-H activation (R = H, alkyl)

b) Proposed C3-C2 migration of the C-Cu bond

Scheme 21. a) Catalytic cycle for copper-catalyzed arylation and b) C3–C2 bond migration.

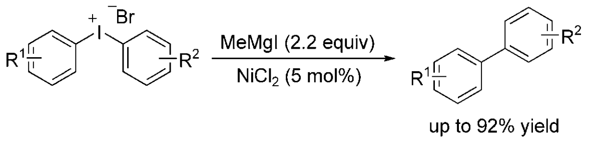


Scheme 22. Biaryl synthesis through C–H activation/arylation a) by Sanford, and b) by Daugulis.



Scheme 23. Proposed Pd^{II}/Pd^{IV} catalytic cycle for the 2-arylation of indoles. IMes = 1,3-dimesitylimidazol-2-ylidene.

Grignard reagents without metal catalysis was largely unsuccessful.[56] The combination of methylmagnesium iodide and nickel(II) chloride in a Kumada coupling proved better, although the application of this method was limited by the mixture of products obtained from unsymmetrical salts (Scheme 24).[109]



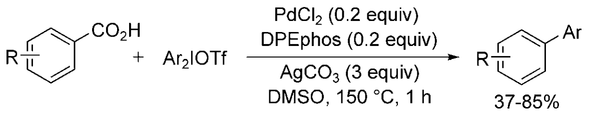
Scheme 24. Mg/Ni-mediated biaryl synthesis.

A double metal-catalyzed coupling of arylmagnesium bromides with diaryliodonium tetrafluoroborates has been reported by Wang and Chen.[110] A mixture of palladium and zinc catalysts was employed to prepare a range of biaryls in excellent yields; in the absence of zinc chloride poor yields were obtained. Similarly, it was found that directed *ortho*-metallation of pyridine-*N*-oxides with a Grignard reagent followed by treatment with diphenyliodonium triflate in the presence of [Pd(PPh$_3$)$_4$] and ZnCl$_2$ delivered the 2-phenylated product.[111] Yamazaki and co-workers reported a reductive coupling of diaryliodonium salts by treatment with a stoichiometric quantity of zinc powder in the presence of a palladium catalyst, furnishing biaryls in excellent yields.[112] Conducting the same reductive coupling under an atmosphere of carbon monoxide afforded arylketones in moderate yield.[113]

Copper-catalyzed arylations have been developed by Kang and co-workers, including both arylation and carbonylative arylation of arylstannanes, and arylation of arylboranes.[114] Nickel-catalyzed arylation and carbonylative arylation of both aryl- and alkynylstannanes were also reported.[115]

Suzuki-type cross-couplings using arylboronic acids can proceed with catalyst loadings of 0.2 mol% [Pd(PPh$_3$)$_4$] at room temperature and in only 5 min, furnishing biaryls in 87–99% yield.[116] Tetraarylborates also make suitable substrates for this reaction, yielding biaryl products in only 20 s under microwave irradiation.[117] Carbonylative arylation has also proved successful, ketones being prepared in good to excellent yields by the reaction of arylstannanes and diaryliodonium salts.[118] More exotic organometallic reagents, such as bismuth[119] and tellurium[120] compounds, have also been investigated.

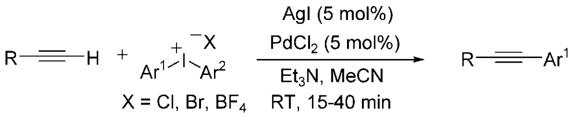
An alternative strategy to both organometallic coupling partners and C–H activation is a decarboxylative coupling as demonstrated by Becht and Le Drian. Using this method, a vast range of highly substituted, nonsymmetrical biaryls could be readily prepared (Scheme 25).[121]



Scheme 25. Decarboxylative coupling strategy.

3.2.2. *Arylation of Alkynes*

Arylation of both aliphatic and aromatic alkynes with diaryliodonium salts has been successfully achieved using a range of transition metals. A recent example of such a reaction is the palladium- and silver-catalyzed method developed by Zhu and co-workers. This mild procedure was applicable to a wide range of aliphatic and aromatic alkynes (Scheme 26).[122] With unsymmetrical diaryliodonium salts, the most electron-rich aryl moiety was selectively transferred.

