3

Hypervalent Iodine Reagents in Organic Synthesis

Compounds of polyvalent iodine have found broad practical application in organic synthesis due to their diverse reactivity combined with benign environmental character and commercial availability. Particularly useful are the organic derivatives of λ^3- and λ^5-iodanes, commonly known as hypervalent iodine reagents. Several inorganic compounds of trivalent, pentavalent and heptavalent iodine have also found wide application in organic chemistry and can be included in this class of reagents. Numerous aryl-substituted λ^3- and λ^5-iodanes, aryliodonium salts and inorganic iodates and periodates are commercially available and used as common reagents in organic synthesis. Typical synthetic applications of these reagents include the following: oxidative halogenation of organic substrates, oxidative functionalization of unsaturated compounds, oxidative conversions of C—H to C—O bonds, various oxidative rearrangements and numerous reactions resulting in the formation of new C—C, C—N and other C—heteroatom or heteroatom—heteroatom bonds [1–3]. Hypervalent iodine compounds have found a particularly important application as selective reagents in the total synthesis of natural products [4], as they are efficient alternatives to toxic and expensive heavy metals for a large range of synthetic transformations. An overview of general principles of reactivity of hypervalent iodine compounds can be found in Section 1.5 of this book. This chapter summarizes specific synthetic applications of polyvalent iodine compounds.

3.1 Reactions of Iodine(III) Compounds

The general reactivity pattern of λ^3-iodanes, $ArIX_2$, is determined by the hypervalent, loose nature of I—X bonds and by a distinct positive charge on the iodine atom. These structural features are responsible for the enhanced electrophilic properties of $ArIX_2$ and explain such typical pathways as ligand exchange and reductive ligand transfer in their reactions with organic substrates (Section 1.5). Owing to these properties, hypervalent iodine(III) compounds have found broad application in organic synthesis as selective oxidants and electrophilic ligand transfer reagents. The growing interest in synthetic application of these compounds is also explained by their ready availability and absence of toxic properties and associated environmental concerns. Synthetic applications of hypervalent iodine(III) compounds have previously been summarized in several books [1–3] and numerous comprehensive reviews [4–12].

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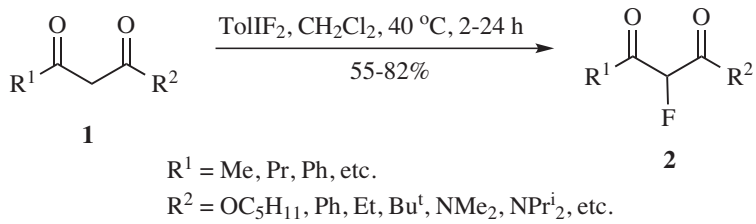


1 2

Scheme 3.1

3.1.1 Fluorinations

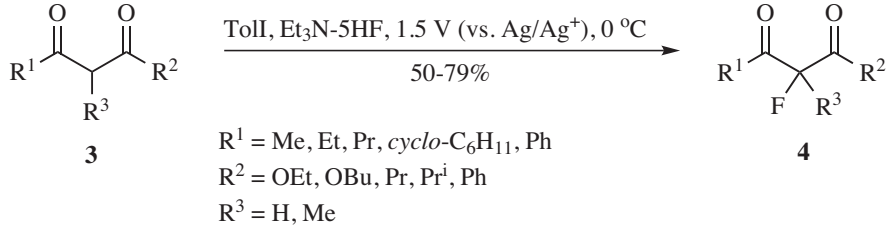
Various fluorinated compounds can be prepared by the fluorination of organic substrates with (difluoroiodo)arenes, which are powerful and selective electrophilic fluorinating reagents. Comparison of several $ArIF_2$ in fluorination reactions revealed that 4-alkyl-substituted (difluoroiodo)benzenes, 4-$MeC_6H_4IF_2$ and 4-$Bu^tC_6H_4IF_2$, are the preferred reagents, owing to their facile preparation and purification by crystallization, relatively high stability and solubility in organic solvents [13–16]. 4-(Difluoroiodo)toluene (also known as difluoroiodotoluene, $TolIF_2$) has become one of the commonly used fluorinating reagents [17].

β-Ketoesters and β-dicarbonyl compounds can be selectively fluorinated at the α-position by difluoroiodotoluene [18–20]. In a specific example, the monofluorinated products **2** can be prepared from β-ketoesters, β-ketoamides, or β-diketones **1** in good yields using difluoroiodotoluene under mild conditions (Scheme 3.1) [20]. A practical and convenient variation of the procedure for fluorination of 1,3-dicarbonyl compounds consists of the generation of $PhIF_2$ *in situ* from aqueous hydrofluoric acid and iodobenzene in dichloromethane [21]. For example, the reaction of ethyl benzoylacetate with the reagent system of aqueous HF and iodobenzene in CH_2Cl_2 affords ethyl 2-fluoro-2-benzoylacetate in 98% yield [21].

A similar fluorination can be performed electrochemically using difluoroiodotoluene as the mediator generated *in situ* from iodotoluene. Thus, the electrolysis of a 1 : 1 mixture of iodotoluene and various β-dicarbonyl compounds **3** in Et_3N/5HF in an undivided cell under constant potential affords the respective α-fluoro-β-dicarbonyl compounds **4** in good yields (Scheme 3.2) [19].

Ketones cannot be directly fluorinated by (difluoroiodo)arenes; however, α-fluoroketones can be prepared by the reaction of silyl enol ethers with difluoroiodotoluene in the presence of $BF_3{\cdot}OEt_2$ and the Et_3N–HF complex [22]. Some steroidal silyl enol ethers can be converted into the respective α-fluoroketones in a moderate yield [23].

Several synthetically useful fluorinations of various organosulfur compounds with difluoroiodotoluene have been reported [13, 24–26]. A clean and selective preparation of *gem*-difluorides **6** can be achieved by the



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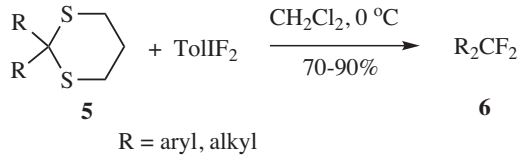
Scheme 3.2



Scheme 3.3

reaction of difluoroiodotoluene with dithioketals **5** (Scheme 3.3) [13]. This fluorination can also be performed electrochemically using a difluoroiodoarene as the in-cell mediator generated *in situ* from catalytic amounts (0.05–0.2 equiv) of 4-methoxyiodobenzene [27].

α-(Phenylthio)acetamides **7** are fluorinated in the α-position to give products **8** when treated with difluoroiodotoluene under mild conditions (Scheme 3.4) [24, 28].

Under similar conditions α-phenylthio esters **9** afford fluorides **10** (Scheme 3.5) [25]. The mechanism of this Pummerer-type reaction involves initial nucleophilic addition of the sulfur atom to the electrophilic iodine center to form the iodosulfonium salt **11.** The liberated fluoride anion acts as a base with resultant formation of the classical Pummerer intermediate **12.** Subsequent trapping of cation **12** with fluoride anion yields the final product **10** (Scheme 3.5) [25].

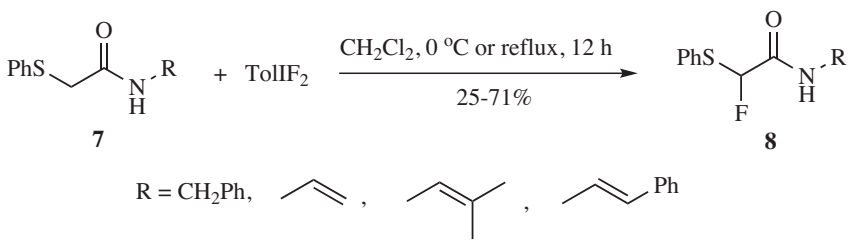
Addition of a second equivalent of difluoroiodotoluene in this reaction (Scheme 3.5) affords α,α-difluoro sulfides and the reaction with three equivalents of $TolIF_2$ leads to α,α-difluoro sulfoxides. This sequential fluorination–oxidation reaction has been exploited in the one-pot synthesis of 3-fluoro-2(5*H*)-furanone starting from (3*R*)-3-fluorodihydro-2(3*H*)-furanone [29].

The reaction of α-phenylthio lactones **13** with two equivalents of difluoroiodotoluene results in fluorination–oxidation to give α-fluoro sulfoxides **14,** which then undergo thermal *syn* elimination to produce vinyl fluorides **15** (Scheme 3.6) [25].

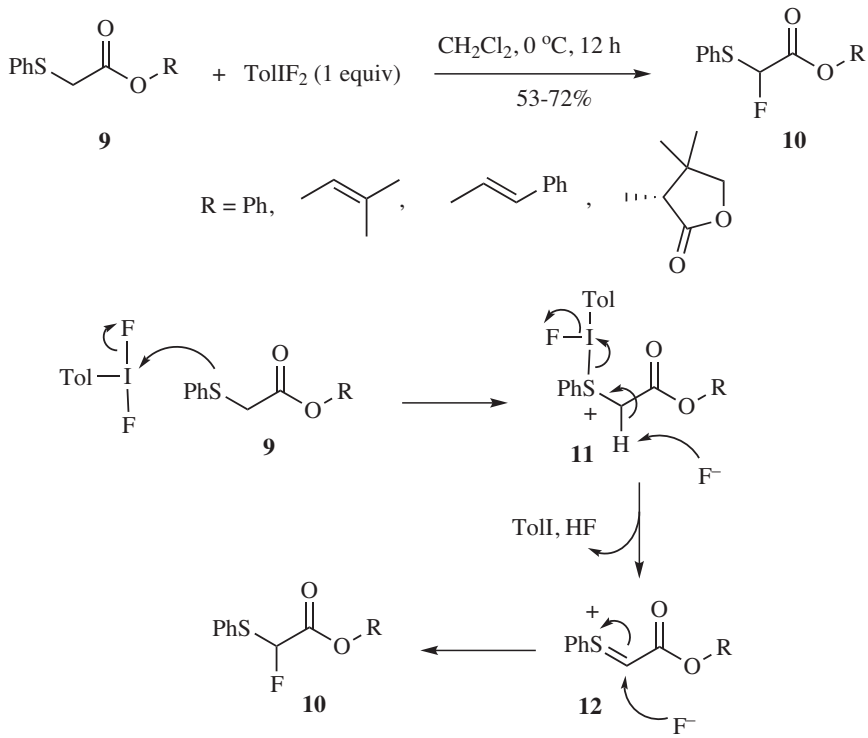
Treatment of the readily available thio- and seleno-glycosides with difluoroiodotoluene gives the corresponding fluoroglycosides in moderate to good yields [15, 26]. In a typical representative example, treatment of the glucose derivative **16** with difluoroiodotoluene under mild conditions affords anomeric fluoroglycosides **17** and **18** in a 3 : 2 ratio (Scheme 3.7) [26].

The reaction of 4-*tert*-butyl(difluoroiodo)benzene with esters of cephalosporin V (**19**) is solvent-dependent: the major product in dichloromethane is fluoroazetidine **20,** while the same reactants in acetonitrile afford oxazoline disulfide **21** (Scheme 3.8) [16].

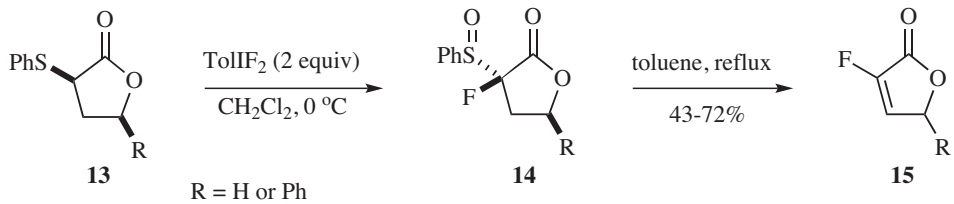
The monofluorination of a series of α-acceptor-substituted selenides **22** using difluoroiodotoluene (Scheme 3.9) has been reported [30]. Although the yields of products **23** are only moderate, the reactions are usually very clean and, under the reaction conditions used, no further oxidized products are observed.



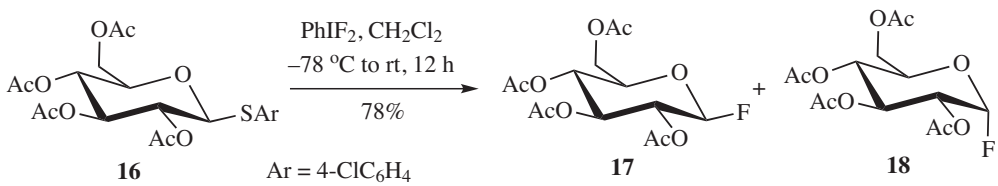
Scheme 3.4



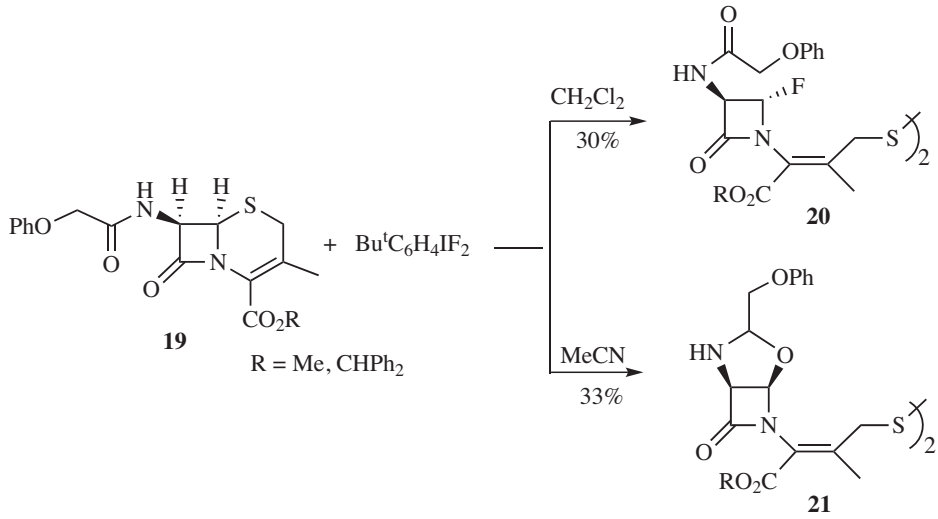
Scheme 3.5



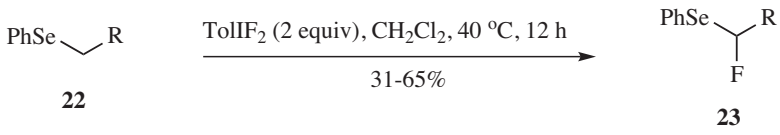
Scheme 3.6



Scheme 3.7



Scheme 3.8

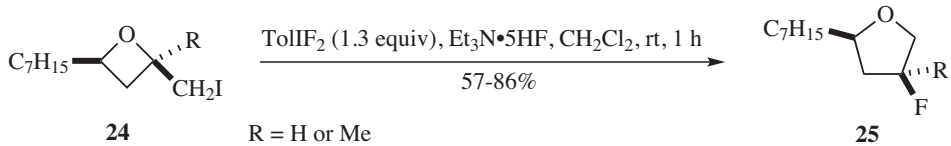


R = CO_2Et, CO_2Ph, $CO_2CH_2CH{=}CH_2$, CONHMe, $CONMe_2$, CN, etc.

Scheme 3.9

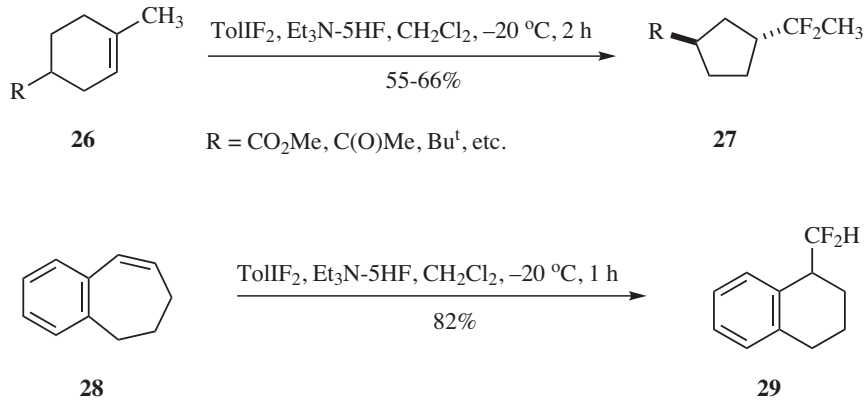
Fluorinated five- to seven-membered cyclic ethers have been stereoselectively synthesized from iodoalkyl substituted four- to six-membered cyclic ethers by fluorinative ring-expansion reaction using difluoroiodotoluene [31]. Scheme 3.10 shows a specific example of a fluorinative ring-expansion reaction of oxetanes **24** leading to five-membered cyclic ethers **25** [31].

(Difluoroiodo)arenes react with aryl-substituted alkenes to afford the rearranged, geminal difluorides, owing to the migration of the aryl group [32, 33]. Likewise, the reaction of substituted cyclic alkenes with difluoroiodotoluene and Et_3N/5HF results in a fluorinative ring-contraction with the selective formation of difluoroalkyl substituted cycloalkanes. Thus, the fluorination of 1-methylcyclohexene derivatives **26** affords



R = H or Me

Scheme 3.10



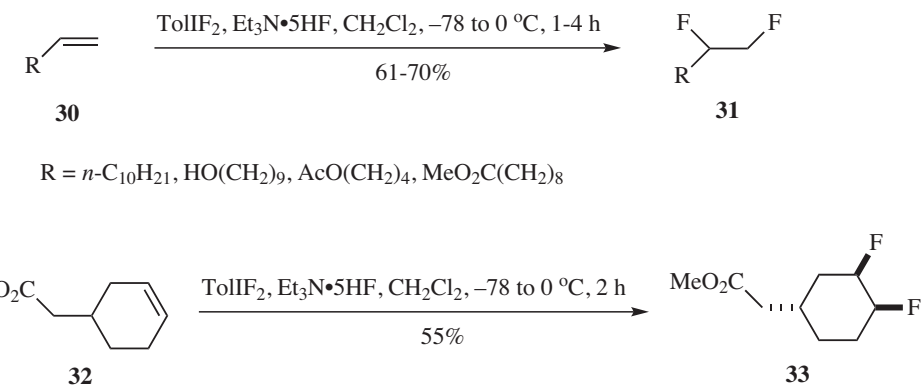
Scheme 3.11

(1,1-difluoroethyl)cyclopentanes **27,** while a similar reaction of benzocycloheptane **28** gives the respective difluoromethyl-substituted benzocyclohexane **29** in high yield (Scheme 3.11) [34].

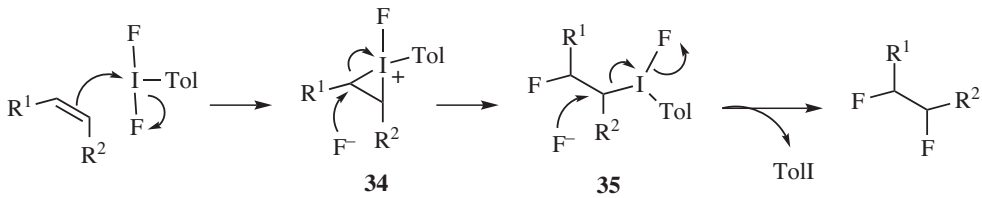
The reaction of difluoroiodotoluene with terminal alkenes **30** furnishes *vic*-difluoroalkanes **31** in moderate yields (Scheme 3.12) [35]. The cyclohexene derivative **32** reacts with this reagent under similar conditions with the stereoselective formation of *cis*-difluoride **33** [35].

The observed *syn*-stereoselectivity of this difluorination is explained by a two-step mechanism involving the *anti*-addition of the reagent to the double bond through cyclic iodonium intermediate **34** in the first step and then nucleophilic substitution of iodotoluene with fluoride anion in **35** in the second step (Scheme 3.13) [35].

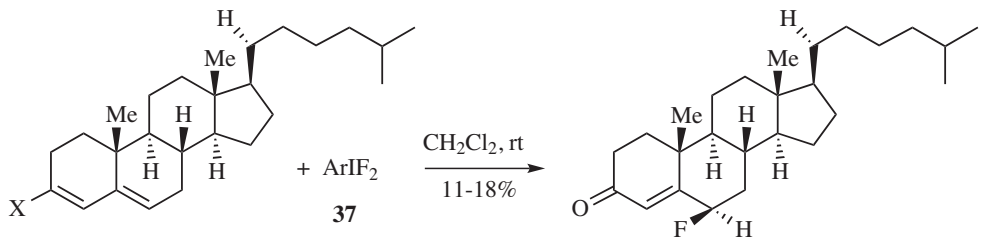
Steroidal dienes **36** react with (difluoroiodo)arenes **37** to afford fluorinated product **38** with a high degree of regioselectivity and stereoselectivity (Scheme 3.14) [14]. (Difluoroiodo)arenes react with terminal alkynes with stereo- and regioselective formation of synthetically useful (*E*)-2-fluoro-1-alkenyliodonium salts [36–39]. A convenient procedure for the preparation of various (*E*)-2-fluoroalkenyliodonium fluorides **39** is based on the addition of difluoroiodotoluene to terminal acetylenes (Scheme 3.15) [37–39]. Products **39** can be



Scheme 3.12



Scheme 3.13

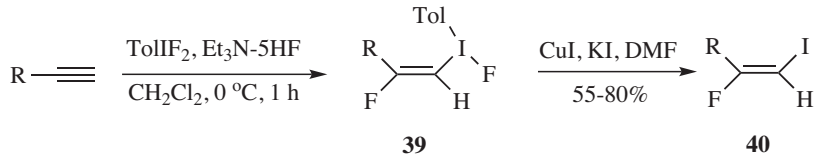


Scheme 3.14

further converted into (*E*)-2-fluoro-1-iodo-1-alkenes **40** without isolation by treatment with KI/CuI [37], or can be used as reagents in the Pd-catalyzed coupling reactions [38, 39].

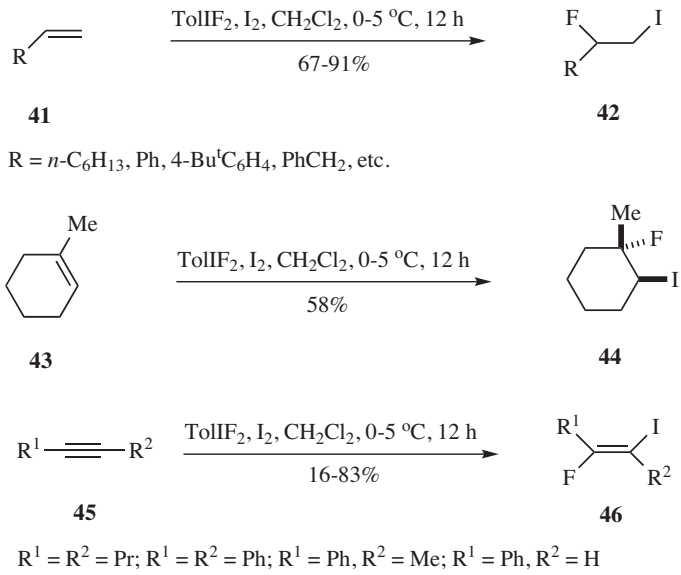
The fluorination of alkenes **41** and **43** and alkynes **45** with difluoroiodotoluene in the presence of iodine affords *vic*-fluoroiodoalkanes **42** and **44** and fluoroiodoalkenes **46** in moderate to good yields (Scheme 3.16) [40]. This reaction proceeds in a Markovnikov fashion and with prevalent *anti*-stereoselectivity via initial addition of the electrophilic iodine species followed by nucleophilic attack of fluorine anion. The analogous reaction of alkenes and alkynes with difluoroiodotoluene in the presence of diphenyl diselenides affords the respective products of phenylselenofluorination in good yields [41].

The reaction of difluoroiodotoluene with a four-, five-, or six-membered carbocycles **47** affords the ring-expanded (*E*)-δ-fluoro-β-halovinyliodonium tetrafluoroborates **48** stereoselectively in high yields (Scheme 3.17) [42]. This reaction proceeds via a sequence of λ^3-iodanation-1,4-halogen shift–ring enlargement–fluorination steps.



R = MeC_9H_{18}, HOC_9H_{18}, ClC_9H_{18}, $MeO_2CC_8H_{16}$, $Bu^tC(O)C_8H_{16}$, etc.

Scheme 3.15



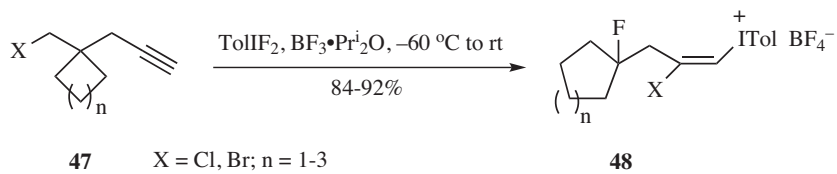
Scheme 3.16

N-Protected anilines can be selectively fluorinated at the *para*-position by bis(*tert*-butylcarbonyloxy)-iodobenzene, $PhI(OPiv)_2$ and hydrogen fluoride/pyridine. This convenient procedure provides facile access to various *para*-fluorinated anilides in moderate to good yields [43].

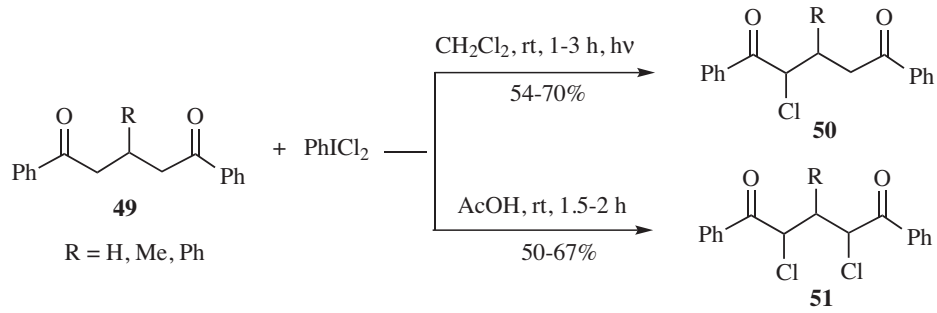
3.1.2 Chlorinations

(Dichloroiodo)arenes are widely used as reagents for chlorination of various organic substrates. Among (dichloroiodo)arenes, (dichloroiodo)benzene, $PhICl_2$, is the most commonly used reagent, which can be conveniently prepared by direct chlorination of iodobenzene (Section 2.1.3). The preparation and reactions of several recyclable, polymer-supported or nonpolymeric iodine(III) chlorides are discussed in Chapter 5.

Typical chlorinations of alkanes or alkenes with (dichloroiodo)benzene proceed via a radical mechanism and generally require photochemical conditions or the presence of radical initiators in solvents of low polarity, such as chloroform or carbon tetrachloride. However, the alternative ionic pathways are also possible due to the electrophilic properties of the iodine atom in $PhICl_2$ or electrophilic addition of Cl_2 generated by the dissociation of the reagent. An alternative synchronous molecular addition mechanism in the reactions of $PhICl_2$ with alkenes has also been discussed and was found to be theoretically feasible [44]. The general reactivity patterns of $ArICl_2$ were discussed in detail in several earlier reviews [8, 45, 46].



Scheme 3.17



Scheme 3.18

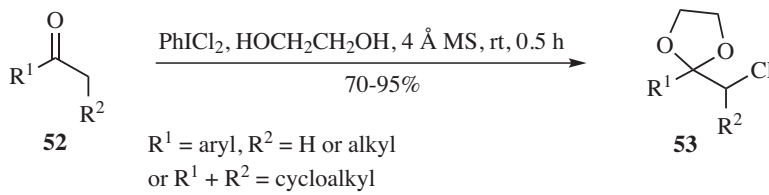
(Dichloroiodo)benzene has been applied for a substitutive chlorination at sp^3-carbon of various organic substrates, such as alkanes, ethers, esters, thioethers, ketones, sulfoxides and so on [45–51]. Ketones can be chlorinated at the α-position under either radical or ionic conditions. In a typical example, 1,5-diketones **49** react with $PhICl_2$ in dichloromethane under radical conditions (dichloromethane, UV-irradiation) to form, predominately, monochlorides **50,** while the same reagents in acetic acid in the dark (ionic conditions) selectively afford dichlorides **51** (Scheme 3.18) [47].

Various ketones, including aliphatic and aromatic ketones **52,** can be directly converted into their corresponding α-chloroketone acetals **53** in high to excellent yields using $PhICl_2$ in ethylene glycol in the presence of molecular sieves at room temperature (Scheme 3.19) [52]. For comparison, a similar reaction using Cl_2 as chlorinating reagent under similar conditions affords only trace amount of chlorides **53.**

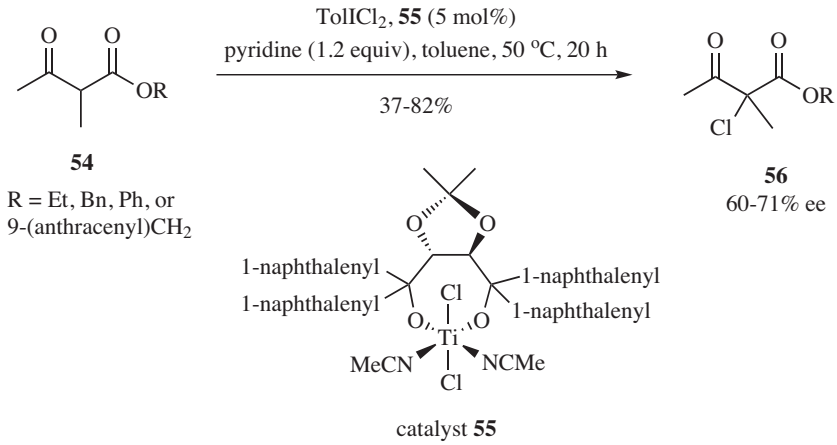
(Dichloroiodo)toluene is a suitable chlorinating reagent in the catalytic asymmetric chlorination of β-keto esters **54,** catalyzed by the titanium complex **55,** leading to the respective α-chlorinated products **56** in moderate to good yields and enantioselectivities (Scheme 3.20) [53]. Interestingly, the enantioselectivity of this reaction shows a strong temperature dependence, with the maximum selectivity reached at 50 °C.

Depending on the conditions, reactions of $ArICl_2$ with alkenes may follow a radical or ionic mechanism [49, 54–56]. Under radical conditions, the reaction gives exclusively the products of 1,2-addition of chlorine, often with high *trans*-stereoselectivity, while under polar conditions chlorination is usually accompanied by skeletal rearrangements. For example, norbornene reacts with $PhICl_2$ in nonpolar solvents to give 1,2-adducts **57** and **58** (Scheme 3.21) as the only detectable products [49]. The same reaction in the presence of trifluoroacetic acid affords exclusively the products of skeletal rearrangement **59–61.** Bicyclic diene **62** reacts with $PhICl_2$ under similar polar conditions to afford the tricyclic, rearranged products **63** and **64** in low yield [50].

Reactions of (dichloroiodo)benzene with various monoterpenes in methanol proceed via the ionic mechanism and afford the respective products of chloromethoxylation of the double bond with high regio- and stereoselectivity [56]. Likewise, the reaction of a recyclable chlorinating reagent, 4,4′-bis(dichloroiodo)biphenyl



Scheme 3.19

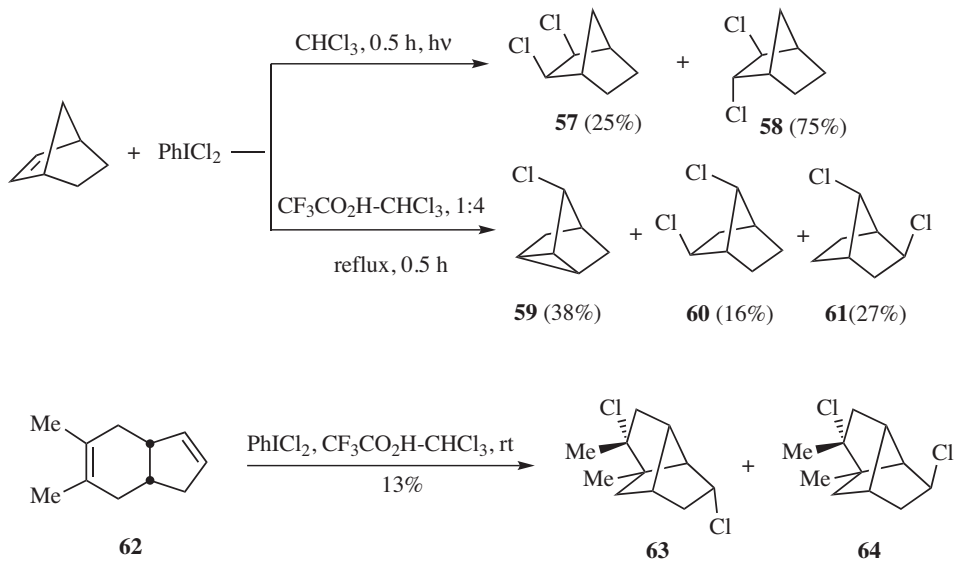


Scheme 3.20

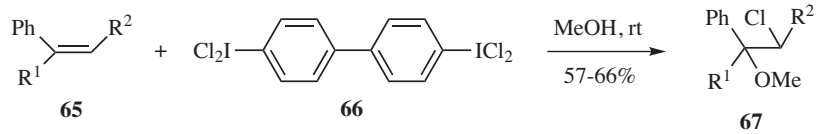
66 (Section 5.3.1), with styrene derivatives **65** in methanol affords exclusively the products of electrophilic chloromethoxylation (**67**) (Scheme 3.22) [54].

The electrophilic reactivity of $PhICl_2$ can be increased by adding Lewis acids or $AgBF_4$ to the reaction mixture. Under these conditions, the reaction of $PhICl_2$ with diene **68** gives exclusively rearranged products **69** and **70,** which clearly result from an ionic mechanism of addition (Scheme 3.23) [51].

An enantioselective dichlorination of allylic alcohols using (dichloroiodo)arenes as chlorine sources in the presence of catalytic amounts of a dimeric cinchona alkaloid derivative $(DHQ)_2PHAL$ has been developed [57]. For example, the dichlorination of *trans*-cinnamyl alcohols **71** with 4-$Ph(C_6H_4)ICl_2$ catalyzed by $(DHQ)_2PHAL$ affords products **72** in good yields and enantioselectivities (Scheme 3.24).



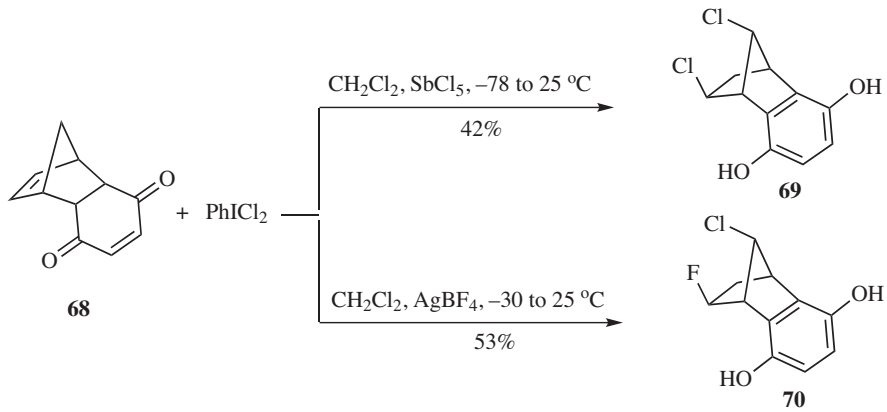
Scheme 3.21



65 **66** **67**

$R^1 = H, R^2 = H$; $R^1 = Ph, R^2 = H$; $R^1 = H, R^2 = Ph$

Scheme 3.22

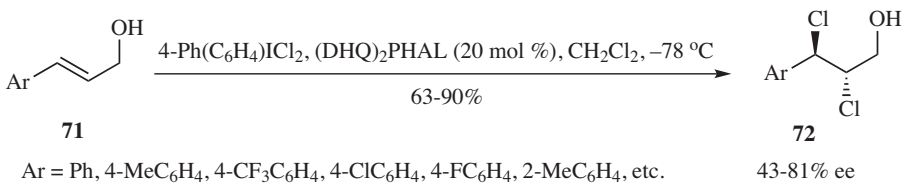


68 **69** **70**

Scheme 3.23

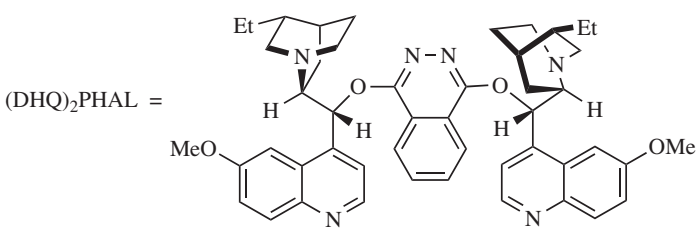
(Dichloroiodo)arenes can also be used for the chlorination of aromatic compounds. Aminoacetophenone **73** is selectively chlorinated with (dichloroiodo)benzene to give product **74** in good yield (Scheme 3.25). This process can be scaled up to afford 24.8 kg of product **74** with 94% purity [58].

Treatment of 5,10,15-trisubstituted porphyrins **75** with (dichloroiodo)benzene affords the corresponding *meso*-chlorinated porphyrins **76** (Scheme 3.26) [59]. The chlorination of 5,10,15,20-tetraarylporphyrins, in

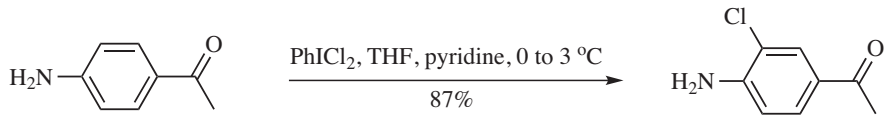


71 **72**

Ar = Ph, 4-MeC_6H_4, 4-$CF_3C_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 2-MeC_6H_4, etc. 43-81% ee

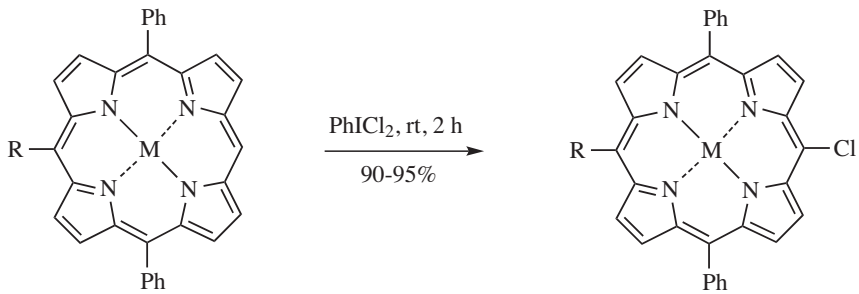


Scheme 3.24



73 **74**

Scheme 3.25



75 M = 2H, Cu, Ni
R = Ph or 4-$CF_3C_6H_4$ **76**

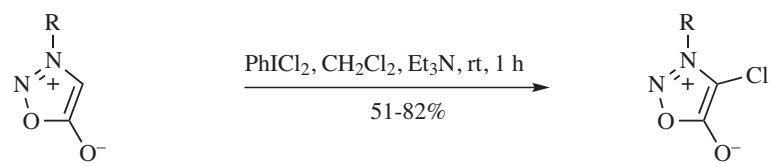
Scheme 3.26

which all *meso*-positions are substituted, under similar conditions affords β-monochlorinated products in high yields.

(Dichloroiodo)benzene in the presence of triethylamine has been used for the selective chlorination of 3-substituted sydnones **77** to furnish the 4-chloro substituted products **78** in good yield (Scheme 3.27) [60].

Fullerene (C_{60}) reacts smoothly with (dichloroiodo)benzene in tetrachloroethane at –25 to 25 °C to give polychlorinated fullerenes **79** (Scheme 3.28) [61]. Laser desorption mass-spectrometry analysis of product **79** shows $C_{60}Cl_7$ and $C_{60}Cl_9$ as the most prevalent species, while elemental analysis of the product is consistent with a molecular composition of $C_{60}Cl_{16}$. The previously reported preparation of $C_{60}Cl_n$ involved the chlorination of C_{60} with chlorine gas at 250 °C or liquid chlorine at –35 °C for one day.

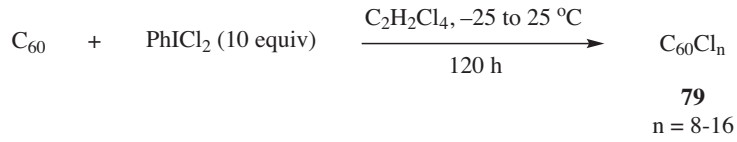
The reaction of N-protected pyrrolidine **80** with *p*-nitro(dichloroiodo)benzene affords α-hydroxy-β,β-dichloropyrrolidine **81** as the main product (Scheme 3.29) via a complex ionic mechanism involving a triple



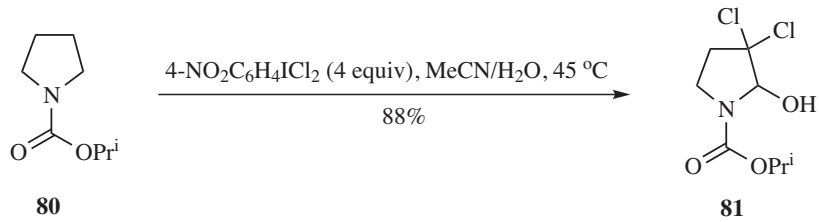
77 **78**

R = Ph, 4-MeC_6H_4, $PhCH_2$, 2-MeC_6H_4, 4-ClC_6H_4
2-AcC_6H_4, 3-$MeOC_6H_4$, 2-$MeO_2CC_6H_4$

Scheme 3.27



Scheme 3.28



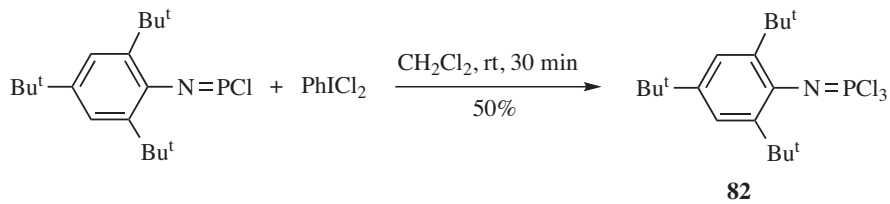
Scheme 3.29

C—H bond activation. This oxidative pathway has been demonstrated to be general for several saturated, urethane-protected nitrogen heterocyclic systems [62].

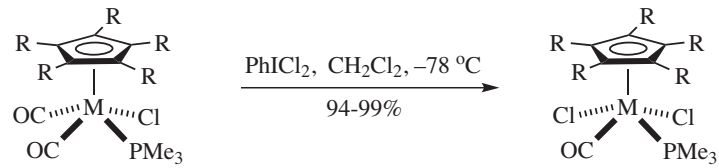
(Dichloroiodo)benzene can be conveniently generated *in situ* from other hypervalent iodine reagents and used for subsequent chlorination of organic substrates. In a specific example, an efficient chlorination of β-keto esters, 1,3-diketones and alkenes has been performed using iodosylbenzene with concentrated HCl, selectively giving α-chloro-β-keto esters, 2-chloro-1,3-diketones and 1,2-dichloroalkanes, respectively [63]. A stereoselective *anti*-addition was observed in the chlorination of indene under these conditions.

Various organic compounds containing heteroatoms can be effectively chlorinated by (dichloroiodo)arenes. Numerous examples of chlorinations at sulfur, phosphorus, selenium, arsenic, antimony and some metals have been reported in older reviews [45, 46]. More recent examples include the oxidation of sulfides to the corresponding sulfoxides and sulfones by 2-(dichloroiodo)benzoic acid [64], the preparation of *N*-chlorotriphenylphosphinimine, Ph_3PNCl, in good yield by the reaction of $Ph_3PNSiMe_3$ with $PhICl_2$ [65] and the synthesis of trichlorophosphine imides **82** (Scheme 3.30) [66].

(Dichloroiodo)benzene is commonly used as a reagent for the chlorination or oxidation of various transition metal complexes. Numerous examples of oxidative chlorination of various molybdenum and tungsten complexes with $PhICl_2$ have been reported in the literature [67–74]. In a representative example, oxidative decarbonylation of the cyclopentadienyl complexes **83** with one equivalent of $PhICl_2$ selectively yields the respective molybdenum(IV) or tungsten(IV) complexes **84** in excellent yields (Scheme 3.31) [73].



Scheme 3.30



83 M = Mo or W; R = H or Me **84**

Scheme 3.31

Additional examples of the reactions of transition metal complexes with $PhICl_2$ include the oxidation of heterobimetallic Pt(II)–Au(I) complexes to Pt(III)–Au(II) complexes [75] and the chlorinations or oxidations of palladium [76–78], cobalt [79], vanadium [80], iridium [81] and gold [82] complexes.

Inorganic iodine(III) chlorides, such as iodine trichloride and tetrachloroiodate salts $M^+ICl_4^-$, can also be used as chlorinating reagents. It has been demonstrated that ICl_3 reacts with alkanes in the presence of light to form chloroalkanes via a radical mechanism [83–85]. Benzyltrimethylammonium tetrachloroiodate, $PhCH_2Me_3N^+ICl_4^-$, is an effective reagent for benzylic chlorination of alkylaromatic compounds under reflux conditions in carbon tetrachloride in the presence of radical initiators [86]. Potassium tetrachloroiodate, $K^+ICl_4^-$, has been used for the chlorination of fullerenes [87, 88].