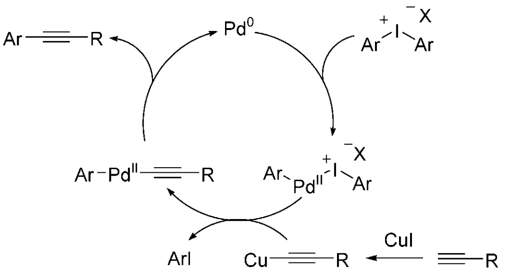


Scheme 26. Pd/Ag-catalyzed Sonogashira reaction.

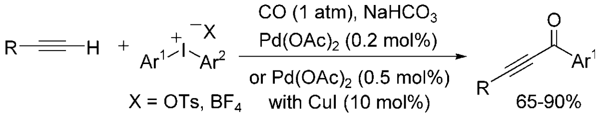
Some years prior to this, a copper-catalyzed variant had been published by Kang et al. using 10 mol% of copper(I) iodide, furnishing the desired products in only 30 min at room temperature.[123] This method was applicable to a wide range of functionalized terminal acetylenes, including acetylinic alcohols and esters. Both copper-catalyzed coupling and carbonylative arylation of alkynylstannanes and diaryliodonium salts had previously been reported by the same group.[114,118] The carbonylative cross-coupling was also successful for aryl and alkenyl substrates.

Alkynes bearing electron-withdrawing groups are generally unreactive in metal-catalyzed couplings with aryl iodides, and diaryliodonium salts provide a means to circumvent this problem. A mixture of palladium and copper catalysts were used by Radhakrishnan and Stang in conjunction with diphenyliodonium tosylate or triflate in the phenylation of enynes, propargylic ketones, and propargylic esters.[124] It was noted that the most electron-rich aryl moiety was transferred to the product when unsymmetrical diaryliodonium salts were used. The proposed mechanism is illustrated in Scheme 27. The same catalyst mixture was used by Beletskaya and co-workers to arylate terminal acetylenes at room temperature in only 10 min.[125]

In addition to the above examples of Sonogashira-type cross-couplings, carbonylative cross-coupling reactions of terminal alkynes catalyzed by palladium acetate have been developed (Scheme 28).[126] Addition of 10 mol% copper(I) iodide was necessary when aliphatic alkynes were employed. Again, the most electron-rich aryl moiety was transferred in unsymmetrical salts.

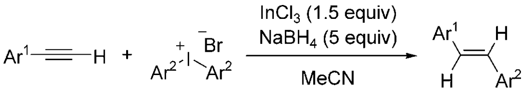


Scheme 27. Stang's proposed mechanism for the $[Pd(PPh_3)_2Cl_2]$/CuI-catalyzed cross-coupling of alkynes and enynes.



Scheme 28. Carbonylative cross-coupling of terminal alkynes with diaryliodonium salts.

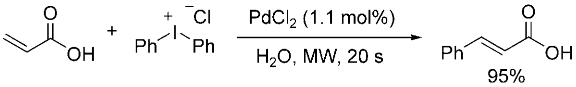
A reductive arylation of terminal alkynes using indium trichloride and sodium borohydride was reported by Xue and co-workers in 2006 (Scheme 29).[127] The reaction was successful for a wide range of aromatic alkynes, furnishing the (*E*)-alkene as the major product with minor amounts of the (*Z*)- and 1,1-substituted alkenes as byproducts.



Scheme 29. Reductive phenylation of aromatic alkynes.

3.2.3. *Arylation of Alkenes*

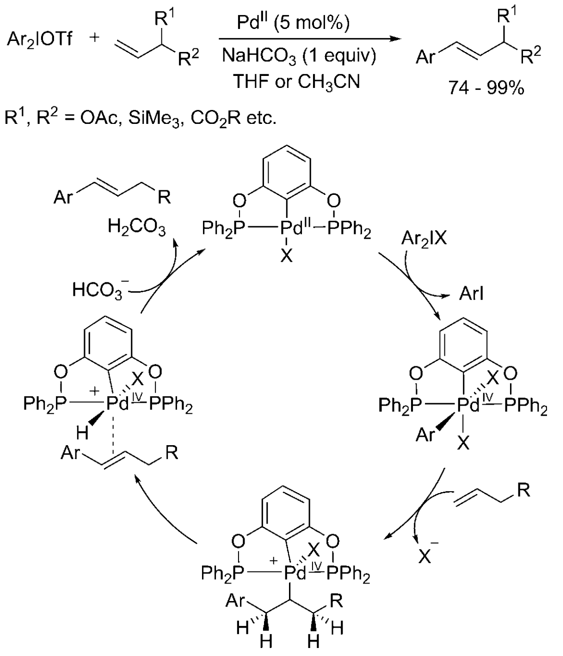
Known for over a decade, the arylation of alkenes using diaryliodonium salts encompasses a range of substrates and is remarkably facile in many cases. Zhu and co-workers reported a Heck-type reaction requiring less than one minute reaction time under aqueous conditions. This procedure was used to prepare a number of *trans*-cinnamic acids and *trans*-cinnamyl alcohols in excellent yields (Scheme 30).[128] They also noted that when an unsymmetrical iodonium salt was used, the most electron-rich arene was transferred to the alkene. A similar Heck-type arylation was performed on methyl vinyl ketone.[129]



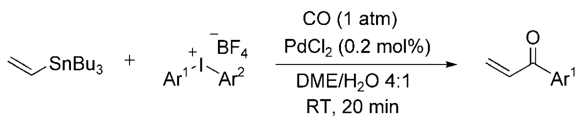
Scheme 30. Synthesis of *trans*-cinnamic acid.

Szabó and co-workers used palladium pincer complexes in the coupling of alkenes with diaryliodonium triflates, which enabled the development of a mild method for the arylation of allylic acetates and electron-rich alkenes (Scheme 31).[130] The reaction was proposed to proceed by a Pd^{II}/Pd^{IV} catalytic cycle, and palladium acetate was also found to be an efficient catalyst for the transformation.

Carbonylative coupling of vinylstannanes with diphenyliodonium triflate using palladium(II) chloride as the catalyst led to the formation of vinyl aryl ketones in high yields within 20 min at room temperature (Scheme 32).[118] A copper-catalyzed variant of this reaction is also known,[114] as is a non-carbonylative Stille coupling.[131]

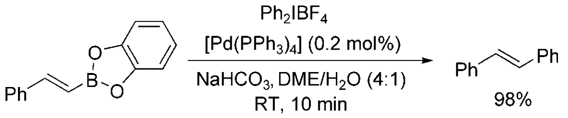


Scheme 31. Catalysis with palladium pincer complexes.



Scheme 32. Carbonylative Stille-type coupling reaction.

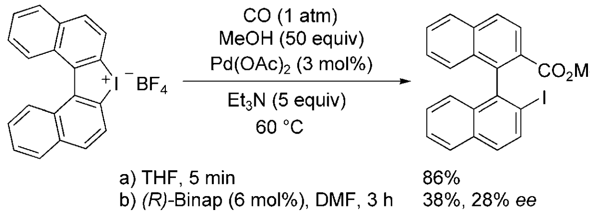
In 1996, Kang et al. published a Suzuki-type cross-coupling using vinylboranes and only 0.2 mol% $[Pd(PPh_3)_4]$ as the catalyst, furnishing the desired product in 10 min at room temperature (Scheme 33).[116] This method was also successful for aryl–aryl couplings (see Section 3.2.1).



Scheme 33. Suzuki reaction employing diphenyliodonium tetrafluoroborate.

3.2.4. *Arylation of Other Substrates*

In addition to the more conventional arylation substrates discussed above, a number of other applications of diaryliodonium salts have come to light. The synthesis of esters by palladium-catalyzed reaction of alcohols with diaryliodonium salts under a carbon monoxide atmosphere was reported in 1998.[132] A similar coupling was subsequently developed by Hayashi and co-workers, in which a dinaphthyliodonium salt was treated with methanol under a carbon monoxide atmosphere, furnishing the corresponding binaphthyl ester in 86% yield (Scheme 34a).[129] Conducting the reaction in the presence of (*R*)-binap gave the product with moderate enantioselectivity (Scheme 34b).