3.1.3 Brominations

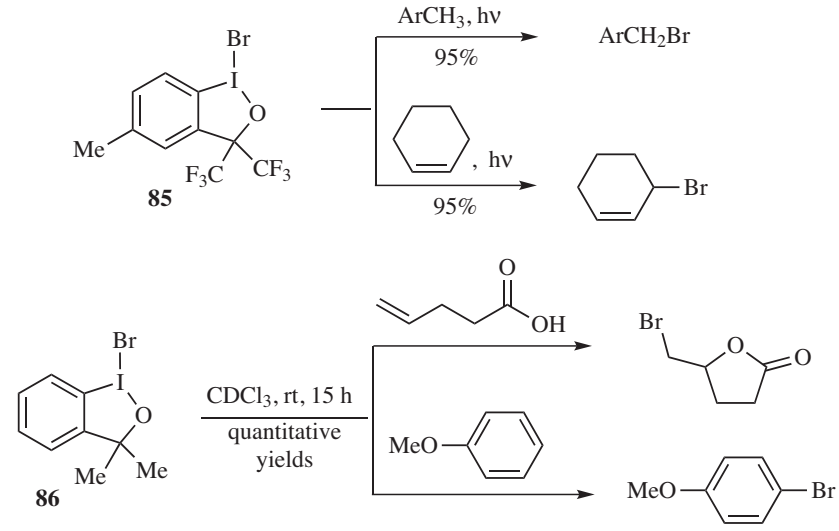
Only a few examples of oxidative brominations utilizing hypervalent iodine(III) reagents have been reported. Stable bromobenziodoxoles (Section 2.1.8.1.1) have been demonstrated to be active brominating agents. In particular, benziodoxole **85** can be used for selective allylic and benzylic brominations under radical conditions [89] and bromobenziodoxole **86** has been utilized for electrophilic bromination of anisole or bromolactonization of 4-pentenoic acid (Scheme 3.32) [90].

Common hypervalent iodine(III) reagents, such as $PhI(OAc)_2$ and PhI(OH)OTs, in the presence of bromide anions can be used for oxidative bromination of organic substrates. The oxidative halogenation of 1,4-dimethoxynaphthalene derivatives with (diacetoxyiodo)benzene and trimethylsilyl bromide or chloride affords the corresponding halogenated or haloacetylated products [91, 92]. For example, the treatment of 1,4-dimethoxynaphthalene (**87**) with $PhI(OAc)_2$ and trimethylsilyl bromide affords 3-bromo-1,4-dimethoxynaphthalene (**88**) in quantitative yield (Scheme 3.33) [92].

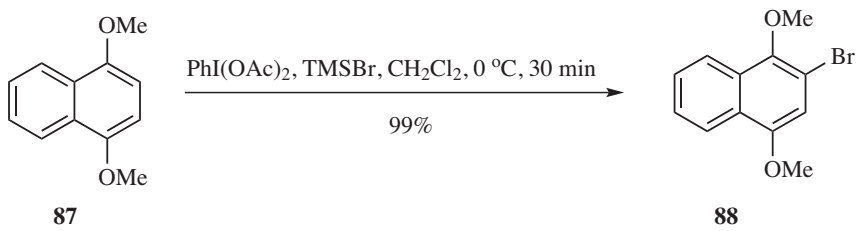
Polyalkylbenzenes react with [hydroxy(tosyloxy)iodo]benzene in the presence of ionic halides or *N*-halosuccinimide to afford the products of ring halogenation in good yields [93–95]. For example, the reaction of mesitylene with PhI(OH)OTs in the presence of sodium bromide selectively gives monobrominated product **89** in excellent yield (Scheme 3.34) [95].

A convenient procedure for the aminobromination of electron-deficient olefins **90** using Bromamine-T (TsNBrNa) as nitrogen and bromine source promoted by (diacetoxyiodo)benzene has been developed [96]. This heavy-metal-free protocol is highly efficient and affords the vicinal bromamines **91** with excellent regio- and stereoselectivities (Scheme 3.35).

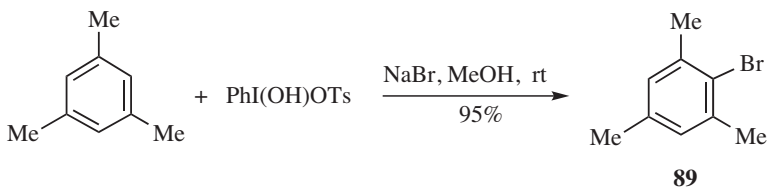
Carboxylic acids are bromodecarboxylated by reaction with (diacetoxyiodo)benzene and bromine under irradiation with a tungsten lamp, leading to respective alkyl or aryl bromides in 50–79% yield [97]. The reaction works very well with carboxylic acids having a primary, secondary or tertiary α-carbon atom, although diphenylacetic acid gives benzophenone. Benzoic acid derivatives are bromodecarboxylated in



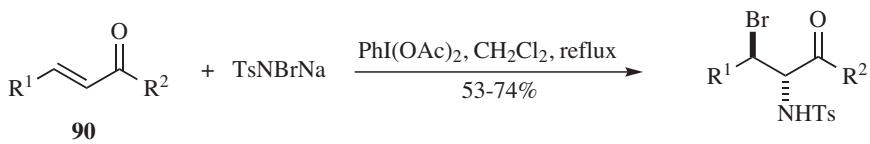
Scheme 3.32



Scheme 3.33



Scheme 3.34



anti/syn >99/1

R^1 = 3,4-$Cl_2C_6H_3$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, Ph, etc.
R^2 = Ph, 4-ClC_6H_4, OMe, NEt_2, etc.

Scheme 3.35

moderate yields if electron-withdrawing substituents are present in the benzene ring, while they are recovered mostly unchanged if the substituents are electron donating.

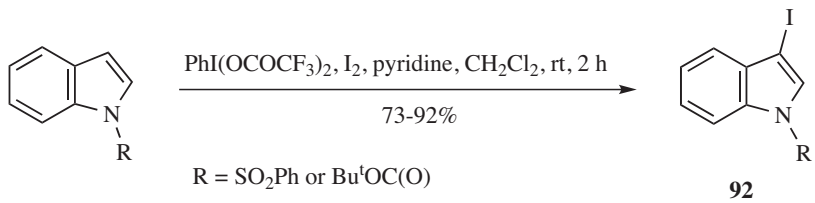
(Diacetoxyiodo)benzene in combination with simple bromide salts in ethanol can be used for the regioselective ethoxybromination of a wide range of enamides, giving synthetically versatile α-bromo hemiaminals [98].

3.1.4 Iodinations

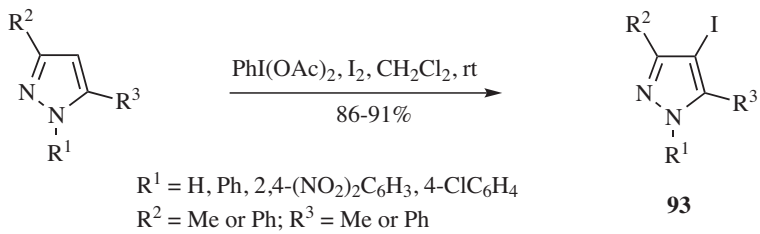
Iodine in combination with [bis(acyloxy)iodo]arenes is a classical reagent combination for the oxidative iodination of aromatic and heteroaromatic compounds [99]. A typical iodination procedure involves the treatment of electron-rich arenes with the $PhI(OAc)_2$–iodine system in a mixture of acetic acid and acetic anhydride in the presence of catalytic amounts of concentrated sulfuric acid at room temperature for 15 min [100, 101]. A solvent-free, solid state oxidative halogenation of arenes using $PhI(OAc)_2$ as the oxidant has been reported [102]. Alkanes can be directly iodinated by the reaction with the $PhI(OAc)_2$–iodine system in the presence of *t*-butanol under photochemical or thermal conditions [103]. Several other iodine(III) oxidants, including recyclable hypervalent iodine reagents (Chapter 5), have been used as reagents for oxidative iodination of arenes [104–107]. For example, a mixture of iodine and [bis(trifluoroacetoxy)iodo]benzene in acetonitrile or methanol iodinates the aromatic ring of methoxy substituted alkyl aryl ketones to afford the products of electrophilic mono-iodination in 68–86% yield [107].

A mild and effective procedure for the iodination of electron-deficient heterocyclic systems using the [bis(trifluoroacetoxy)iodo]benzene–iodine system has been reported [108]. The usefulness of this procedure can be illustrated by the preparation of 3-iodoindole derivatives **92** (Scheme 3.36), which are difficult to obtain by other methods due to their chemical instability. Sensitive protecting groups such as acetyl, Boc and *tert*-butyldimethylsilyl are stable under these iodination reaction conditions [108].

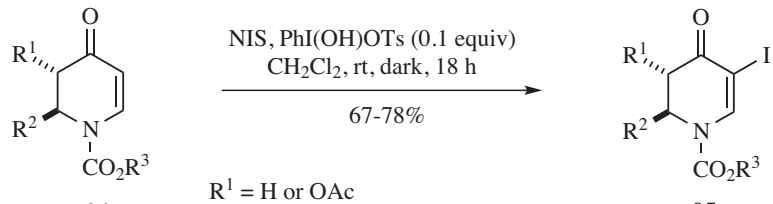
Substituted pyrazoles can be iodinated to the corresponding 4-iodopyrazole derivatives **93** by treatment with iodine and $PhI(OAc)_2$ at room temperature (Scheme 3.37) [109].



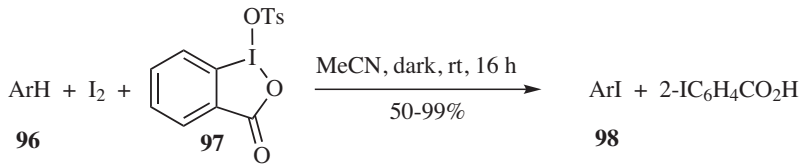
Scheme 3.36



Scheme 3.37



Scheme 3.38



ArH = 1,3,5-$(MeO)_3C_6H_3$, 1,3,5-$(i\text{-}Pr)_3C_6H_3$, 1,3,5-$Me_3C_6H_3$, 1-MeO-4-$MeCO_2C_6H_4$, 1-MeO-4-BrC_6H_4, 1,4-$Me_2C_6H_4$, 1,3-$Me_2C_6H_4$, $MeOC_6H_5$, $Bu^tC_6H_5$, $AcOC_6H_5$, naphthalene, 2,3-benzothiophene, etc.

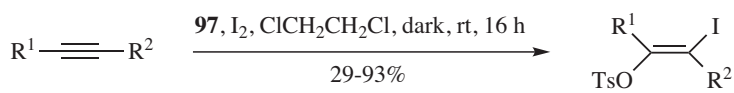
Scheme 3.39

Various dihydropyridone derivatives **94** can be efficiently iodinated by treatment with *N*-iodosuccinimide (NIS) in the presence of [hydroxy(tosyloxy)iodo]benzene to give products **95** (Scheme 3.38) [110].

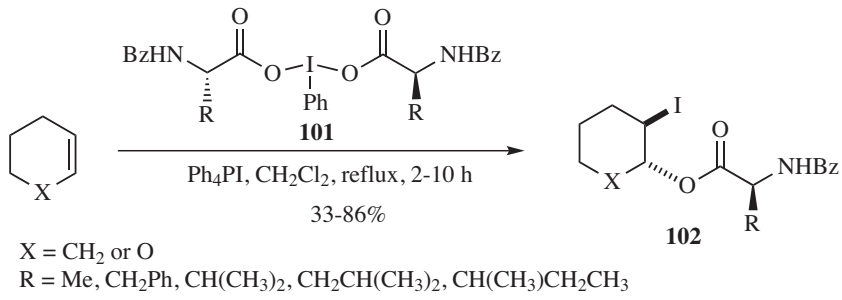
It has been demonstrated that tosyloxybenziodoxole **97** (Section 2.1.8.1.3) can be used as an effective reagent for the oxidative iodination of aromatic compounds [111, 112]. Treatment of various aromatic compounds **96** with reagent **97** and I_2 gives the corresponding iodinated compounds **98** in good yields (Scheme 3.39). As compared with other trivalent iodine compounds, the tosylate **97** shows the best reactivity as an oxidant for oxidative halogenation [112].

In addition, the reagent **97**–iodine system can be used for the iodotosyloxylation of alkynes **99** to give the addition products **100** in good yields (Scheme 3.40) [112]. These reactions presumably proceed via the intermediate formation of arenesulfonyl hypoiodites.

Kirschning and coworkers have developed several experimental procedures for the stereoselective bromoacetoxylation or iodoacetoxylation of alkenes based on the interaction of $PhI(OAc)_2$ with iodide or bromide anions [113, 114]. The actual reacting electrophilic species in these reactions are the diacetylhalogen(I) anions, $(AcO)_2I^-$ and $(AcO)_2Br^-$, which can also be prepared as the polymer-supported variant [114].



Scheme 3.40



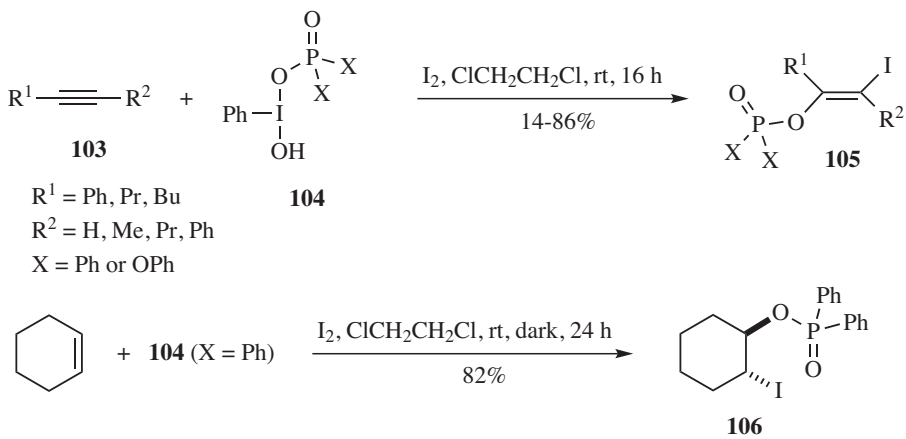
Scheme 3.41

The reaction of $PhI(OAc)_2$–I_2 system with alkenes in the presence of external nucleophiles has been used for the preparation of various β-functionalized iodoalkanes [115]. A similar iodocarboxylation of alkenes using amino acid-derived phenyliodine(III) dicarboxylates **101** (Section 2.1.5) selectively affords the respective amino acid esters **102** in moderate yields (Scheme 3.41) [116].

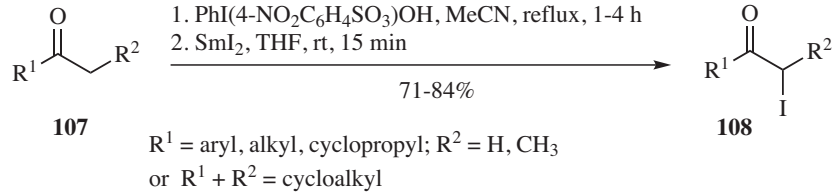
Similarly, [hydroxy(phosphoryloxy)iodo]benzenes **104** (Section 2.1.7) are useful reagents for iodophosphoryloxylation of alkynes and alkenes [117]. Specifically, alkynes **103** can be converted into the corresponding 1,2-iodophosphoryloxylated compounds **105** in moderate to good yields upon treatment with reagents **104** in the presence of iodine (Scheme 3.42). Under similar conditions, cyclohexene is converted into the corresponding adduct **106** in high yield [117].

The reaction of ketones **107** with [hydroxy(4-nitrobenzenesulfonyloxy)iodo]benzene and subsequent treatment with samarium iodide has been used for a one-pot preparation of α-iodoketones **108** (Scheme 3.43) in high yields [118]. 2-Iodosylbenzoic acid can also be used as a convenient recyclable hypervalent iodine oxidant for the synthesis of α-iodoketones by oxidative iodination of ketones [119].

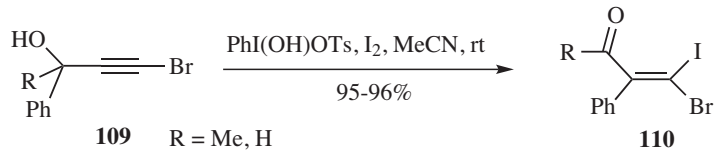
The $PhI(OAc)_2$–I_2 system has been used for the oxidative decarboxylation/iodination of carboxylic acids [120–123]. This reaction was employed in the efficient syntheses of enantiopure 1-benzoyl-2(*S*)-*tert*-butyl-3-methylperhydropyrimidin-4-one [120] and 2-substituted-5-halo-2,3-dihydro-4(*H*)-pyrimidin-4-ones [123].



Scheme 3.42



Scheme 3.43



Scheme 3.44

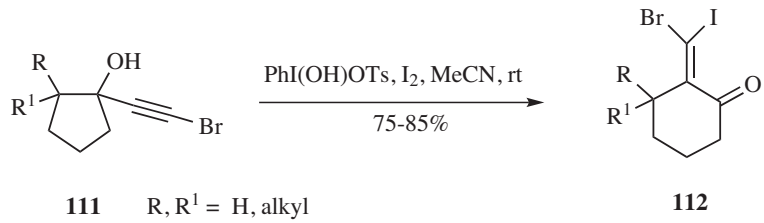
1-Iodoalkynes can be prepared in good to excellent yields by the oxidative iodination of terminal alkynes with $PhI(OAc)_2$, potassium iodide and copper(I) iodide [124].

In a series of communications, McNelis and coworkers have reported the scope of reactions of the reagent combination PhI(OH)OTs–halogen or PhI(OH)OTs–*N*-halosuccinimide with alkynols, resulting in the formation of various haloenones [125–133]. All these oxidative rearrangements involve iodonium intermediates and are highly regio- and stereoselective. For example, bromoethynyl alcohols **109** are cleanly converted into β,β-dihaloenones **110** by reaction with the PhI(OH)OTs–I_2 system (Scheme 3.44) [127, 128].

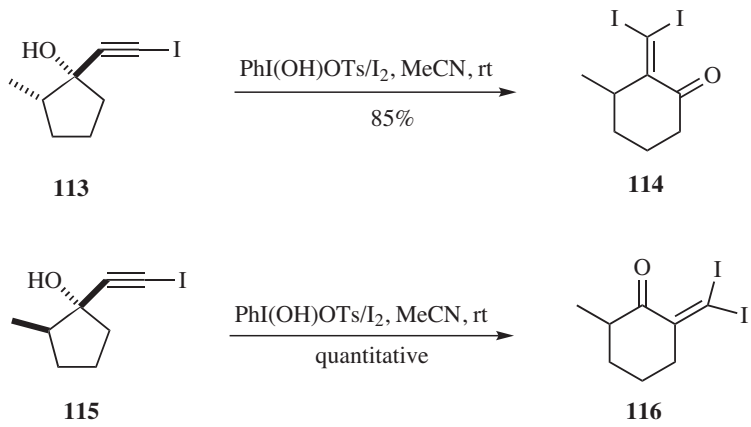
Reactions of this type (Scheme 3.44) are especially useful for the preparation of cyclic β,β-dihaloenones by ring expansions of alkynyl cyclopentanols or alkynyl cyclohexanols. 1-Bromoethynylcyclopentanols **111** react with equimolar amounts of iodine and PhI(OH)OTs under mild conditions to produce cyclohexanone derivatives **112** with a high degree of stereoselectivity (Scheme 3.45) [129].

Likewise, stereoselective ring expansions in 1-iodoethynyl-2-methylcyclopentanols **113** and **115** affords β,β-diiodoenones upon treatment with PhI(OH)OTs and iodine (Scheme 3.46) [134]. Depending on the relative stereochemistry of the methyl and the hydroxyl groups in the starting cyclopentanol, the products are 2-(diiodomethylidene)-3-methylcyclohexanone (**114**), from *cis*-cyclopentanol **113** and 2-(diiodomethylidene)-6-methylcyclohexanone (**116**) from *trans*-cyclopentanol **115** [134].

A similar reaction was used in the synthesis of phenanthrenone **118** from the readily available fluorenone derivative **117** (Scheme 3.47) [130].



Scheme 3.45



Scheme 3.46

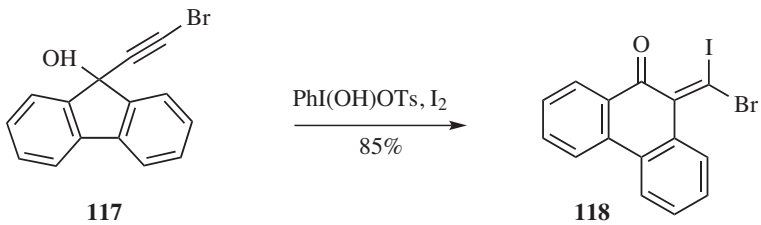
Ring expansion of camphor (**119**) and adamantanone (**121**) derivatives under the same conditions afforded the respective (*Z*)-bromoiodoenones **120** and **122** in good yields and in high stereoselectivity (Scheme 3.48) [131–133].

The treatment of iodoalkynol derivatives of xylose **123** with PhI(OH)OTs and iodine under similar conditions furnishes β,β-diiodoenol ethers **124** with a furo[3, 4-*b*]furan heterocyclic core (Scheme 3.49) [135].

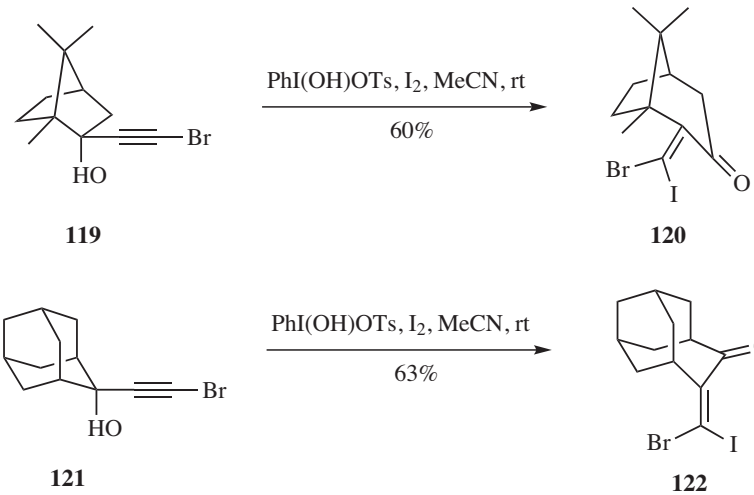
3.1.5 Oxidation of Alcohols

In contrast with λ^5-iodanes (Section 3.2), hypervalent iodine(III) reagents are not effective oxidants of alcohols in the absence of catalysts. Kita and coworkers were the first to find that, in the presence of bromide salts, iodosylbenzene or (diacetoxyiodo)benzene can be used as an efficient reagent for selective oxidation of alcohols [136, 137]. The iodosylbenzene–KBr system is applicable to the oxidation of various primary and secondary alcohols, even in the presence of sensitive functional groups such as ether, ester, sulfonamide and azido groups. Primary alcohols under these conditions afford carboxylic acids (Scheme 3.50), while the oxidation of various secondary alcohols under similar conditions affords the appropriate ketones in almost quantitative yield [136].