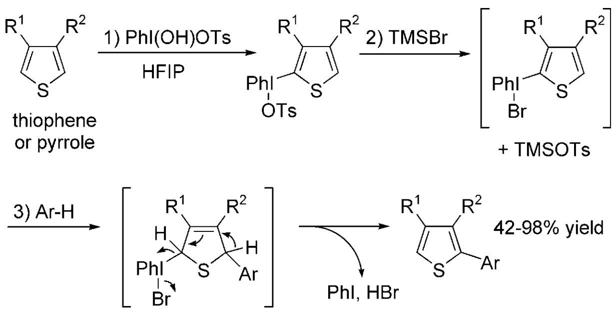


Scheme 34. Carbonylative coupling of dinaphthyliodonium tetrafluoroborate.

Palladium(0)-catalyzed arylation of acylzirconocene chlorides,[133] allenes,[134] allenyl *N*-tosylcarbamates,[135] α-allenic alcohols,[136] allylic cyclic carbonates,[137] and aryl-, alkenyl, and alkynylfluorosilanes[138] have been reported by Kang and co-workers. Allylic alcohols have been arylated using a range of symmetrical diaryliodonium salts with a polymer-bound palladium catalyst.[139] Chen and Chen reported the preparation of polymeric diaryliodonium salts and their subsequent cross-coupling with salicylaldehydes.[17] Chromium(II)-mediated umpolung reactions of diaryliodonium tetrafluoroborates with aldehydes were investigated in detail by Ochiai.[140] Using this method, a range of aryl alcohols could be prepared in moderate yield.

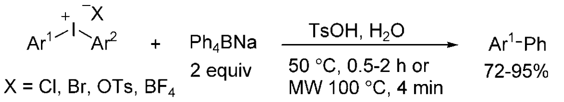
3.3. *Metal-Free Cross-coupling Reactions*

Despite the current trend towards developing environmentally benign synthetic methods, relatively few transition-metal-free cross-couplings using diaryliodonium salts have been reported. In 2009, Kita and co-workers reported a metal-free oxidative cross-coupling reaction of heteroarenes and electron-rich arenes through C–H activation. The reaction proceeds by in situ formation of a diaryliodonium salt from an electron-rich heteroarene and Koser's reagent. Sequential addition of trimethylsilyl bromide and an electron-rich aromatic coupling partner then furnished the biaryl product (Scheme 35).[141] This mild route is tolerant of a wide range of arenes and heterocycles. It is proposed that the intermediate diaryliodonium species undergoes activation on addition of TMSBr, followed by hydroarylation with the added arene.



Scheme 35. Kita's oxidative cross-coupling reaction. HFIP = hexafluoroisopropanol.

Yan and co-workers have been prolific in the area of metal-free cross-coupling reactions, their results include the synthesis of biphenyls by the reaction of sodium tetraphenylborate and various diaryliodonium salts in aqueous media (Scheme 36).[142] They report that diaryliodonium bromides react much more efficiently than the corresponding tetrafluoroborate salts, giving both increased yields and reduced reaction times. It was again found that the most electron-rich arene was transferred when unsymmetrical diaryliodonium salts were used, in keeping with the findings in transition-metal-catalyzed couplings.[124,126,128] An obvious drawback of this method is the necessity for one of the aryl moieties to be a phenyl group, limiting the range of biaryls that can be prepared.



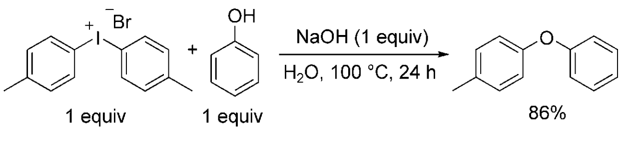
Scheme 36. Yan's transition-metal-free cross-coupling reactions.