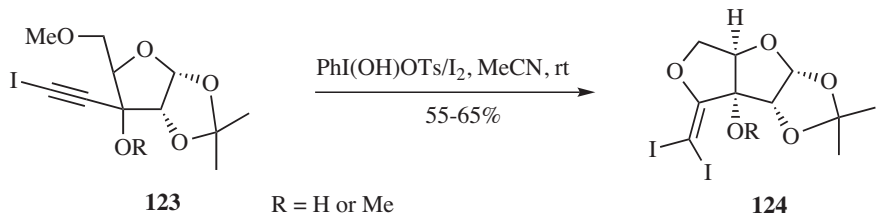
[Bis(acyloxy)iodo]arenes in the presence of KBr in water can oxidize primary and secondary alcohols analogously to the iodosylbenzene–KBr system [137]. The oxidation of primary alcohols affords carboxylic acids or esters [136, 138], while the oxidation of secondary alcohols under same conditions



Scheme 3.47



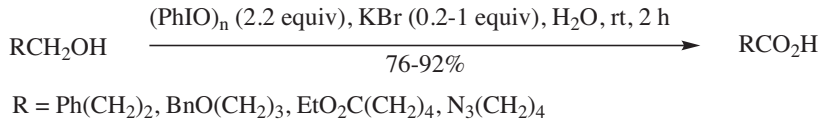
Scheme 3.48



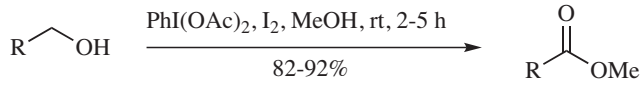
Scheme 3.49

leads to the respective ketones in excellent yields [139]. Aldehydes can be converted into methyl esters by a similar procedure using $PhI(OAc)_2$ and NaBr [140]. Molecular iodine can serve as an efficient catalyst in the oxidation of secondary alcohols to ketones and primary alcohols to carboxylic acids using $PhI(OAc)_2$ as an oxidant in acetonitrile solution [141]. The oxidation of primary alcohols or aldehydes with the $PhI(OAc)_2$–I_2 system in methanol solution yields the respective methyl esters in excellent yields (Scheme 3.51) [141, 142].

An efficient procedure for the oxidation alcohols with $PhI(OAc)_2$ in the presence of catalytic amounts of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), originally developed by Piancatelli, Margarita and coworkers [143], has been frequently used in recent years [144–150]. This procedure works well for the

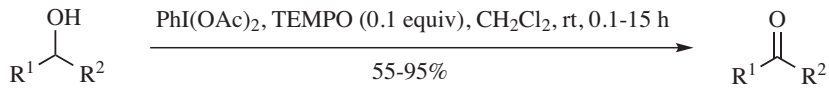


Scheme 3.50



R = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, C_9H_{19}, C_7H_{15}, $PhCH_2CH_2$, PhCH=CH, etc.

Scheme 3.51



R^1, R^2 = H, alkyl, aryl, alkenyl, etc.

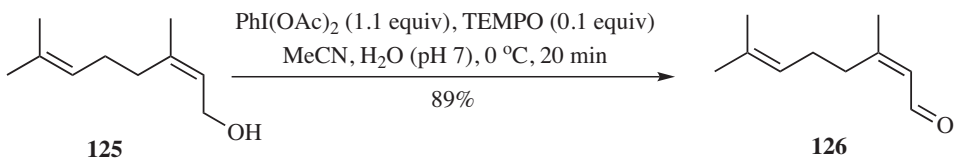
Scheme 3.52

conversion of various primary and secondary alcohols into carbonyl compounds in generally high yields (Scheme 3.52) [143].

This procedure (Scheme 3.52) exhibits a very high degree of selectivity for the oxidation of primary alcohols to aldehydes, without any noticeable overoxidation to carboxyl compounds and a high chemoselectivity in the presence of either secondary alcohols or of other oxidizable moieties. An optimized protocol, published in *Organic Synthesis* for the oxidation of nerol (**125**) to nepal (**126**) (Scheme 3.53), is based on the treatment of the alcohol **125** solution in buffered (pH 7) aqueous acetonitrile with $PhI(OAc)_2$ and TEMPO (0.1 equiv) at 0 °C for 20 min [145].

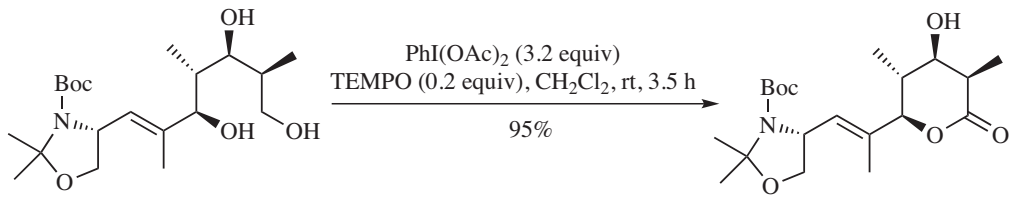
A similar oxidative protocol has been used for the oxidation of (fluoroalkyl)alkanols, $R_F(CH_2)_nCH_2OH$, to the respective aldehydes [146], in the one-pot selective oxidation/olefination of primary alcohols using the $PhI(OAc)_2$–TEMPO system and stabilized phosphorus ylides [147] and in the chemo-enzymatic oxidation–hydrocyanation of γ,δ-unsaturated alcohols [148]. Other [bis(acyloxy)iodo]arenes can be used instead of $PhI(OAc)_2$ in the TEMPO-catalyzed oxidations, in particular the recyclable monomeric and the polymer-supported hypervalent iodine reagents (Chapter 5). Further modifications of this method include the use of polymer-supported TEMPO [151], fluorous–tagged TEMPO [152, 153], ion-supported TEMPO [154] and TEMPO immobilized on silica [148].

Based on the ability of the $PhI(OAc)_2$–TEMPO system to selectively oxidize primary alcohols to the corresponding aldehydes in the presence of secondary alcohols, Forsyth and coworkers have developed the selective oxidative conversion of various highly functionalized 1°,2°-1,5-diols into the corresponding δ-lactones [155]. A representative example, showing the conversion of substrate **127** into the δ-lactone



125 **126**

Scheme 3.53



127 **128**

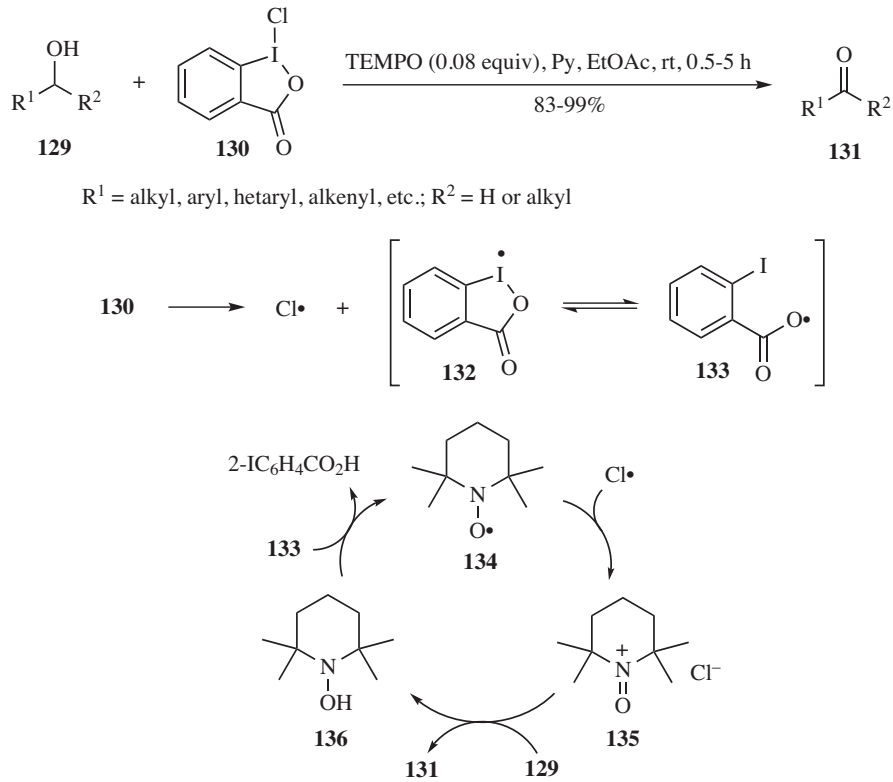
Scheme 3.54

128, is given in Scheme 3.54. Monitoring of this reaction revealed initial formation of the intermediate lactol species, which then undergoes further oxidation to the lactone [155]. A similar $PhI(OAc)_2$–TEMPO promoted γ-lactonization has been utilized in the asymmetric total synthesis of the antitumor agent (+)-eremantholide A [156].

An efficient and mild procedure has been described for the oxidation of different types of alcohols to carbonyl compounds using TEMPO as the catalyst and (dichloroiodo)benzene as a stoichiometric oxidant at 50 °C in chloroform solution in the presence of pyridine [157]. Under these conditions, 1,2-diols are oxidized to β-hydroxyketones or β-diketones depending upon the amount of $PhICl_2$ used. Interestingly, a competitive study has shown that this system preferentially oxidizes aliphatic secondary alcohols over aliphatic primary alcohols [157], while the $PhI(OAc)_2$–TEMPO system selectively converts primary alcohols into the corresponding aldehydes in the presence of secondary alcohols.

A similar TEMPO-catalyzed system for the oxidation of alcohols using 1-chloro-1,2-benziodoxol-3(1*H*)-one (**130**) (Section 2.1.8.1.1) as the terminal oxidant in ethyl acetate in the presence of pyridine at room temperature has been reported [158]. Various alcohols **129** can be oxidized to the corresponding carbonyl compounds in high to excellent yields under these conditions (Scheme 3.55). The oxidation of primary alcohols (**129,** $R^2 = H$) in this reaction proceeds generally faster compared to the secondary alcohols. Different heteroaromatic rings (e.g., pyridine, furan and thiophene) and carbon–carbon double bonds are well tolerated under the reaction conditions. Moreover, reagent **130** can be easily recycled from the reaction mixture and reused. The mechanism of this reaction includes initial homolytic cleavage of the I—Cl bond providing a chlorine atom and the iodanyl radical **132,** which is in equilibrium with the benzoyloxy radical **133.** TEMPO (**134**) is oxidized by the chlorine atom to oxoammonium salt **135,** which then oxidizes the alcohol **129** to the corresponding carbonyl compound **131** and is itself reduced to hydroxylamine **136.** The benzoyloxy radical **133** accomplishes the regeneration of TEMPO **134** from hydroxylamine **136,** giving rise to 2-iodobenzoic acid and the catalytic cycle is complete (Scheme 3.55) [158].

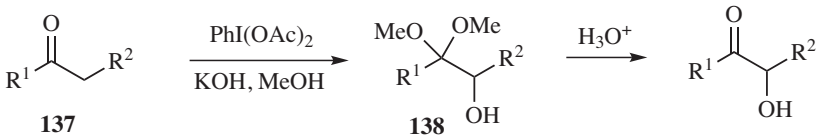
Only a few examples of uncatalyzed oxidation of alcohols with hypervalent iodine(III) reagents have been reported [159–162]. Vicinal diols can be cleaved to aldehydes in dichloromethane at room temperature by polymer-supported (diacetoxyiodo)benzene (Chapter 5) [159]. Substituted benzyl alcohols can be oxidized by [bis(trifluoroacetoxy)iodo]benzene in aqueous acetic acid to the corresponding benzaldehydes [160]. Benzylic alcohols can also be oxidized with [hydroxy(tosyloxy)iodo]benzene under solvent-free microwave irradiation conditions to afford the corresponding aldehydes or ketones in excellent yields [162]. Vicinal fullerene diol is oxidized to fullerene dione in 80% yield by $PhI(OAc)_2$ in benzene at 35 °C [161]. Oligomeric iodosylbenzene sulfate, $(PhIO)_3 \cdot SO_3$, can oxidize benzyl alcohol in aqueous acetonitrile at room temperature to afford benzaldehyde in 92% yield [163]. Alcohols can be selectively oxidized to the corresponding aldehydes or ketones with $(PhIO)_3 \cdot SO_3$ in water in the presence of β-cyclodextrin [164]. Transition metal catalyzed oxidations of alcohols using hypervalent iodine reagents as stoichiometric oxidants are discussed in Section 3.1.20.



Scheme 3.55

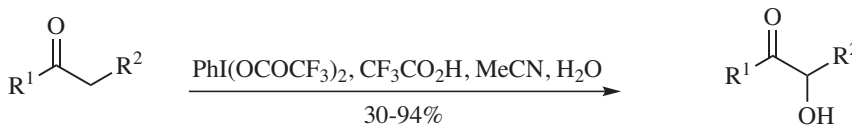
3.1.6 Oxidative Functionalization of Carbonyl Compounds

Hypervalent iodine reagents are commonly used for oxidative α-functionalization of carbonyl compounds [165]. The α-hydroxycarbonyl group is of interest to synthetic organic chemists due to its ubiquity in nature, occurring in polyketide, terpenoid and alkaloid natural products. In the 1980s Moriarty and coworkers developed a particularly useful methodology for the oxidative α-hydroxylation of enolizable carbonyl compounds using iodosylbenzene, (diacetoxyiodo)benzene, or other hypervalent iodine oxidants [166]. The reagent system $PhI(OAc)_2$/KOH/MeOH is especially efficient for hydroxylation of enolizable ketones **137** via the initially formed α-hydroxydimethylacetals **138** (Scheme 3.56) [167–173]. This procedure has been further extended to the α-hydroxylation of carboxylic esters [167, 174].



R^1 = aryl, heteroaryl, alkyl; R^2 = H or alkyl

Scheme 3.56



R^1 = aryl, heteroaryl, alkyl; R^2 = H or alkyl

Scheme 3.57

R^1, R^2 = alkyl, aryl; R^3 = Me, 4-MeC_6H_4, etc.

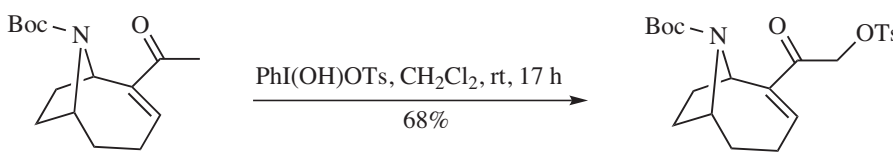
Scheme 3.58

Hydroxylation of some substituted acetophenones under these conditions (Scheme 3.56) is especially useful for the synthesis of various oxygen-containing heterocyclic compounds [175–179]. Applications of this methodology in organic synthesis, especially in the chemistry of heterocyclic compounds, have been summarized in several reviews [166, 180–182].

A similar hydroxylation of aromatic, heteroaromatic and aliphatic ketones can also be performed using [bis(trifluoroacetoxy)iodo]benzene under acidic conditions (Scheme 3.57) [183]. A plausible mechanism for this hydroxylation involves initial electrophilic addition of $PhI(OCOCF_3)_2$ to the enolized ketone and subsequent nucleophilic substitution in the iodonium intermediate.

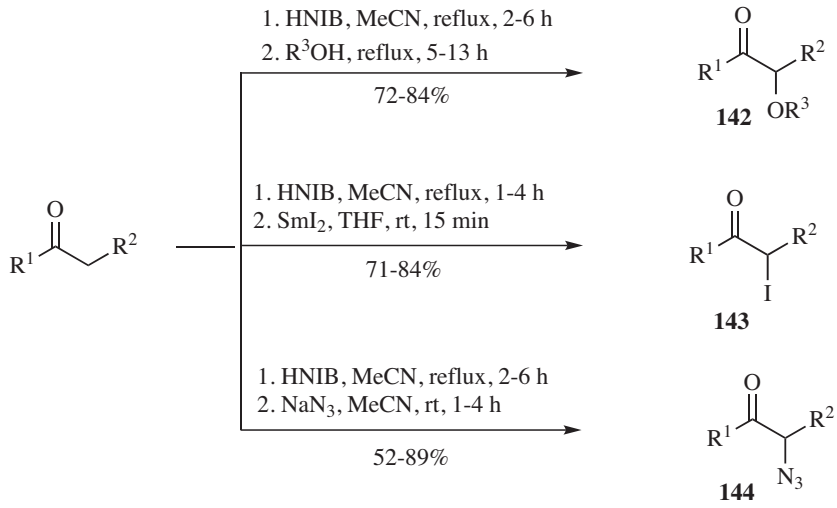
The functionalization of carbonyl compounds at the α-carbon is the most typical reaction of [hydroxy(organosulfonyloxy)iodo]arenes **139** (Scheme 3.58) [184].

Of particular use is the reaction of [hydroxy(tosyloxy)iodo]benzene (HTIB, also known as Koser's reagent) with ketones leading to α-tosyloxyketones [185–187]. This is a highly chemoselective reaction; different functional groups, aromatic rings and carbon–carbon double bonds are well tolerated under the reaction conditions [188]. Scheme 3.59 shows a representative example of synthetic application of HTIB for the functionalization of the azabicyclic alkaloid anatoxin-a, which is one of the most potent nicotinic antagonists. Specifically, the reaction of *N*-Boc anatoxin-a **140** with HTIB is the method of choice for the preparation of the synthetically versatile α-tosyloxy ketone **141** (Scheme 3.59) [189].



140 **141**

Scheme 3.59



HNIB = PhI(4-$NO_2C_6H_4SO_3$)OH
R^1 = aryl, alkyl; R^2 = H, alkyl or $R^1 + R^2$ = cycloalkyl
R^3 = Me, Et, Ac

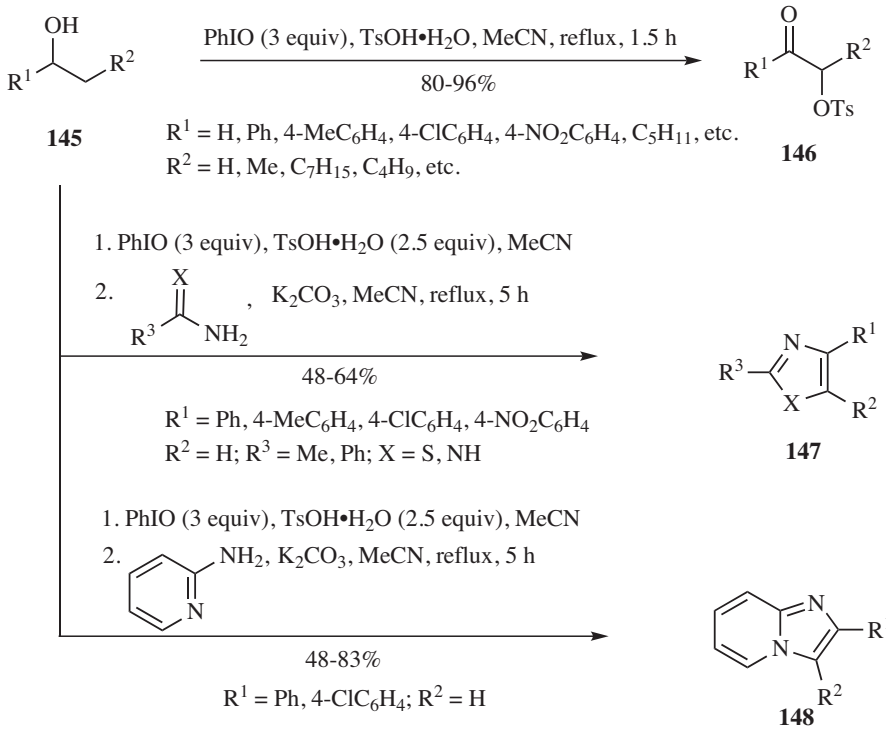
Scheme 3.60

This reaction of ketones with [hydroxy(organosulfonyloxy)iodo]arenes followed by treatment with an appropriate nucleophile *in situ* offers a convenient entry into various other α-substituted ketones, or can lead to various heterocycles via cyclization of the initially formed α-tosyloxyketones [176, 177, 184, 190, 191]. For example, the reaction of various ketones with [hydroxy(*p*-nitrobenzenesulfonyloxy)iodo]benzene (HNIB) and subsequent treatment with the appropriate nucleophile has been used for a one-pot preparation of secondary α-alkoxy or α-acetoxy ketones **142** [192], α-iodoketones **143** [118] and α-azidoketones **144** [193] in generally high yields (Scheme 3.60).

The tosyloxylation of suitable ketones followed by heterocyclization has been utilized in the syntheses of the following heterocyclic systems: 2-aroylbenzo[*b*]furans [194], 3-aryl-5,6-dihydroimidazo[2,1-*b*][1,3]-thiazoles [194], 6-arylimidazo[2,1-*b*]thiazoles [195], (1*S*,2*R*)-indene oxide [196], 2-mercaptothiazoles [197], triazolo-[3,4-*b*]-1,3,4-thiadiazines [198], dihydroindeno[1,2-*e*][1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazines [199], furo[3,2-*c*]coumarins [200], 4,5-diarylisoxazoles [201], 2-substituted 4,5-diphenyloxazoles [202], quinoxaline [203], 3-carbomethoxy-4-arylfuran-2-(5*H*)-ones [204], thiazol-2(3*H*)-imine-linked glycoconjugates [205] and other important heterocycles.

Based on the oxidation–tosyloxylation sequence, Togo and coworkers have developed the preparation of α-tosyloxy ketones and aldehydes **146** in good yields from alcohols **145** by treatment with iodosylbenzene and *p*-toluenesulfonic acid monohydrate (Scheme 3.61) [206]. This method can also be used for the direct preparation of thiazoles (**147,** X = S), imidazoles (**147,** X = NH) and imidazo[1,2-*a*]pyridines **148** from alcohols in good to moderate yields by successive treatment with iodosylbenzene and *p*-toluenesulfonic acid monohydrate, followed by thioamides, benzamidine and 2-aminopyridine, respectively (Scheme 3.61) [206].

Carboxylic anhydrides can be functionalized at the α-carbon using [hydroxy(organosulfonyloxy)-iodo]arenes. Treatment of carboxylic anhydrides **149** with reagents **150** at about 100 °C followed by esterification of the reaction mixture with methanol affords 2-sulfonyloxycarboxylate esters **151** in moderate to good yields (Scheme 3.62) [207].

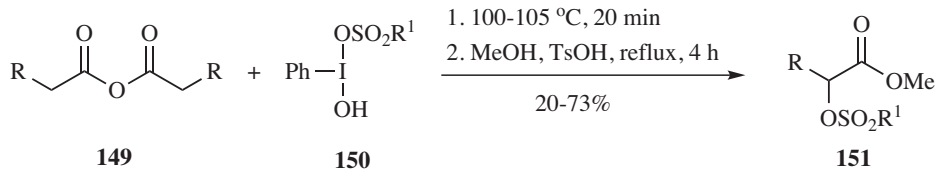


Scheme 3.61

[Hydroxy(phosphoryloxy)iodo]benzenes **153** (Section 2.1.7) are useful reagents for the introduction of phosphonate or phosphinate groups at the α-position to ketone or ester carbonyl groups of carbonyl compounds **152** to produce the corresponding products **154** (Scheme 3.63) [208].

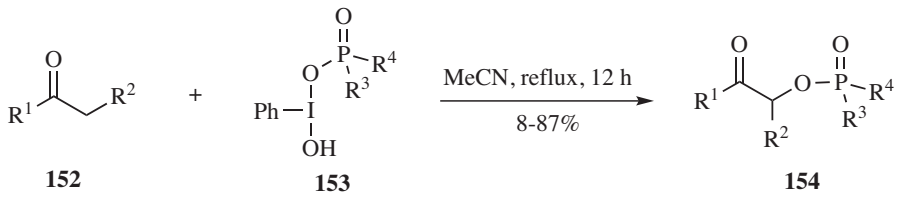
3.1.7 Oxidative Functionalization of Silyl Enol Ethers

Reactions of silyl enol ethers with iodosylbenzene in the presence of $BF_3{\cdot}Et_2O$ can be used to form new carbon–carbon bonds [209], prepare α-substituted ketones [210] and synthesize oxygen-containing



R = Me, Et, Pr, Bu, C_8H_{17}, $C_{10}H_{21}$, MeOOC, Pr^i, Bu^i, $PhCH_2CH_2$
R^1 = 4-MeC_6H_4, Me, 4-$NO_2C_6H_4$, (+)-10-camphoryl

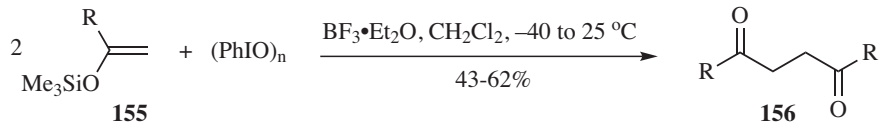
Scheme 3.62



152 **153** **154**

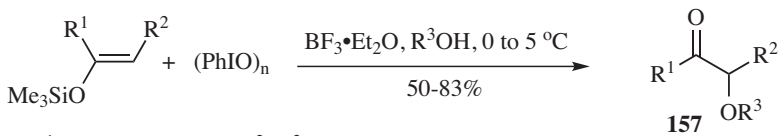
R^1 = Me, Ph; R^2 = H, PhCO, CO_2Me; $R^1 + R^2 = (CH_2)_4$
$R^3 = CH_3$, R^4 = OPh; $R^1 = R^2$ = Ph; $R^1 = R^2$ = Me

Scheme 3.63



155 **156**

R = aryl, heteroaryl, Bu^t



157

R^1 = aryl, heteroaryl; R^2, R^3 = H, alkyl

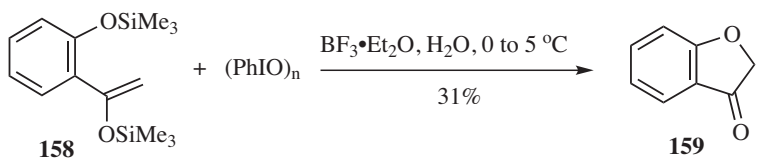
Scheme 3.64

heterocyclic compounds [176–178]. For example, the reaction of silyl enol ethers **155** with PhIO–BF_3 in non-nucleophilic solvents usually affords 1,4-butanediones **156** as major products [211], while in the presence of water or alcohols these reactants give α-hydroxy- or α-alkoxyketones **157** (Scheme 3.64) [212].

A similar intramolecular oxidation of silyl enol ether **158** affords oxygen heterocycle **159** (Scheme 3.65) [213].

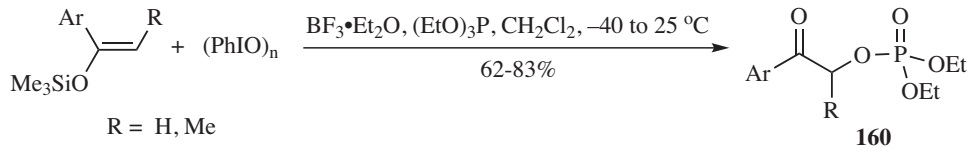
The reaction of silyl enol ethers with PhIO–BF_3 in the presence of triethyl phosphite as an external nucleophile yields β-keto phosphonates **160** in good yield (Scheme 3.66) [214].

Various Lewis acids and strong Brønsted acids can be used instead of $BF_3 \cdot Et_2O$ to catalyze reactions of iodosylbenzene with unsaturated compounds. For example, the reaction of iodosylbenzene with silyl enol ethers in the presence of trimethylsilyl triflate affords α-trifluoromethanesulfonyloxyketones **161** (Scheme 3.67) [215].

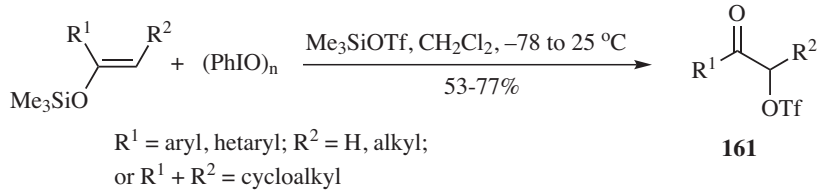


158 **159**

Scheme 3.65



Scheme 3.66



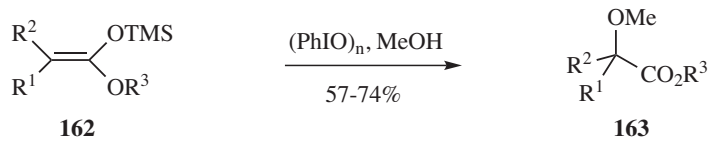
Scheme 3.67

Trimethylsilyl ketene acetals of esters **162** and lactones **164** react with iodosylbenzene in methanol to give the corresponding α-methoxylated esters **163** or α-methoxylated lactones **165** in good yields (Scheme 3.68) [216]. It is assumed that the actual oxidizing monomeric species in this reaction is $PhI(OMe)_2$.

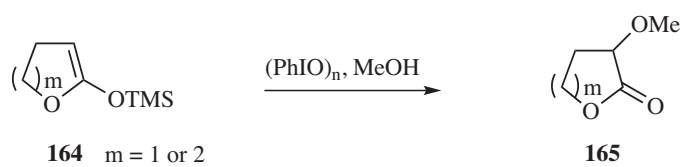
In some reactions (difluoroiodo)arenes can be used as general oxidizing reagents. For example, Koser and coworkers applied a difluoroiodotoluene/phosphoric acid mixture as a reagent for direct conversion of silyl enol ethers into tris-ketol phosphates **166** (Scheme 3.69) [217].

3.1.8 Oxidation of Alkenes and Alkynes

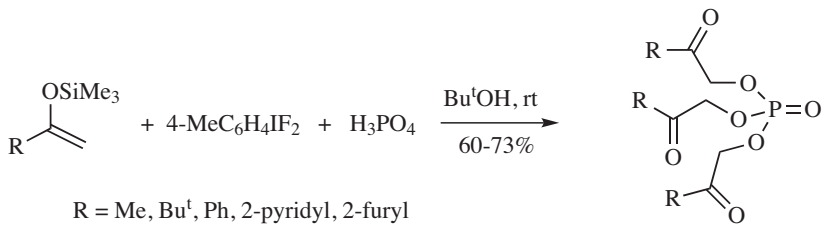
Alkenes and alkynes can be oxidatively functionalized by electrophilic λ^3-iodanes, such as iodosylbenzene, [bis(acyloxy)iodo]arenes and organoiodine(III) derivatives of strong acids. Iodosylbenzene itself has a low reactivity to alkenes due to the polymeric structure. However, the relatively weak electrophilic reactivity of $(PhIO)_n$ can be increased considerably in the presence of $BF_3 \cdot Et_2O$ or other Lewis acids. This activation



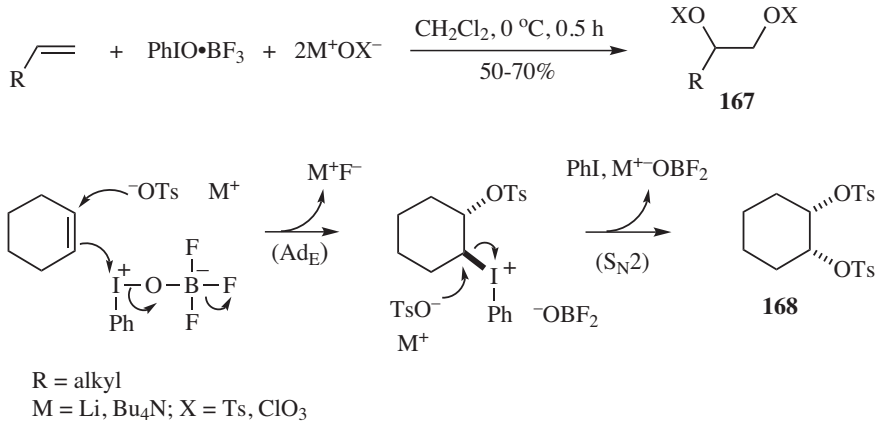
R^1 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4; R^2 = H, Me; R^3 = Me, Et



Scheme 3.68



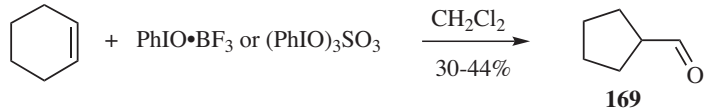
Scheme 3.69



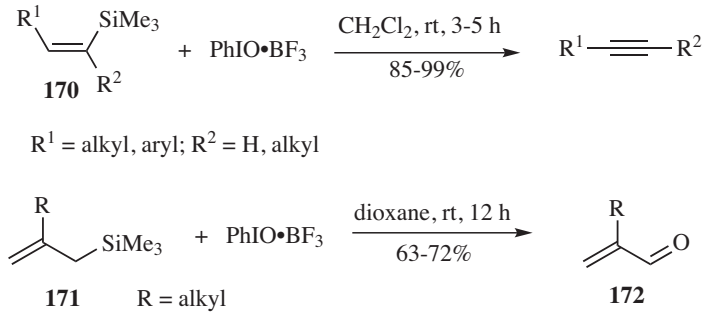
Scheme 3.70

is usually explained by the formation of non-isolable, highly electrophilic complexes such as $PhI^{+}OBF_3^{-}$. Reactions of these complexes with unsaturated organic substrates can afford various products depending on the reaction conditions and structure of the organic substrate. Alkenes react with activated iodosylbenzene in the presence of perchlorate or tosylate anions as external nucleophiles to give 1,2-diperchlorates or 1,2-ditosylates **167** as major products (Scheme 3.70) [218]. Cyclohexene in this reaction gives exclusively *cis*-ditosylate **168** resulting from the electrophilic addition–nucleophilic substitution sequence outlined in Scheme 3.70.

Under similar conditions, but in the absence of external nucleophiles, cyclohexene with $PhI^{+}OBF_3^{-}$ affords formylcyclopentane (**169**) (Scheme 3.71) [219]. The rearranged product **169** is also formed in the reaction of cyclohexene with oligomeric iodosylbenzene sulfate, $(PhIO)_3SO_3$ [163], or with $(PhIO)_n$ in aqueous H_2SO_4 [220].



Scheme 3.71



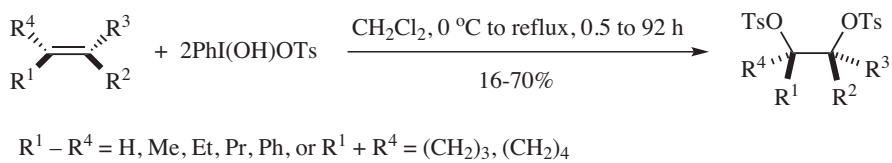
Scheme 3.72

Various products can be prepared by the reaction of $PhI^+OBF_3^-$ with unsaturated silylated substrates, such as silylalkenes and silylalkynes. (*E*)-Vinylsilanes react with $PhI^+OBF_3^-$ to give stable alkenyl(phenyl)iodonium tetrafluoroborates (Section 2.1.9.2), whereas (*Z*)-vinylsilanes **170** undergo dehydrosilylation to afford alkynes in high yields (Scheme 3.72) [221–223]. Allylsilanes **171** are oxidized with $PhI^+OBF_3^-$ to give conjugated enals **172** [224].

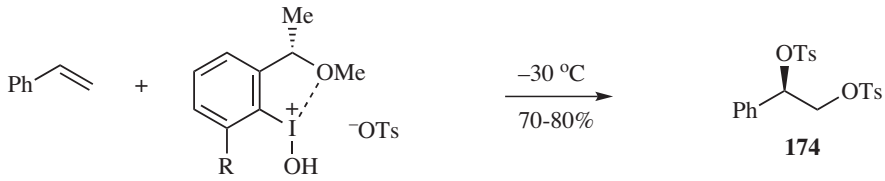
HTIB [PhI(OH)OTs] has high reactivity toward alkenes and alkynes. Reactions of HTIB with alkenes afford *vic*-ditosyloxyalkanes in moderate yield (Scheme 3.73) [225–227]. With cyclohexene and alkyl-substituted alkenes, this reaction proceeds as a stereoselective *syn*-addition, whereas phenyl-substituted alkenes and norbornene give products of skeletal rearrangements.

The reactions of HTIB with alkenes (Scheme 3.73) can be rationalized by a polar addition–substitution mechanism similar to the one shown in Scheme 3.70. The first step in this mechanism involves electrophilic *anti*-addition of the reagent to the double bond and the second step is nucleophilic substitution of the iodonium fragment by tosylate anion with inversion of configuration. Such a polar mechanism also explains the skeletal rearrangements in the reactions of HTIB with polycyclic alkenes [227], the participation of external nucleophiles [228] and the intramolecular participation of a nucleophilic functional group with the formation of lactones and other cyclic products [229–231]. An analogous reactivity pattern is also typical of [hydroxy(methanesulfonyloxy)iodo]benzene [232] and other [hydroxy(organosulfonyloxy)iodo]arenes.

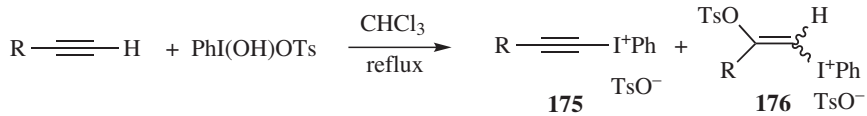
Chiral [hydroxy(organosulfonyloxy)iodo]arenes **173** (Section 2.1.6.1) have been evaluated as enantioselective electrophilic reagents towards alkenes and ketones. Enantioselectivities as high as 65% have been achieved in the dioxytosylation of styrene to give products **174** (Scheme 3.74). The maximum selectivity is observed in the reactions of *ortho*-ethyl compounds **173,** with lower selectivity being observed for reagents **173** bearing both smaller and larger substituents R. X-Ray structure analysis and *ab initio* calculations have been used to develop a model to rationalize the stereoselectivities in the reactions of chiral hypervalent iodine reagents **173.** In this model, high enantiomeric excess in the reaction correlates with the relative population of a conformation in which a methyl group on the asymmetric carbon atom is in the axial position [233].



Scheme 3.73



Scheme 3.74



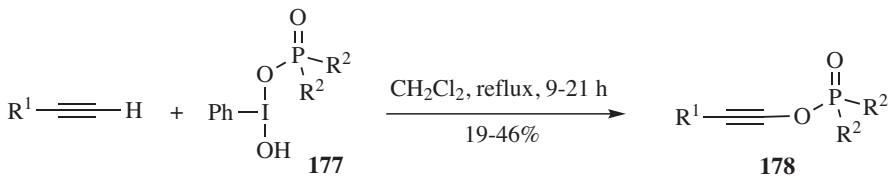
Scheme 3.75

The reaction of HTIB with alkynes generally affords two products: alkynyl- (**175**) and alkenyl-(phenyl)iodonium (**176**) tosylates (Scheme 3.75) [234–238]. Alkynyl(phenyl)iodonium tosylates **175** are major products in the reactions of terminal alkynes bearing bulky substituents (R = *tert*-butyl, *sec*-butyl, cyclohexyl, aryl, etc.), while alkenyliodonium tosylates **176** are formed from non-sterically hindered terminal alkynes or from internal alkynes.

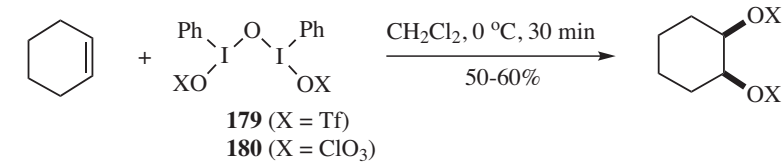
[Hydroxy(dialkylphosphoryloxy)iodo]benzenes **177** (Section 2.1.7) react with terminal alkynes under anhydrous conditions to afford alkynyl phosphates **178** (Scheme 3.76) via intermediate formation of the respective alkynyl(phenyl)iodonium phosphates [239].

μ-Oxo-bridged triflate **179** and perchlorate **180** (Section 2.1.7) react with alkenes to afford *vic*-diperchlorates or ditriflates; in the case of cyclohexene this reaction proceeds as a stereospecific *syn*-addition (Scheme 3.77) [218, 240–242]. Likewise, the reaction of alkenes and cycloalkenes with a reagent generated *in situ* from (diacetoxyiodo)benzene and magnesium perchlorate (Section 2.1.7) affords 1,2-diperchlorates **181** and **182** [243].

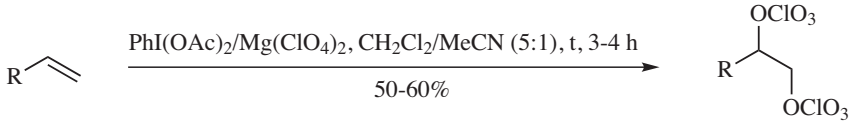
Adducts of iodosylbenzene with sulfur trioxide (**183** and **185**) (Section 2.1.7) react with alkenes under mild conditions to give the respective cyclic sulfate esters, such as **184, 186** and **187** (Scheme 3.78) [218, 244]. Likewise, phenyliodine(III) sulfate **185,** generated from iodosylbenzene and trimethylsilyl chlorosulfonate



Scheme 3.76

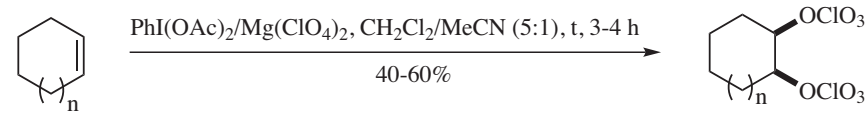


179 (X = Tf)
180 (X = ClO_3)



R = C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, cyclohexyl

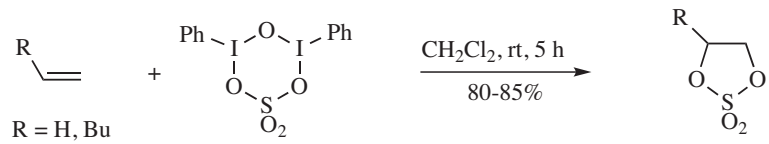
181



n = 1, 2, 3

182

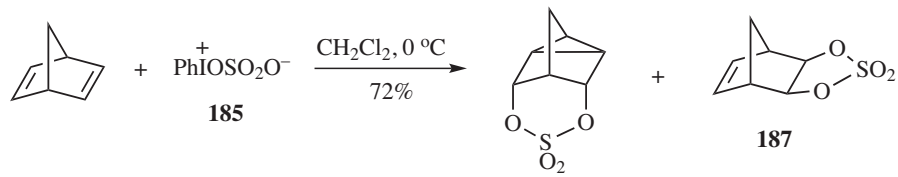
Scheme 3.77



R = H, Bu

183

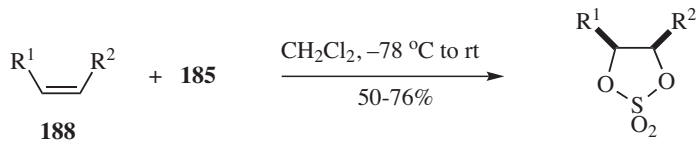
184



185

186

187

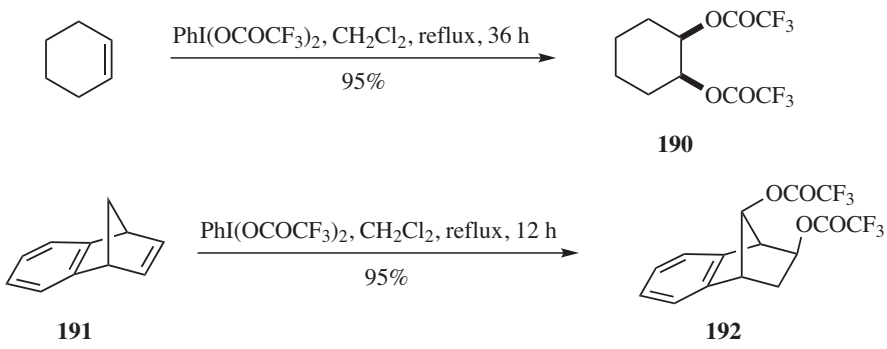


188

R^1 = Me_3Si, Me_2PhSi, Bu; R^2 = H or Bu

189

Scheme 3.78



Scheme 3.79

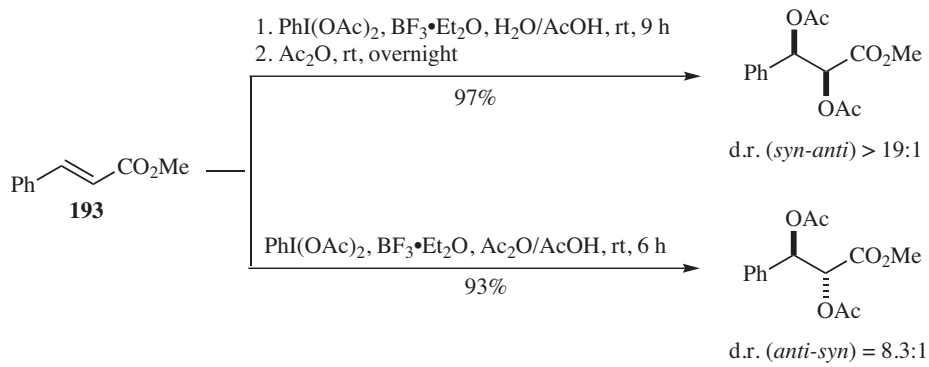
(Section 2.1.7), has been used for the preparation of cyclic sulfates **189** from alkenes and vinylsilanes **188** [245, 246].

Numerous examples of oxidative transformations of alkenes using [bis(acyloxy)iodo]arenes have been reported [11, 247–253]. [Bis(trifluoroacetoxy)iodo]benzene reacts with alkenes in the absence of any additive or catalyst, affording vicinal bis(trifluoroacetates), which can be converted into the corresponding glycols or carbonyl compounds by hydrolysis [248, 253]. For example, cyclohexene reacts with $PhI(OCOCF_3)_2$ in dichloromethane under reflux conditions to give *cis*-1,2-bis(trifluoroacetate) **190** in almost quantitative yield (Scheme 3.79) [248]. With bicyclic alkenes, such as norbornene or benzonorbornadiene **191,** the rearranged products (e.g., **192**) are predominantly formed. Similar rearranged products are formed in the reactions of alkenes with $PhI(OAc)_2$ in the presence of strong acids [254].

Mechanistic studies of the diacetoxylation of alkenes using (diacetoxyiodo)benzene have demonstrated a protio-catalytic nature of this reaction [255]. Systematic studies into the catalytic activity in the presence of proton-trapping and metal-complexing additives indicate that strong acids act as catalysts in the reaction. When trifluoromethanesulfonic acid is used as catalyst, the selectivity and reaction rate of the conversion is similar or superior to most efficient metal-based catalysts, such as Pd(II) and Cu(II) metal cations. Based on a kinetic study as well as *in situ* mass spectrometry, a mechanistic cycle for the proton-catalyzed reaction was proposed in this work [255].