3.4. Arylation of Heteroatom Nucleophiles

The use of diaryliodonium salts in arylation of heteroatom nucleophiles has been known for more than 80 years. As with the initial work on α-arylation of carbonyl compounds, Beringer's group paved the way for future discoveries. In 1953, the phenylation of a wide range of organic and inorganic bases including alkoxides, phenoxides, benzoates, nitrites, sulfonamides, amines, sulfites, sulfinates, and cyanides was achieved in moderate to good yields.[143] The reactions were predominantly run in aqueous solution under reflux for several hours. This research provided a foundation for many subsequent investigations, including the copper(I)-catalyzed reaction of diphenyliodonium-2-carboxylate with a range of nucleophiles.[144] More recently, metal-catalyzed arylation methods have been developed and were reviewed by Ley and Thomas in 2003.[145]

3.4.1. Arylation of Oxygen Nucleophiles

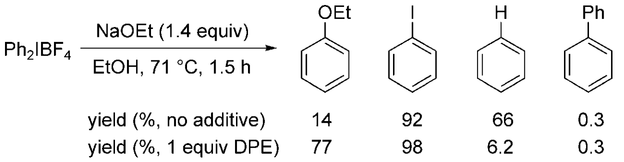
A decade after Beringer's investigation, Crowder et al. reported the preparation of diaryl ethers using a similar method. Initial studies showed that the highest yield of diphenyl ether (72 %) was obtained by refluxing diphenyliodonium bromide in water with an equimolar amount of sodium phenoxide. Substituted phenols gave diaryl ethers in 63–86 % yields (Scheme 37).[146]



Scheme 37. Arylation of sodium phenoxides.

This method has been applied to the synthesis of many polybrominated diphenyl ethers, which have a range of industrial applications.[147] Polymer-supported diaryliodonium salts have been used to prepare diaryl ethers and thioethers in moderate to good yields by reaction with either sodium aryloxides or arylthiolates.[18]

In 1975, a detailed investigation into the reaction of diaryliodonium salts with sodium alkoxides was published by McEwen and co-workers.[148] It was found that treatment of diphenyliodonium tetrafluoroborate with sodium ethoxide in ethanol for 90 min yielded four products (Scheme 38). Addition of 1,1-diphenylethylene (DPE) as a radical trap significantly altered the product distribution and thus a radical mechanism was proposed to explain the formation of the byproducts.[149]

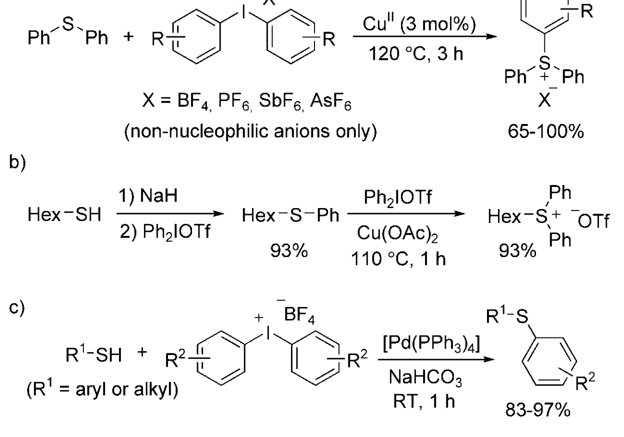


Scheme 38. Products obtained from the reaction between diphenyliodonium tetrafluoroborate and sodium ethoxide.

Diaryliodonium salts have also been employed in the formation of esters via benzynes (see Section 3.5.2).

3.4.2. Arylation of Sulfur and Selenium Nucleophiles

In 1978, Crivello and Lam reported a copper(II)-catalyzed arylation of both diarylsulfides and diarylselenides using a range of symmetrical diaryliodonium salts. The reaction delivered triarylsulfonium and -selenonium salts in good to excellent yields (Scheme 39 a).[60] More recently, the phenylation of thiols and thioethers was described by Krief et al. (Scheme 39 b).[150] A high-yielding palladium-catalyzed preparation of thioethers from thiols using symmetrical diaryliodonium salts was developed by Wang and Chen in 2001 (Scheme 39 c).[151]

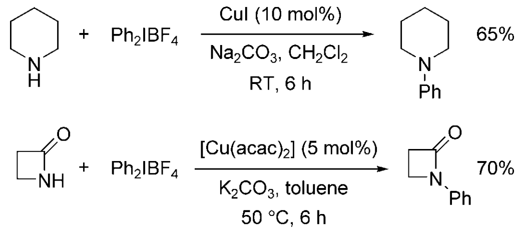


Scheme 39. Arylation of thiols and thioethers.