Selective *syn* and *anti* diacetoxylations of alkenes can be achieved using a $PhI(OAc)_2$–$BF_3{\cdot}OEt_2$ system at room temperature in the presence and absence of water, respectively [256]. Various alkenes, including styrenes, aliphatic alkenes, cycloalkenes, α,β-unsaturated esters, furnish the corresponding vicinal diacetates in good to excellent yields and diastereoselectivity under these conditions. A multigram-scale diastereoselective diacetoxylation of methyl cinnamate (**193**) (Scheme 3.80) has also been also accomplished, maintaining the same efficiency as the small-scale reaction.

It is assumed that the reversal of *syn*/*anti* selectivity in these reactions can be explained by a mechanism involving the 1,3-dioxolan-2-yl cation **194** (Scheme 3.81) [255–259] similar to that proposed for the I_2/silver salt mediated Prevost [260] and Woodward [261] reactions. Reactions of alkenes with chiral [bis(acyloxy)iodo]arenes (Section 2.1.5.1) can be used for enantioselective acetoxylations [257, 262, 263]. For example, in the reaction of alkene **195** with chiral reagent **196** initiated by injection of boron trifluoride diethyl etherate in a dichloromethane solution containing acetic acid at –80 °C and terminated at –40 °C by addition of water, a regioisomeric mixture of the monoacetoxy products **197** and **198** is obtained. Acetylation of this regioisomeric mixture gives *syn*-diacetate **199** as a single diastereomer with the (1*S*,2*S*) configuration in high enantiomeric purity (Scheme 3.82) [257]. When the reaction of alkene **200** is similarly started at



Scheme 3.80

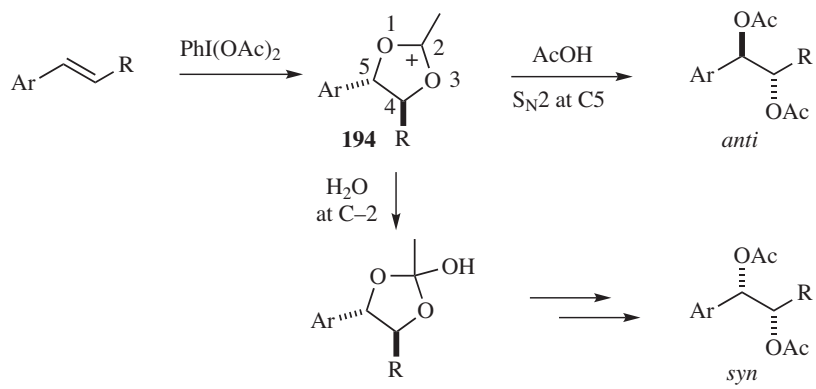
–80 °C and the reaction mixture is allowed to warm to room temperature, *anti*-diacetate **201** with the (1*R*,2*S*) configuration is preferentially obtained.

The reversal of *syn*/*anti* selectivity in this reaction (Scheme 3.82) can be explained by a mechanism similar to that shown in Scheme 3.81. The chiral, non-racemic 1,3-dioxolan-2-yl cation intermediates **194** are initially generated during enantioselective dioxyacetylation of alkene with chiral [bis(acyloxy)iodo]arene **196.** Regioselective attack of a nucleophile toward the intermediate results in reversal of enantioselectivity of the dioxyacetylation [257].

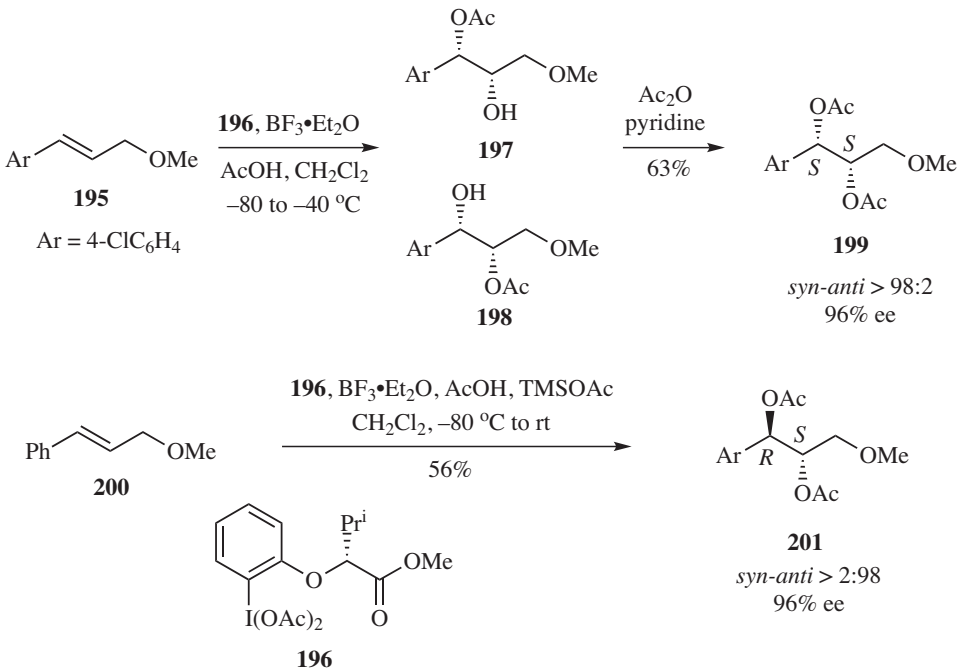
The oxylactonization of *ortho*-alkenylbenzoates with lactate-derived optically active hypervalent iodine(III) reagents proceeds with a high degree of regio-, diastereo- and enantioselectivity leading to the asymmetric synthesis of 3-alkyl-4-oxyisochroman-1-ones [263]. A specific example – the enantioselective oxylactonization of substrate **202** with reagent **203** – is shown in Scheme 3.83.

Iodosylbenzene and [bis(acyloxy)iodo]arenes are useful reagents for nucleophilic epoxidation of electron-deficient alkenes, such as tetrasubstituted perfluoroalkenes [264] and α,β-unsaturated carbonyl compounds [265, 266]. In particular, iodosylbenzene reacts with enones **204** to furnish the corresponding epoxides **205** in generally high yields (Scheme 3.84) [265].

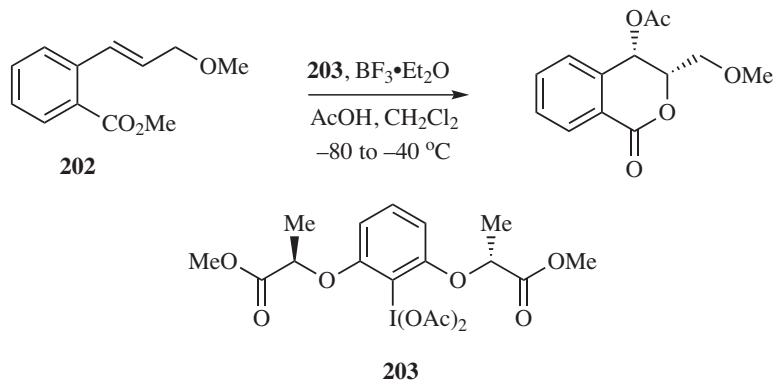
Likewise, [bis(acyloxy)iodo]arenes can be used as the oxidants in organocatalytic, asymmetric epoxidation of α,β-unsaturated aldehydes using chiral imidazolidinone catalyst **207** [266]. In a specific example, the



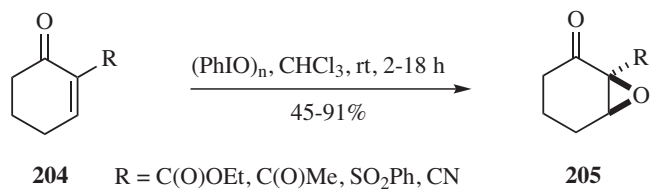
Scheme 3.81



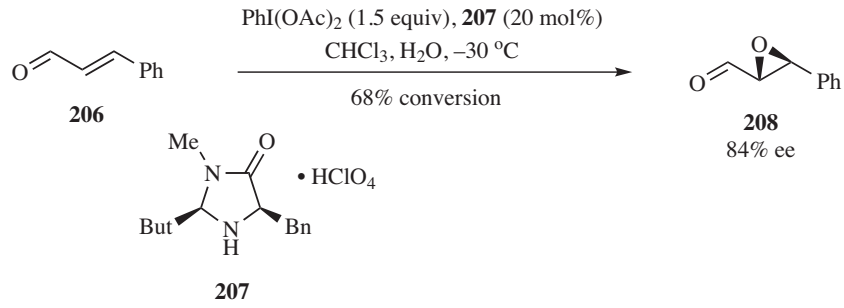
Scheme 3.82



Scheme 3.83



Scheme 3.84



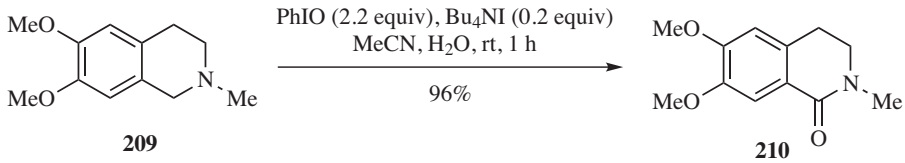
Scheme 3.85

reaction of aldehyde **206** with (diacetoxyiodo)benzene affords epoxide **208** with good enantioselectivity (Scheme 3.85).

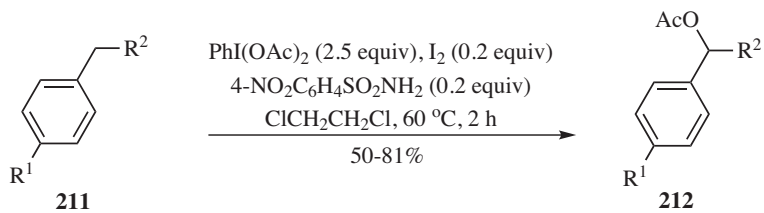
3.1.9 Oxidations at the Benzylic or Allylic Position

Oxidations of C—H bonds at the benzylic or allylic position using λ^3-iodanes can be achieved only in the presence of catalysts, such as, iodine, peroxides and transition metals (Section 3.1.20). For example, the oxidation of tetrahydroisoquinoline **209** by iodosylbenzene in the presence of tetrabutylammonium iodide proceeds at the benzylic position to give the lactam **210** (Scheme 3.86) [267].

Likewise, treatment of alkylbenzenes **211** with (diacetoxyiodo)benzene in the presence of catalytic amounts of molecular iodine and *p*-toluenesulfonamide or *p*-nitrobenzenesulfonamide in 1,2-dichloroethane at 60 °C gives the corresponding (α-acetoxy)alkylbenzenes **212** in generally good yields (Scheme 3.87) [268]. A plausible mechanism for this reaction involves the initial generation of $ArSO_2NH^{\bullet}$ radicals from $PhI(OAc)_2$, I_2 and $ArSO_2NH_2$, which further promote radical substitution at the benzylic carbon [268].

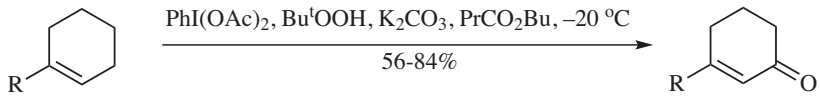


Scheme 3.86



R^1 = H, Br, Bu^t, NO_2, CO_2Me, Ph, etc.; R^2 = Me, Et, Pr, etc.

Scheme 3.87



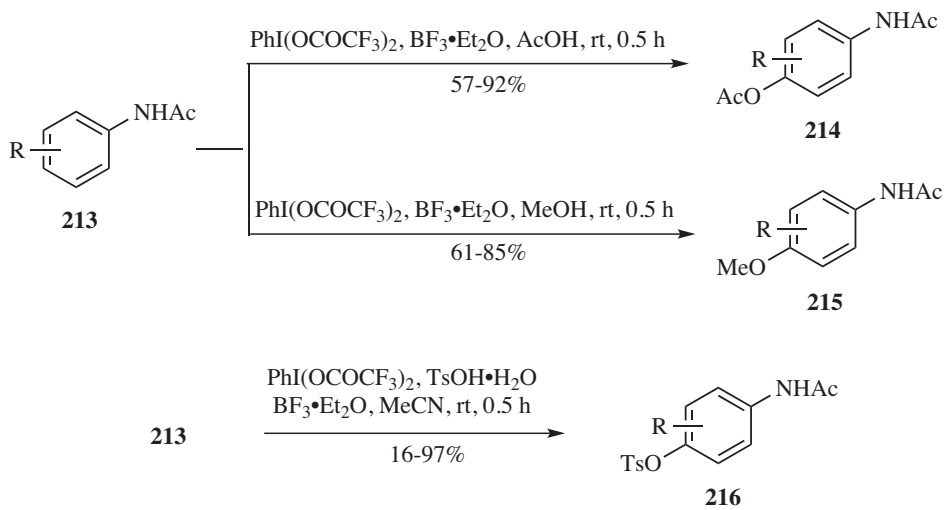
R = alkyl, aryl, OAc, CN, NO_2, etc.

Scheme 3.88

(Diacetoxyiodo)benzene in the presence of *tert*-butyl hydroperoxide readily oxidizes alkenes at the allylic position (Scheme 3.88) [269]. This reaction proceeds via initial formation of the *tert*-butylperoxy radical and it can be extended to the oxidation of unactivated C—H bonds in alkyl esters and amides to give the corresponding keto compounds under mild conditions [270].

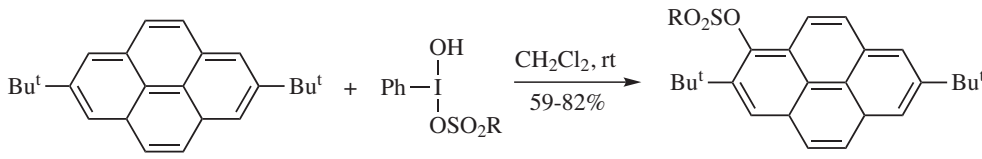
3.1.10 Oxidative Functionalization of Aromatic Compounds

The reactions of aromatic compounds with λ^3-iodanes usually afford products of oxidative dearomatization (Section 3.1.11) or oxidative coupling (Section 3.1.12). Only a few examples of non-catalytic oxygenation of aromatic C—H bonds have been reported in the literature. Direct acetoxylation and etherification of anilides can be achieved using [bis(trifluoroacetoxy)iodo]benzene in the presence of Lewis acids [271]. In particular, treatment of various anilides **213** with 1.5 equiv of $PhI(OCOCF_3)_2$ and 1.0 equiv of boron trifluoride etherate in acetic acid at room temperature affords the corresponding *para*-acetoxylated products **214** in good yields and with high regioselectivity (Scheme 3.89). Likewise, the reaction of anilides **213** with alcohols and 2.0 equiv of $PhI(OCOCF_3)_2$ in the presence of 2.0 equiv of $BF_3{\cdot}OEt_2$ provides the corresponding *para*-etherified products **215** in good yields [271]. The direct tosyloxylation of anilides **213** has been performed in a similar fashion by the treatment of anilides with $PhI(OCOCF_3)_2$ under mild conditions in the presence of $BF_3{\cdot}OEt_2$ and toluenesulfonic acid to give *para*-tosyloxylated products **216** with high regioselectivity [272].



R = H, 2-Me, 3-Me, 2-OMe, 2-F, 2-Cl, 2-Br, 2-CO_2Me, 3-OAc, 2,5-Me_2, 3,5-Me_2, etc.

Scheme 3.89



217 **218** **219**

R = Me, 4-MeC$_6$H$_4$, 2,4-(NO$_2$)$_2$C$_6$H$_3$, (1*R*)-10-camphoryl

Scheme 3.90

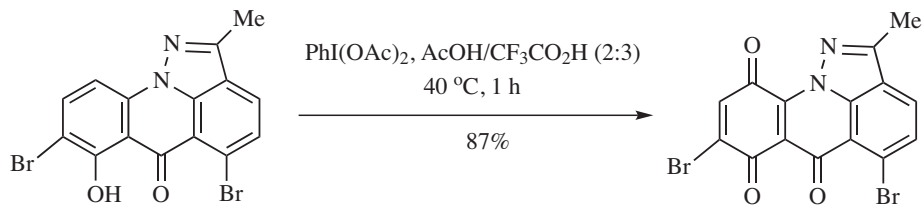
para-Triflates from anilides have been prepared similarly by direct oxidative triflation using PhI(OCOCF$_3$)$_2$ as the oxidant and AgOTf as the source of triflate anion [273].

[Hydroxy(organosulfonyloxy)iodo]benzenes can be used for the oxidative functionalization of arenes. Various polycyclic arenes, such as pyrene, anthracene, phenanthrene, perylene and others, undergo regioselective oxidative substitution reactions with [hydroxy(organosulfonyloxy)iodo]benzenes in dichloromethane at room temperature to give the corresponding aryl sulfonate esters in moderate to good yields [274]. For example, treatment of 2,7-di-*tert*-butylpyrene (**217**) with iodine(III) organosulfonate reagents **218,** containing tosylate, mesylate, (+)-10-camphorsulfonate and 2,4-dinitrobenzenesulfonate ligands, affords the respective organosulfonyloxy derivatives **219** in good yields and with high regioselectivity (Scheme 3.90) [274].

3.1.11 Oxidative Dearomatization of Phenols and Related Substrates

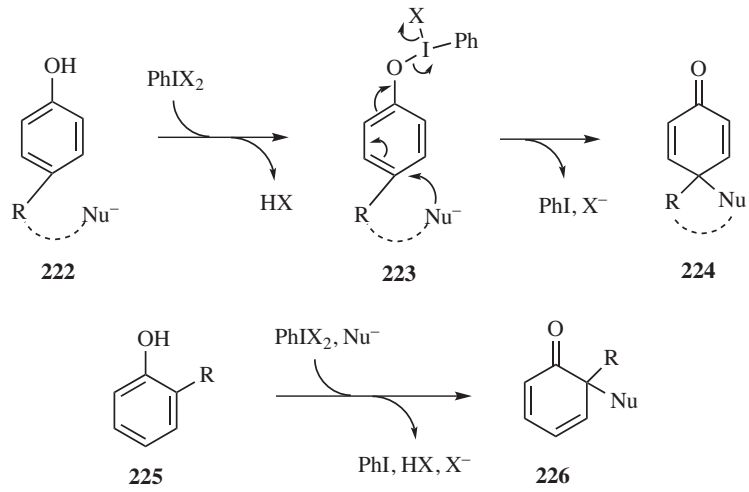
Hypervalent iodine compounds are commonly used as the reagents for various synthetically useful oxidative transformations of phenols and other electron-rich aromatic substrates. The oxidation of various *ortho*-substituted phenols or *o*- and *p*-hydroquinones with [bis(acyloxy)iodo]arenes usually affords the corresponding benzoquinones in excellent yields [275–282]. (Diacetoxyiodo)benzene is a reagent of choice for the oxidation of various substituted *o*- and *p*-hydroquinones to the corresponding benzoquinones [277–279]. The oxidation generally proceeds in a methanol solution at room temperature to give benzoquinones in almost quantitative yield [277]. This procedure has been utilized in organic synthesis; for example, the oxidation of phenol **220** with (diacetoxyiodo)benzene has been used for the preparation of quinone **221** (Scheme 3.91), which is a key intermediate in the synthesis of an important class of antitumor agents [278]. [Bis(trifluoroacetoxy)iodo]benzene can selectively oxidize polychlorinated phenols to the respective benzoquinones in aqueous media [280]. This reaction has been utilized in the sensitive electrochemical identification of pentachlorophenol, which is one of the most toxic polychlorinated phenols.

Of particular use are the reactions of oxidative dearomatization of 4- or 2-substituted phenols **222** and **225** with λ^3-iodanes in the presence of an external or internal nucleophile (Nu) leading to the respective



220 **221**

Scheme 3.91



R = alkyl, aryl, halogen, O–alkyl, etc.
X = OAc or $OCOCF_3$

Scheme 3.92

cyclohexadienones **224** or **226** according to Scheme 3.92. The mechanism of this reaction most likely involves the initial formation of phenoxyiodine(III) species **223** followed by elimination of PhI and the generation of cationic phenoxenium intermediates, which finally combine with the nucleophile [283].

Various nucleophiles, such as water, alcohols, fluoride ion, carboxylic acids, amides, oximes and carbon nucleophiles, have been used successfully in these reactions (Scheme 3.92) in either an inter- or intramolecular mode. Synthetic applications of oxidative dearomatization reactions of phenols and related substrates have been summarized in several reviews [284–292].

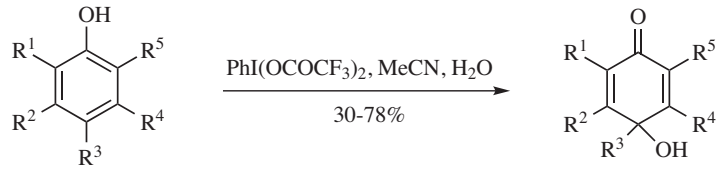
3.1.11.1 Oxidative Dearomatization of 4-Substituted Phenols

Oxidative dearomatization of 4-substituted phenols **222** with [bis(acyloxy)iodo]arenes in the presence of an external nucleophile provides a convenient approach to various 3,3-disubstituted cyclohexadienones **224** according to Scheme 3.92. Several examples of this reaction are provided below in Schemes 3.93–3.97.

The oxidation of various substituted phenols **227** with [bis(trifluoroacetoxy)iodo]benzene in aqueous acetonitrile affords *p*-quinols **228** in moderate to good yields (Scheme 3.93) [293]. Even higher yields of *p*-quinols are obtained when trimethylsilyl ethers of phenols are used as starting material. In particular, it was shown that the oxidation of trimethylsilyl ethers **229** affords *p*-quinols **230** in greatly improved yields due to the minimization of oligomer side-product formation compared to the oxidation of free phenol [294].

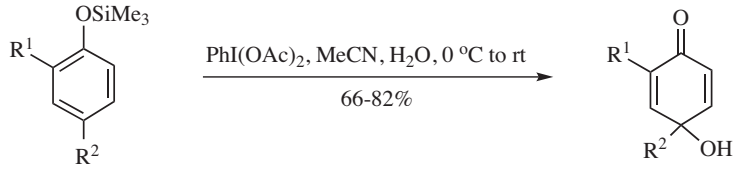
A similar oxidation of *p*-alkoxyphenols or 4-methoxynaphthols with (diacetoxyiodo)benzene in the presence of alcohols affords the respective quinone monoketals (Scheme 3.94) [277, 295, 296].

Further examples of synthetic application of the *para*-alkoxylation reaction include the preparation of dimethoxy ketal **231,** which is an essential precursor in the enantioselective synthesis of the potent antifungal agent (–)-jesterone [297], the synthesis of various dimethoxy ketals of *para*- and *ortho*-benzoquinones [298] and the methoxylation of various phenolic substrates, such as **232,** using (diacetoxyiodo)benzene in methanol (Scheme 3.95) [299–301].



227 **228**

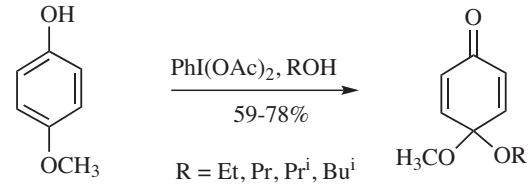
R^1, R^2, R^4, R^5 = H, alkyl, Br, CO_2Et; R^3 = Me, Bu^t, CH_2CO_2Et



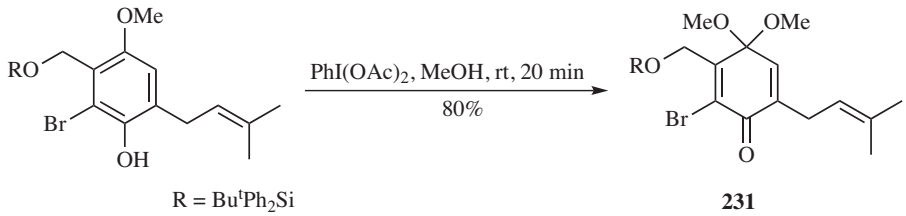
229 **230**

R^1 = H or Br; R^2 = Me, Ph, 2-FC_6H_4, 3-$NO_2C_6H_4$

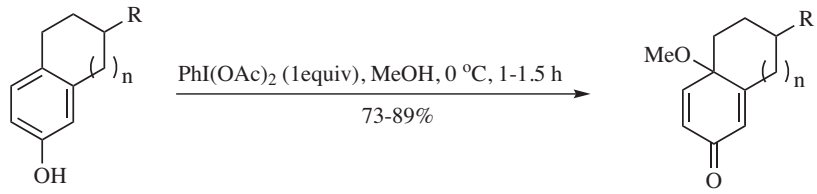
Scheme 3.93



Scheme 3.94

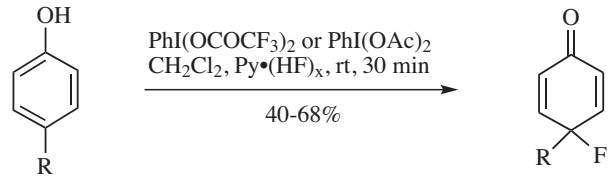


R = Bu^tPh_2Si **231**

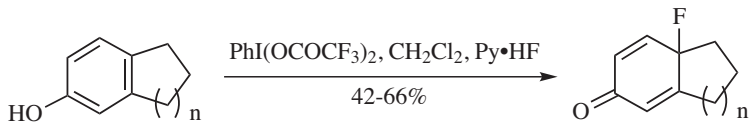


232 n = 0 or 1; R = H, Me, Et, etc.

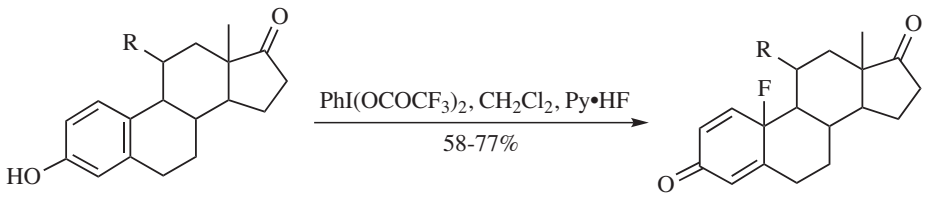
Scheme 3.95



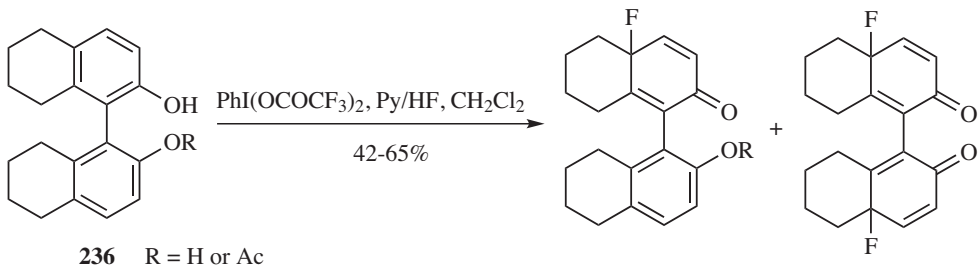
233 R = Me, Et, CH_2CH_2Br, F, Cl, etc.



n = 1 or 2 **234**

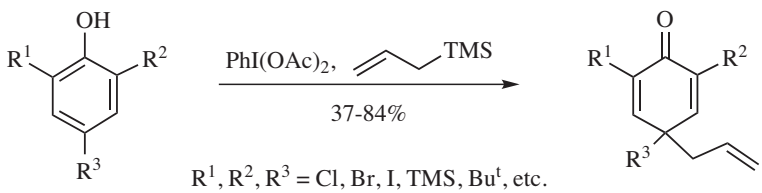


R = H, OH **235**



236 R = H or Ac

Scheme 3.96



R^1, R^2, R^3 = Cl, Br, I, TMS, Bu^t, etc.

237

Scheme 3.97

The oxidation of 4-alkylphenols **233** with [bis(acyloxy)iodo]arenes in the presence of pyridinium polyhydrogen fluoride, $Py{\cdot}(HF)_x$, as the source of fluoride anion results in nucleophilic *ipso*-fluorination (Scheme 3.96) [302–304]. This reaction has been used for the preparation of polycyclic 4-fluorocyclohexa-2,5-dienones **234** and **235** [302] and for the nucleophilic *para*-fluorination of tetrahydro-2-naphthol **236** [305].

Carbon nucleophiles can also be used as external nucleophiles, as illustrated by the oxidative allylation of phenols **237** (Scheme 3.97) [306].

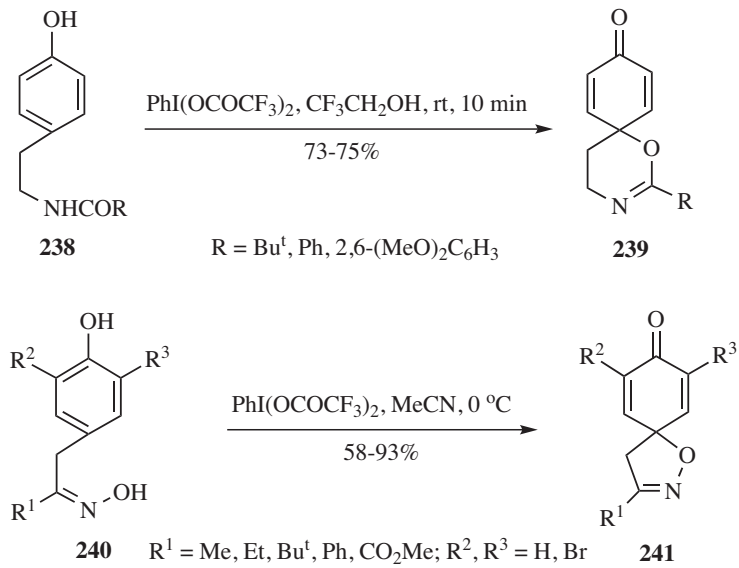
The oxidation of phenolic substrates in the intramolecular mode has been widely exploited as a powerful synthetic tool for the construction of a spirodienone fragment. Numerous oxidative spirocyclizations of phenolic substrates containing an internal oxygen, nitrogen, or carbon nucleophile have been reported and utilized in natural product syntheses. Representative examples of spirocyclizations employing oxygen-based internal nucleophiles are shown below in Schemes 3.98–3.102.

Oxidative cyclizations of amides **238** and ketoximes **240** by the action of [bis(trifluoroacetoxy)iodo]benzene in non-nucleophilic solvents afford the respective spirohexadienones **239** and **241** in good yields (Scheme 3.98) [307–309].

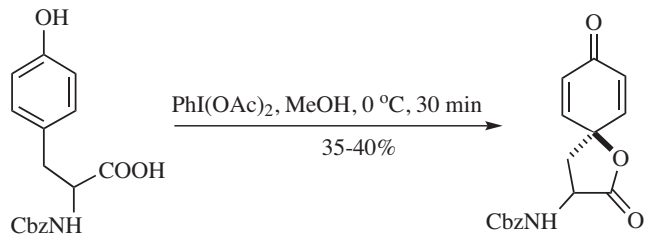
The oxidatively induced cyclization of N-protected tyrosine **242** has been used as an approach to the spirocyclic core intermediate product **243** (Scheme 3.99), which is an important step in the total synthesis of the antitumor antibiotic aranorosin [310].

A similar oxidation of tyrosine derivative **244** with an excess of (diacetoxyiodo)benzene in cold acetonitrile followed by quenching with aqueous sodium bromide furnished brominated spirolactone **246** in 80% overall yield. A plausible mechanism for this reaction involves the iodonium derivative **245** as an intermediate product and subsequent substitution of each phenyliodonium group with a bromide anion (Scheme 3.100) [311].

The spirocyclic product **248** has been prepared by a hypervalent iodine-induced oxidation of catechol **247** in a key step of the enantiospecific synthesis of the antituberculosis marine sponge metabolite (+)-puupehenone (Scheme 3.101) [312]. A similar oxidative cyclodearomatization approach has been utilized in

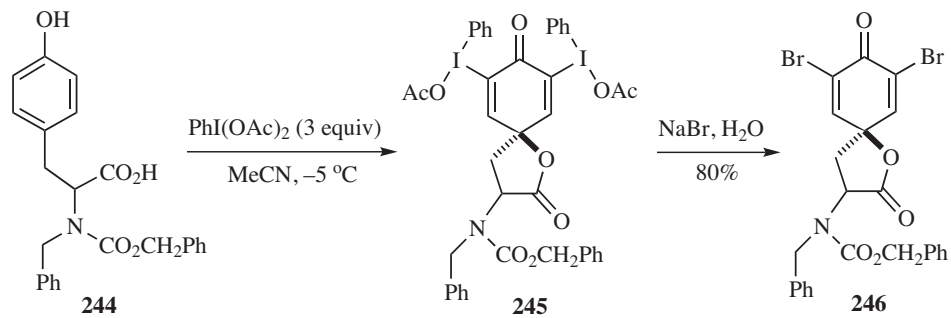


Scheme 3.98



242 Cbz = $PhCH_2O_2C$– **243**

Scheme 3.99



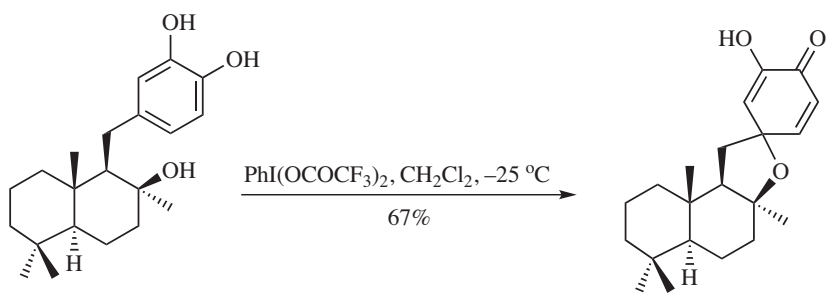
244 **245** **246**

Scheme 3.100

the stereocontrolled synthesis of a complex pentacycle embodying the molecular architecture of the cortistatin class of natural products [313].

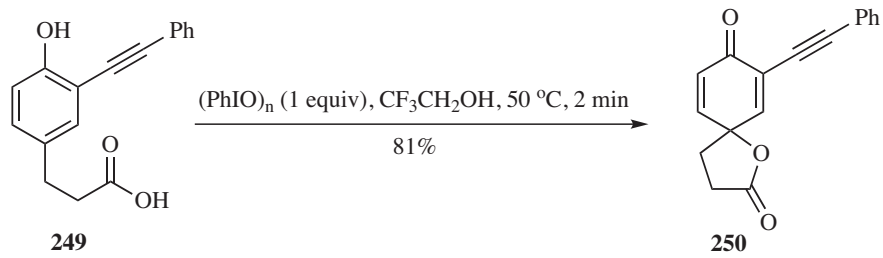
Iodosylbenzene-induced oxidative dearomatization of 3-(3-alkynyl-4-hydroxyphenyl)propanoic acid (**249**) affords spirolactone **250** (Scheme 3.102), which is a key intermediate in the a convergent and efficient synthetic approach to furoquinolinone and angelicin derivatives [314].

The oxidative spirocyclization of phenolic substrates containing an internal nitrogen nucleophile provides a useful tool for the construction of nitrogen heterocycles [287, 315–318]. For example, the hypervalent iodine-induced cyclization of phenolic oxazolines **251** affords the synthetically useful spirolactam products



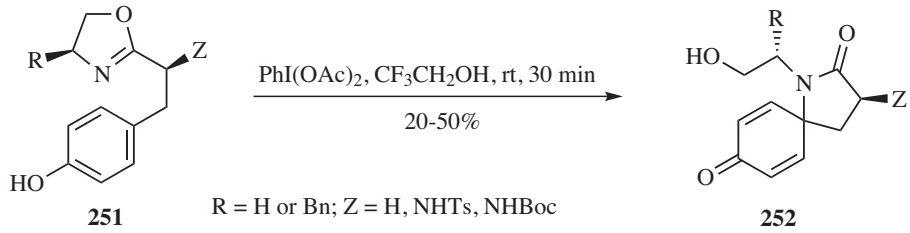
247 **248**

Scheme 3.101



249 **250**

Scheme 3.102



251 R = H or Bn; Z = H, NHTs, NHBoc **252**

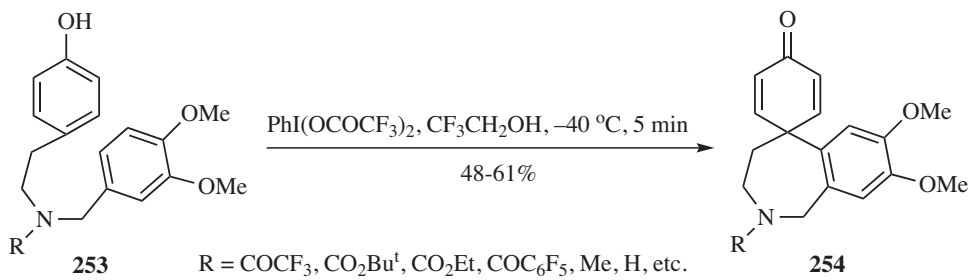
Scheme 3.103

252 (Scheme 3.103) [287, 315–318]. This methodology has been applied in the total synthesis of tricyclic azaspirane derivatives of tyrosine, FR901483 and TAN1251C [318, 319].

Of particular interest are hypervalent iodine-induced cyclizations of phenolic precursors in which carbon–carbon bond formation is achieved. Representative examples of spirocyclizations employing carbon-based internal nucleophiles are shown below in Schemes 3.104–3.111.

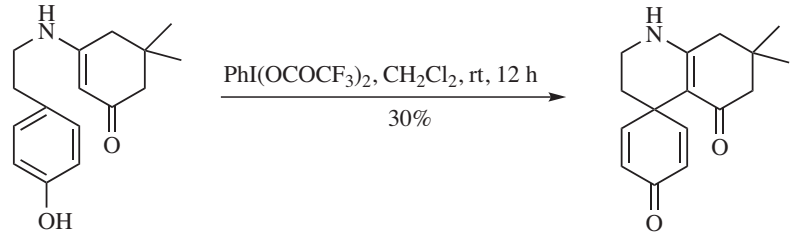
Kita and coworkers have applied the oxidative coupling of various phenolic derivatives towards the synthesis of several pharmacologically interesting natural products [320–323]. For example, spirodienone compounds **254,** which are intermediates for the synthesis of an Amaryllidaceae alkaloid, (+)-maritidine, were selectively obtained by the reaction of phenolic precursor **253** and [bis(trifluoroacetoxy)iodo]benzene (Scheme 3.104) [323].

The analogous oxidation of phenolic enaminone derivatives **255** has been used to prepare spirocyclohexadienones **256** (Scheme 3.105) [324].



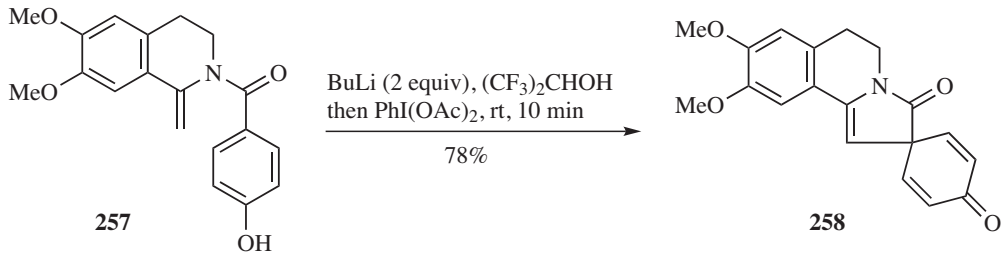
253 R = $COCF_3$, CO_2Bu^t, CO_2Et, COC_6F_5, Me, H, etc. **254**

Scheme 3.104



255 **256**

Scheme 3.105



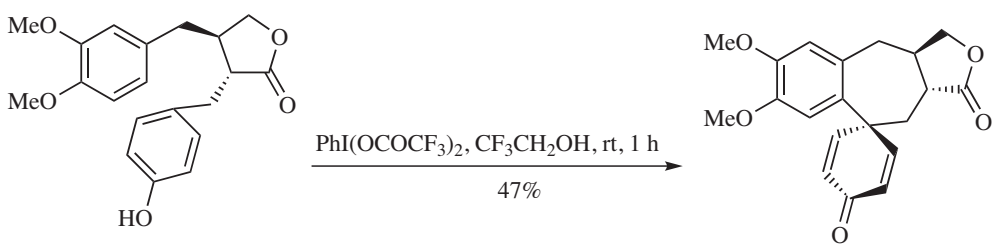
257 **258**

Scheme 3.106

The hypervalent iodine-promoted oxidation of enamide **257** in the presence of a base leads to the spiroenamide **258,** which is a key intermediate product in the total synthesis of annosqualine (Scheme 3.106) [325]. A similar oxidative cyclodearomatization approach has been utilized in the total synthesis of a proaporphine alkaloid, (±)-stepharine [326].

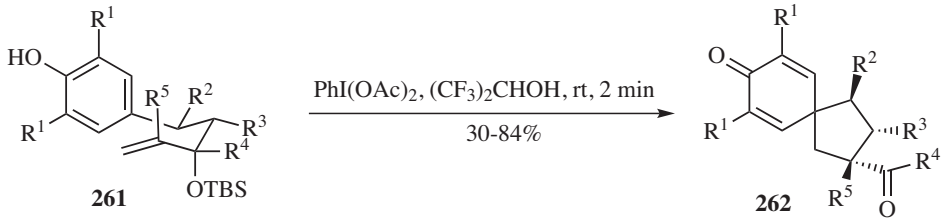
Treatment of the dibenzylbutyrolactone **259** with [bis(trifluoroacetoxy)iodo]benzene in trifluoroethanol for one hour gives as the major product spirodienone **260,** which has been postulated as an intermediate in the biosynthesis of tetrahydrodibenzocyclooctene lignans (Scheme 3.107) [327].

Canesi and coworkers have developed several synthetically useful tandem rearrangements on the basis of hypervalent iodine-promoted phenolic oxidation [328–331]. An oxidative Prins–pinacol tandem process mediated by a hypervalent iodine reagent allows the stereoselective transformation of simple phenols **261** into highly elaborate spirocyclic dienone cores **262** containing several quaternary carbon centers (Scheme 3.108).



259 **260**

Scheme 3.107



R^1 = H or Br; R^2 = H or Me; R^3 = H, Me, $CH_2CH{=}CH_2$
R^4 = Me, $CH{=}CH_2$, Ph; R^5 = H or Me
TBS = Bu^tMe_2Si

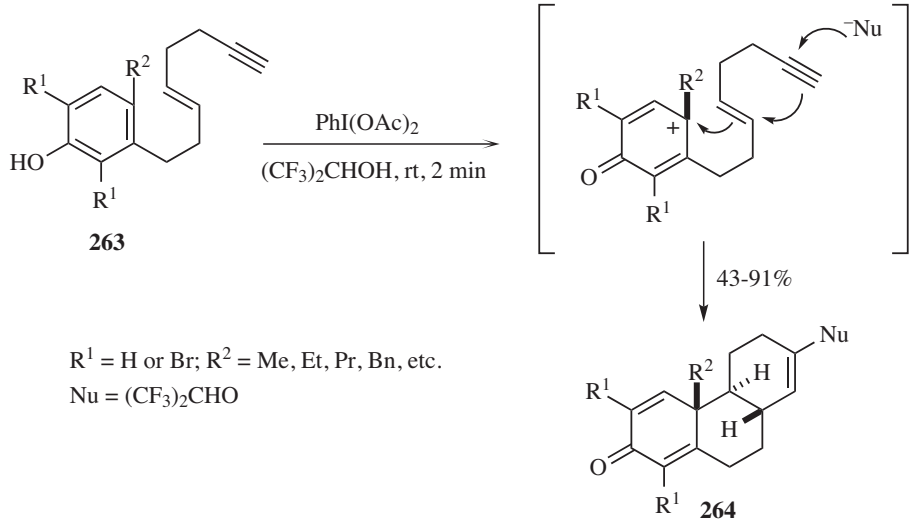
Scheme 3.108

This stereoselective process has been directly applied toward the formal synthesis of (–)-platensimycin, an important antibiotic agent [328].

Activation of phenol derivatives **263** with a hypervalent iodine reagent promotes the formation of bicyclic and tricyclic (**264**) products via a cationic cyclization process (Scheme 3.109). The method allows efficient one-step syntheses of scaffolds present in several natural products and occurs with total stereocontrol [329].

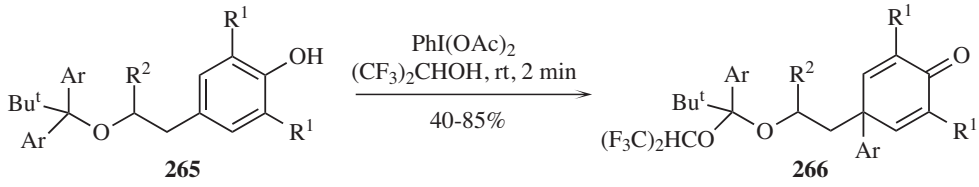
An oxidative *ipso*-rearrangement mediated by a hypervalent iodine reagent that enables rapid generation of a functionalized dienone system **266** containing a quaternary carbon center has been developed (Scheme 3.110) [330]. The process occurs through transfer of an aryl group from a silyl segment present on the lateral chain of the phenol derivative **265.** This transformation has been utilized in a total synthesis of an alkaloid sceletenone [330].

Oxidative 1,2- and 1,3-alkyl shifts mediated by a hypervalent iodine reagent using simple and inexpensive phenol derivatives **267** enable rapid construction of highly functionalized scaffolds containing a prochiral



R^1 = H or Br; R^2 = Me, Et, Pr, Bn, etc.
Nu = $(CF_3)_2CHO$

Scheme 3.109



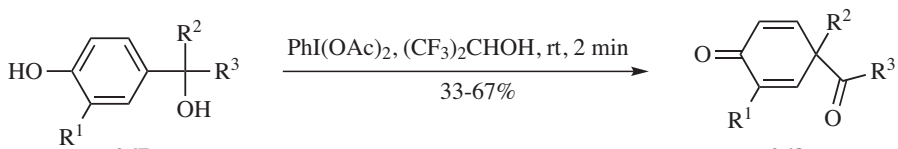
R^1 = H, Br, OMe, Bu^t; R^2 = H or Me
Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4

Scheme 3.110

dienone system (**268**) (Scheme 3.111) [331]. An efficient enantioselective version of this process resulting in the formation of a challenging quaternary carbon center has also been developed. As an illustration of the synthetic potential of this method, the rapid synthesis of several functionalized polycyclic systems as well as a formal synthesis of acetylaspidoalbidine, a hexacyclic alkaloid belonging to the Aspidosperma family, has been described [331].