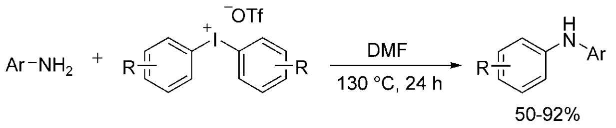
Arylation of sulfur nucleophiles using diaryliodonium salts is not limited to the preparation of thioethers and sulfonium species. *S*-aryl thiocarboxylates were prepared from the corresponding potassium thiocarboxylate salt in moderate to good yields using symmetrical diaryliodonium chlorides and iodides.[152] Arylation of potassium thiosulfonates to afford *S*-aryl thiosulfonates has also been reported.[153] In addition, it is possible to synthesize unsymmetric diaryl selenides by treating sodium areneselenolates with a diaryliodonium salt.[154] Aryl esters of dithiocarbamic acids were prepared by the reaction of the sodium dithiocarbamides with various symmetrical diaryliodonium chlorides, bromides, iodides, and acetates.[155] It was reported that the use of chloride and acetate salts led to superior yields.

3.4.3. *Arylation of Nitrogen Nucleophiles*

While heterocycles have formed the bulk of the N-arylation investigations, it is nevertheless possible to arylate aliphatic substrates. For example, Kang et al. reported a method suitable for arylating secondary aliphatic amines, aromatic amines, azoles, and amides using either copper(I) iodide or [Cu(acac)$_2$] (Scheme 40).[156] Palladium-mediated phenylation of secondary amines using diphenyliodonium tetrafluoroborate has also been reported.[157] More recently, Carroll and Wood published a transition-metal-free route to diarylamines in good yields where they also investigated the influence of the anion and chemoselectivity aspects (Scheme 41).[158]

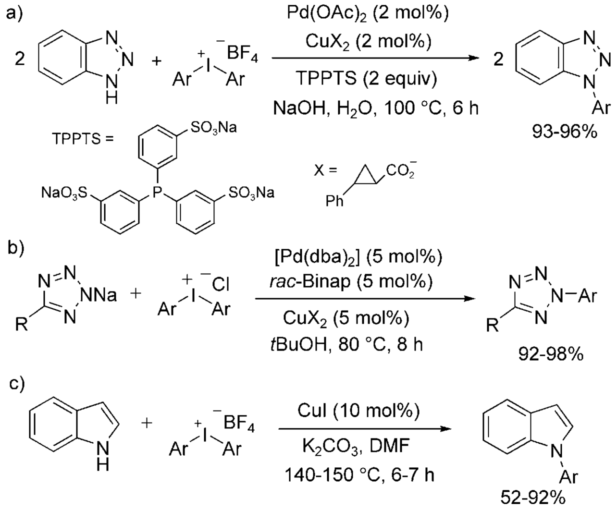


Scheme 40. Kang's arylation of aliphatic amines and amides.



Scheme 41. Metal-free arylation of anilines.

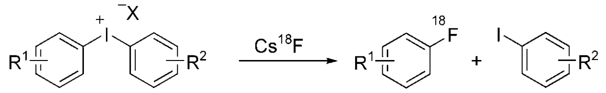
Efforts to arylate nitrogen nucleophiles using diaryliodonium salts have mainly, although not exclusively, focused on nitrogen-containing heterocycles. Copper catalysis also features prominently in this area of research. Davydov and Beletskaya published N-arylation methods for benzotriazoles and tetrazoles (Scheme 42 a,b).[159] N-arylation of both indoles[160] and benzimidazoles[161] was developed by Zhou and Chen in moderate to good yields (Scheme 42 c). For arylation of indoles in the 2- or 3-position, see section 3.2.1.



Scheme 42. Approaches to arylation of benzotriazoles, tetrazoles, and indoles.

3.4.4. *Arylation of Fluorine Nucleophiles*

Fluorine-18 labeled arenes and heterocycles are used in positron-emission tomography (PET). The synthesis of such radiolabeled compounds through nucleophilic attack of [^{18}F]fluoride on diaryliodonium salts has been studied extensively by Carroll and Widdowson (Scheme 43).[162] Advantages of using diaryliodonium salts as precursors are that arenes with a range of substitution patterns can be readily prepared, and that the need for reagents such as [^{18}F]F$_2$ is circumvented. Mechanistic aspects of this reaction have recently been reviewed,[163] and the effect of the counterion and reaction kinetics have been investigated in detail by Coenen and co-workers.[164]



Scheme 43. Preparation of radiolabeled ligands for positron-emission tomography.

3.4.5. *Arylation of Other Heteroatom Nucleophiles*

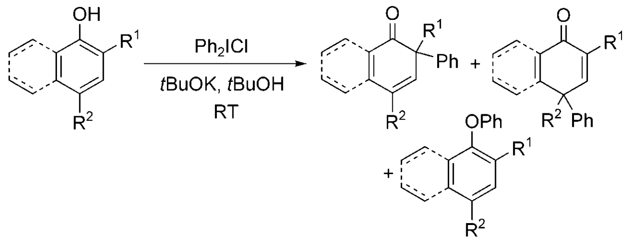
There are a limited number of publications describing the arylation of other heteroatom nucleophiles. *O*,*O*-Dialkyl phosphites can be arylated using 5 mol% [Pd(PPh$_3$)$_4$] as the catalyst.[165] Reaction of sodium telluride (Na$_2$Te) with symmetrical diaryliodonium salts affords symmetrical diaryltellurides in high yields.[166] Sodium aryltellurides (NaTeAr) react with diaryliodonium salts to give unsymmetrical diaryltellurides.[167] Treatment of diphenyliodonium triflate with metallic ytterbium in the presence of methylphenylsilane yields methyldiphenylsilane, thus arylation of silicon is also possible.[168]

3.5. Other Applications

Diaryliodonium salts have found applications in a range of areas, which are briefly outlined below. The biologically activity of diaryliodonium salts is reviewed elsewhere.[5,6]

3.5.1. Dearomatization of Phenols

Ozanne-Beaudenon and Quideau discovered a novel application of diaryliodonium salts as reagents for the dearomatization of phenols.[169] In their elegant procedure, a wide range of substituted phenols could be dearomatized (Scheme 44). It was found that the presence of a small electron-donating substituent at either the *ortho* or *para* position of the phenol determines the regioselectivity of the reaction. A detailed investigation of the reaction mechanism was conducted and it was determined that a radical mechanism is not operative. O-phenylation was observed for some substrates and this was proposed to be the result of an intramolecular ligand coupling.

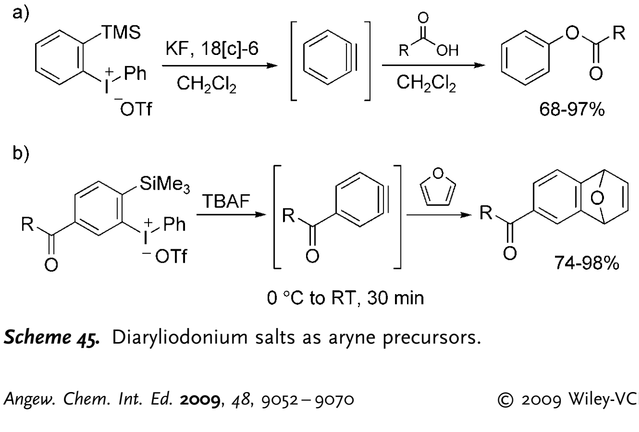


Scheme 44. Dearomatization of phenols.

3.5.2. Benzyne Precursors

(Phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate is a mild and efficient benzyne precursor that can be readily prepared on a multigram scale.[170] It is a crystalline, non-hygroscopic, air-stable solid and can be used at room temperature under neutral conditions. Addition of a fluoride source, for example, tetrabutylammonium fluoride liberates the aryne, which can then be trapped using a range of species.[171]

This approach was used by Xue and Huang in the O-arylation of a range of carboxylic and sulfonic acids (Scheme 45 a).[172] Kitamura et al. used an acylated benzyne precursor in cycloadditions of acylbenzynes and furan (Scheme 45 b).[173] Various other diaryliodonium salts, including heteroaromatic ones, have also been employed as benzyne precursors.[174]



Scheme 45. Diaryliodonium salts as aryne precursors.

3.5.3. Macromolecular Chemistry

Stang and co-workers have been particularly prolific in the application of diaryliodonium salts in macrocyclic chemistry. Various salts have been employed in the synthesis of macrocycles,[175] molecular boxes,[176] and chiral macrocyclic molecular squares.[177] Some general structures are illustrated in Figure 2.

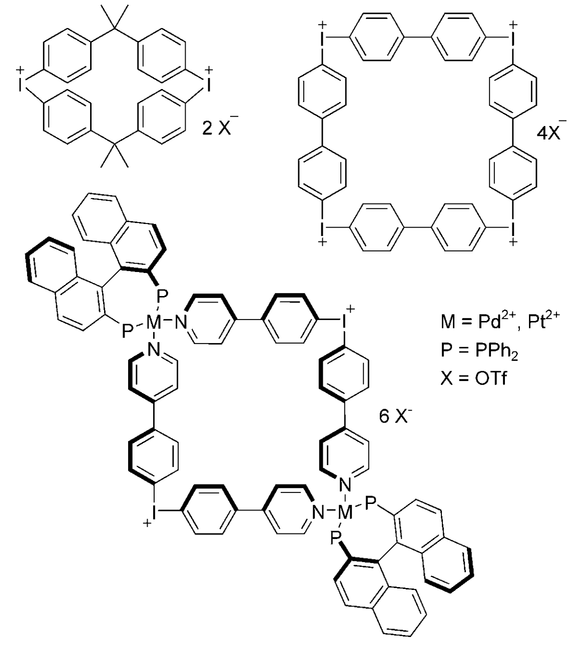
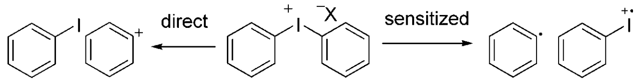


Figure 2. Stang's use of diaryliodonium salts in macrocyclic applications.

3.5.4. Photochemistry and Polymerization

The photochemical properties of diaryliodonium salts have been known for a considerable length of time,[178] and this has led to their widespread use as cationic photoinitiators,[179] for example, in the polymerization of epoxides[180] and oxetanes.[181] Diaryliodonium salts are especially desirable in industrial applications as they do not contain heavy metals, do not cleave into toxic byproducts, and they can be prepared with a range of substituents to aid solubility. A recent application is the use of diaryliodonium salts to graft layers onto carbon electrodes.[182]

A detailed investigation into the photochemical properties of diaryliodonium salts was carried out by Dektar and Hacker in 1990, who isolated the products obtained on photolysis of diphenyliodonium triflate in various solvents.[183] It was surmised that direct photolysis of the salt favored heterolytic cleavage, yielding the phenyl cation and iodobenzene. Sensitized photodecomposition led to homolytic cleav-



Scheme 46. Direct versus sensitized photolysis.

age to the phenyl radical and the iodobenzene radical cation (Scheme 46).

4. Summary and Outlook

The facile and efficient synthetic routes to diaryliodonium salts that have recently been developed have obviated the need for toxic reagents and potentially explosive intermediates in the synthesis of these compounds. A great variety of structures can now be obtained in an operationally simple and efficient manner. It is hoped that these advances will enable more of these compounds to become commercially available, which is necessary for applications in industry.

The application of diaryliodonium salts in organic chemistry is a rapidly emerging area with many exciting developments over the last few years. Future challenges include development of more atom-efficient reactions, as a stoichiometric amount of iodoarene is formed as a byproduct. A catalytic process, where the diaryliodonium salts is formed in situ, would further lessen the environmental impact of these reactions. Another intriguing avenue of research is the use of diaryliodonium salts in asymmetric arylation reactions.

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