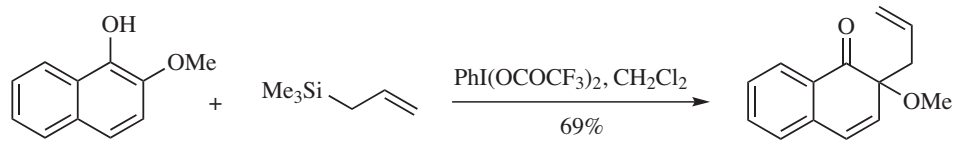
Additional examples of the hypervalent iodine-induced oxidative phenolic cyclizations include the following studies: the preparation of different heterocyclic rings such as dihydrofuranobenzofurans, tetrahydrofuranobenzofurans, tetrahydropyranofurans and dihydrobenzofurans by the treatment of various substituted phenols with (diacetoxyiodo)benzene in the presence of furan, allylsilanes, or cyclic enol ethers [332], the synthesis of galanthamine, a natural alkaloid isolated from the Amaryllidaceae family [333], the asymmetric total syntheses of the pentacyclic Stemona alkaloids tuberostemonine and didehydrotuberostemonine [334], the fully stereocontrolled total syntheses of (–)-cylindricine C and (–)-2-epicylindricine C [335], the asymmetric total synthesis of platensimycin [336], the total synthesis of a potent antitumor alkaloid, discorhabdin A [337], the total synthesis of the Amaryllidaceae alkaloid (+)-plicamine [338] and the development of a flow process for the multistep synthesis of the alkaloid natural product oxomaritidine [339].

(Diacetoxyiodo)benzene and [bis(trifluoroacetoxy)iodo]benzene are the most commonly used reagents for oxidative dearomatization of phenols. It has been demonstrated, however, that μ-oxo-bridged phenyliodine trifluoroacetate, $PhI(OCOCF_3)O(OCOCF_3)IPh$, is a more efficient oxidant in these reactions. The use of the μ-oxo-bridged phenyliodine trifluoroacetate instead of $PhI(OAc)_2$ and $PhI(OCOCF_3)_2$ in the oxidative cyclization of phenols involving carbon–oxygen, carbon–nitrogen and carbon–carbon bond formations affords spirocyclized cyclohexadienones in generally better yields [282, 340, 341]. Application of hypervalent iodine(V) oxidants, such as stabilized 2-iodoxybenzoic acid (SIBX, see Section 2.2.3.1), in the oxidative dearomatization of phenols has also been documented [291].



R^1 = H or Me; R^2 = $CH_2CH{=}CH_2$, $CH{=}CH_2$, Ph, Bu
R^3 = Me, Et, CH_2OTBS, Bu, $CH_2CH{=}CH_2$

Scheme 3.111



269 **270**

Scheme 3.112

3.1.11.2 Oxidative Dearomatization of 2-Substituted Phenols

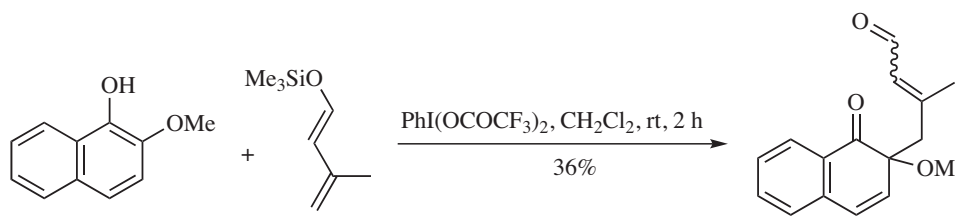
Oxidative dearomatization of 2-substituted phenols **225** with [bis(acyloxy)iodo]arenes in the presence of external or internal nucleophile provides a convenient approach to 6,6-disubstituted cyclohexa-2,4-dienones **226** according to general Scheme 3.92. Specific examples of this reaction are provided below in Schemes 3.112–3.114.

Quideau and coworkers have developed a hypervalent iodine-mediated regioselective protocol for the oxidative dearomatization of 2-alkoxyarenols in the presence of external carbon-based nucleophiles, such as allylsilanes or silyl enol ethers [342–345]. For example, the oxidation of 2-alkoxynaphthol **269** with [bis(trifluoroacetoxy)iodo]benzene in the presence of allylsilane affords 2,4-cyclohexadienone derivative **270** (Scheme 3.112) [342].

This is a synthetically valuable process, as illustrated by the hypervalent iodine-mediated oxidative nucleophilic substitution of **269** with the silyl enol ether **271,** leading to the highly functionalized naphthoid cyclohexa-2,4-dienone **272** (Scheme 3.113), which is an important intermediate product in the synthesis of aquayamycin-type angucyclinones [343, 344].

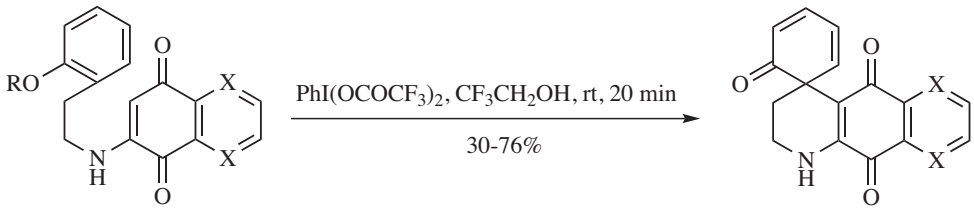
Synthetic application of the oxidative dearomatization of *ortho*-substituted phenolic substrates in the intramolecular mode is exemplified by the preparation of azacarbocyclic spirodienones **274** from phenol derivatives **273** (Scheme 3.114) [322].

Hypervalent iodine induced oxidative dearomatization of *ortho*-substituted phenolic substrates in the intramolecular mode has been realized as an enantioselective reaction. In particular, Kita and coworkers have developed the enantioselective spirocyclization reaction of the *ortho*-substituted phenolic substrates **275** using chiral aryliodine(III) diacetate **276** having a rigid spirobiindane backbone (Scheme 3.115) [346]. Similar enantioselective oxidative spirocyclization reactions of the *ortho*-substituted phenolic substrates under catalytic conditions in the presence of chiral iodoarenes or chiral quaternary ammonium iodide catalysts are discussed in Sections 4.1.6 and 4.4.



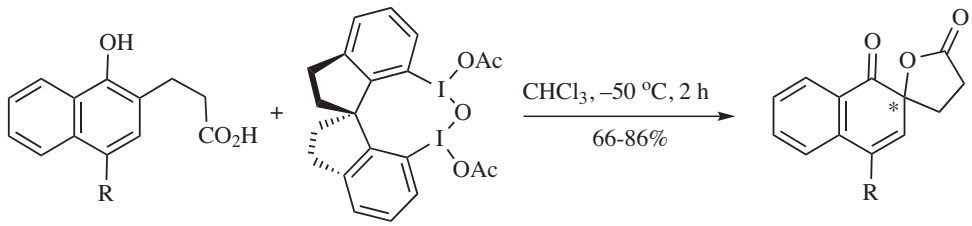
269 **271** **272** (*E*/*Z* 1.3:1)

Scheme 3.113



273 R = H, TMS, TBDM; X = CH or N **274**

Scheme 3.114

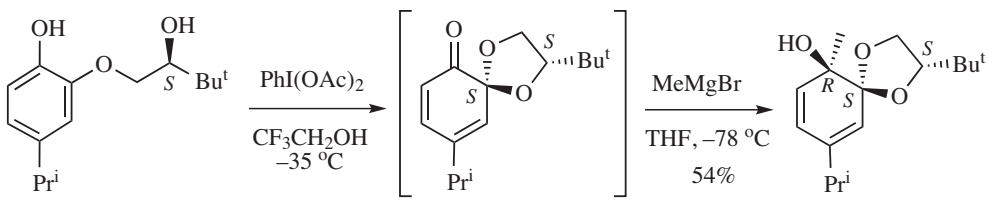


275 R = H, Et, Bn, cyclohexyl **276** up to 86% ee

Scheme 3.115

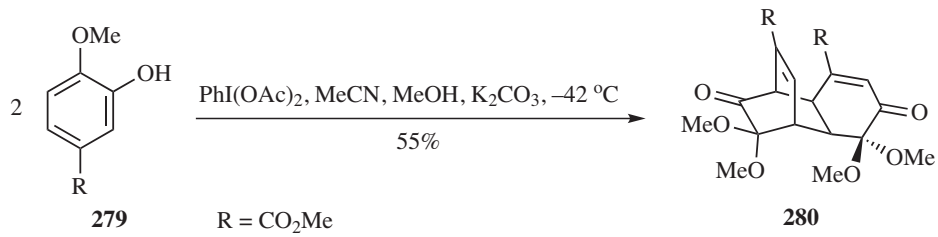
A versatile chiral substrate **278** for asymmetric synthesis has been prepared through the hypervalent iodine induced spiroketalization of phenols **277** with a chiral substituted ethanol unit O-tethered to the *ortho* position (Scheme 3.116) [347]. This reaction has been successfully utilized in the asymmetric total synthesis of the natural product (+)-biscarvacrol.

The oxidative dearomatization of *ortho*-substituted phenols **225** leads to 6,6-disubstituted cyclohexa-2,4-dienones **226** (Scheme 3.92), which can be conveniently utilized *in situ* as dienes in the Diels–Alder cycloaddition reaction. When the oxidation of phenols is performed in the absence of an external dienophile, a dimerization via [4+2] cycloaddition often occurs spontaneously at ambient temperature to afford the corresponding dimers with an extraordinary level of regio-, site- and stereoselectivity [348–350]. A detailed experimental and theoretical investigation of such hypervalent iodine induced Diels–Alder cyclodimerizations



277 **278** d.r. 95:5

Scheme 3.116



279 R = CO_2Me **280**

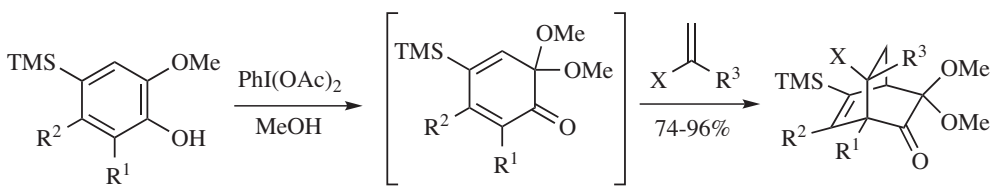
Scheme 3.117

has been published by Quideau and coauthors [349]. Scheme 3.117 shows a representative example of an oxidative Diels–Alder cyclodimerization of a phenolic substrate **279** to the dimer **280** [349].

If the oxidation is performed in the presence of an external dienophile, the respective products of [4+2] cycloaddition are formed [351–356]. Typical examples are illustrated by a one-pot synthesis of several silyl bicyclic alkenes **283** by intermolecular Diels–Alder reactions of 4-trimethylsilyl substituted masked *o*-benzoquinones **282** generated by oxidation of the corresponding 2-methoxyphenols **281** [351] and by the hypervalent iodine-mediated oxidative dearomatization/Diels–Alder cascade reaction of phenols **284** with allyl alcohol affording polycyclic acetals **285** (Scheme 3.118) [352]. This hypervalent iodine-promoted tandem phenolic oxidation/Diels–Alder reaction has been utilized in the stereoselective synthesis of the bacchopetiolone carbocyclic core [353].

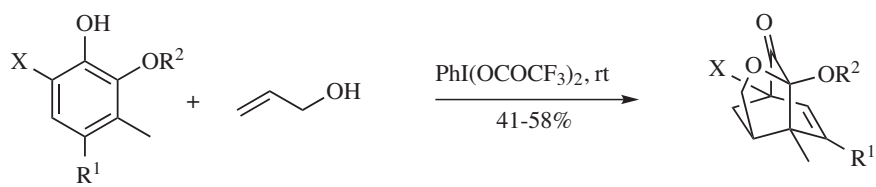
3.1.11.3 Oxidative Dearomatization of Anilines

Aniline derivatives can be oxidatively dearomatized analogously to the phenol derivatives. In particular, the oxidative *ipso*-fluorination of *para*-substituted tosylated anilines **286** using hypervalent iodine reagents



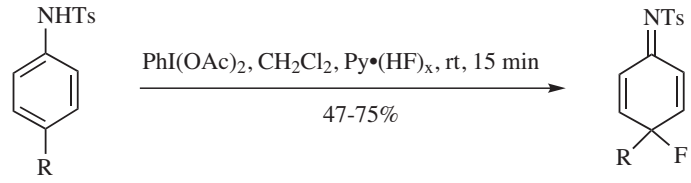
281 **282** **283**

R^1, R^2, R^3 = H or Me; X = CO_2Me



284 X = Br or H; R^1 = CO_2Me or OTs; R^2 = Me or Bn **285**

Scheme 3.118



286 R = Me, Et, F, Cl, etc. **287**

Scheme 3.119

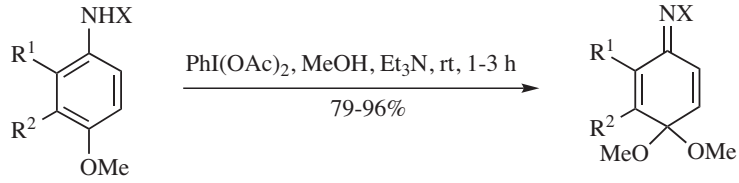
in combination with pyridinium polyhydrogen fluoride affords 4-fluorocyclohexa-2,5-dienimines **287** in generally good yields (Scheme 3.119) [357].

Likewise, the oxidative dearomatization of *para*-methoxy substituted N-protected anilines **288** using (diacetoxyiodo)benzene in the presence of methanol gives *p*-quinone monoimide ketals **289** (Scheme 3.120) [358]. If the oxidation of aniline derivatives is performed in the presence of water, the final isolated products are the respective *p*-benzoquinones or *p*-benzoquinone monoketals resulting from the hydrolysis of initially formed monoimide ketals **289** [358, 359].

The oxidative dearomatization of *para*-substituted *o*-alkynylanilines **290** using (diacetoxyiodo)benzene affords 2-alkynyl cyclohexadienimines **291,** which can act as active substrates for reaction with electron-rich styrenes **292** in the presence of metal salts: the $Bi(OTf)_3$-catalyzed reactions give 3,4-dihydrocyclopenta[*c,d*]indoles **293** and the AgOTf-catalyzed reactions provide tricyclic pyrrole derivatives **294** (Scheme 3.121) [360].

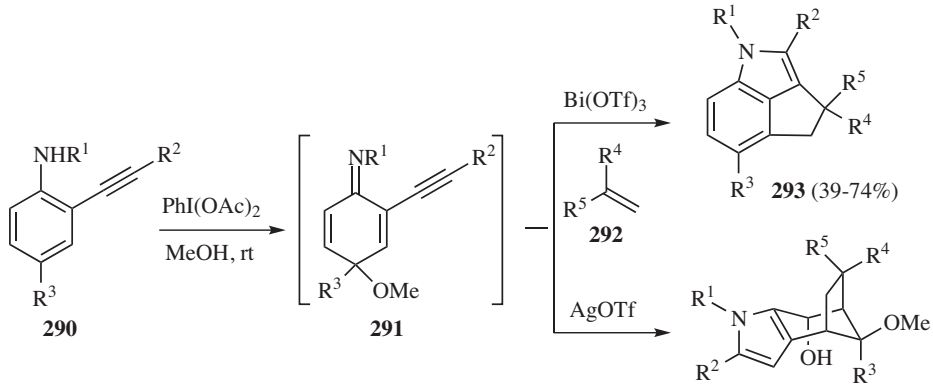
3.1.12 Oxidative Coupling of Aromatic Substrates

Oxidative coupling typically occurs in the reactions of phenol ethers or other electron-rich aromatic substrates with [bis(acyloxy)iodo]arenes in polar, non-nucleophilic solvents, under conditions favorable for single-electron transfer (SET) reactions (Section 1.5.3). The formation of the cation–radical intermediates **296** (R^1–Nu = $CH_2CH_2CH_2OH$) was experimentally confirmed by ESR spectroscopy in a detailed mechanistic study of the hypervalent-iodine-promoted oxidative cyclization reaction of phenol ethers **295** bearing an intramolecular hydroxyl group (Scheme 3.122) [361]. The initially generated cation–radical intermediates **296** combine with external or internal nucleophiles, affording the products of dearomatization (**297**) or coupling (**298**). Various factors determining the ratio of products **297** and **297** and their consequent transformations have been discussed by Kita and coauthors [361].



288 X = Boc or Ac
R^1 = H, R^2 = H, Cl, OMe
or R^2 = H, R^1 = H, Me, OMe **289**

Scheme 3.120

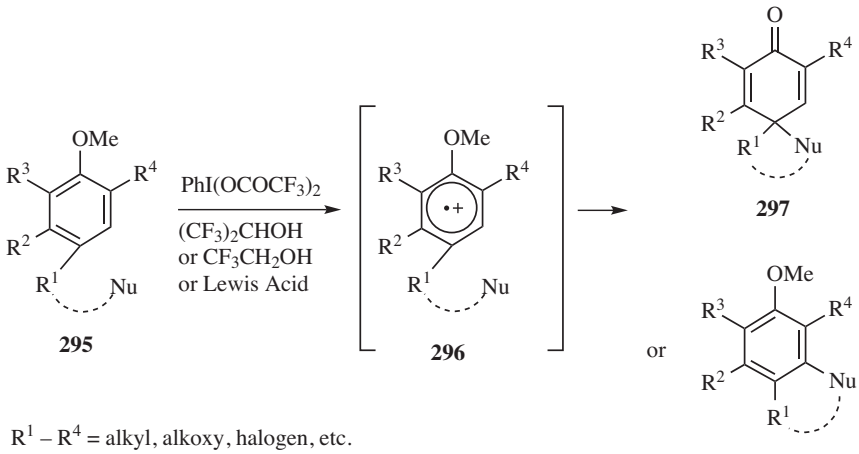


290 **291** **292** **293** (39-74%) **294** (51-93%)

R^1 = Ts, $MeSO_2$
R^2 = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-thienyl, 2-pyridyl, cyclopropyl
R^3 = Me, Et, Bu
R^4 = Ph, 4-$MeOC_6H_4$, 4-$BnOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 4-Br-4,5-$(MeO)_2C_6H_2$, 4-MeC_6H_4
R^5 = H or Me

Scheme 3.121

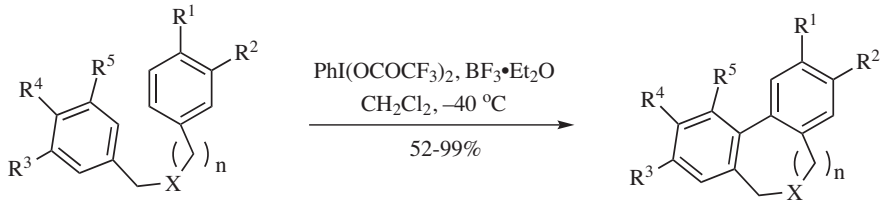
The direct nucleophilic substitution of electron-rich phenol ethers using hypervalent iodine oxidants in the presence of Lewis acid or fluorinated alcohols and involving aromatic cation–radical intermediates was originally developed by Kita and coworkers in 1994 [362]. Since then this procedure with some variations has been extensively applied by Kita and other researchers for various oxidative transformations. In the intermolecular mode, this reaction (Scheme 3.122) has been utilized for the preparation of the products **298** from N_3^-, AcO^-, ArS^-, SCN^-, β-dicarbonyl compounds and other external nucleophiles [320]. The oxidative coupling reaction in the intramolecular mode provides a powerful synthetic tool for the preparation of various



295 **296** **297** **298**

$R^1 - R^4$ = alkyl, alkoxy, halogen, etc.
Nu = external or internal nucleophilic group, including electron-rich aromatics

Scheme 3.122



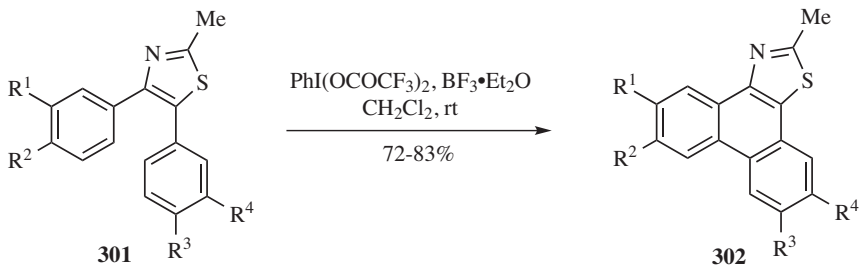
299 **300**

X = CH_2, $NCOCF_3$, O, S; n = 1, 2
R^1 = OMe; R^2 = H, OMe or $R^1 + R^2 = OCH_2O$
R^3 = OMe; R^4 = OMe, OTBS, OAc or $R^3 + R^4 = OCH_2O$
R^5 = H, OMe

Scheme 3.123

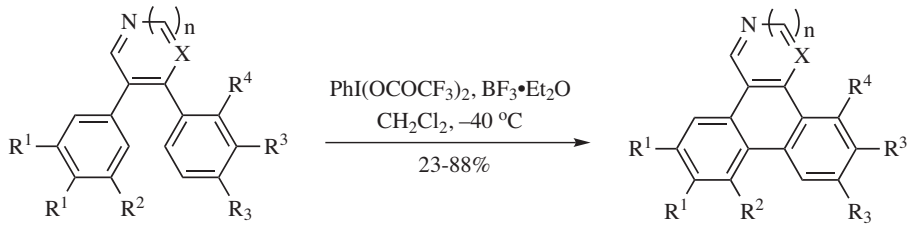
carbocyclic and heterocyclic compounds [321, 363–369]. Specific examples of synthetic applications of this reaction are provided below in Schemes 3.123–3.129.

Numerous dibenzoheterocyclic compounds **300** have been prepared by the oxidation of phenol ether derivatives **299** with [bis(trifluoroacetoxy)iodo]benzene in the presence of $BF_3 \cdot Et_2O$ in dichloromethane (Scheme 3.123) [363–365].



301 **302**

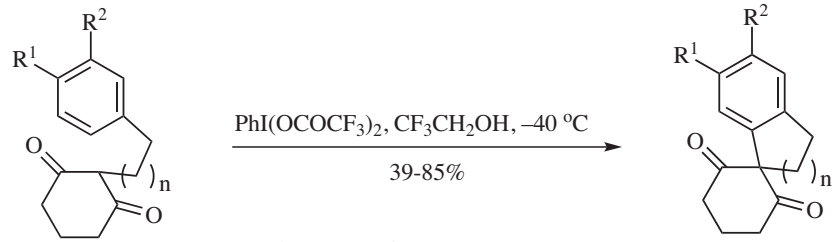
$R^1 = R^2 = R^3 = R^4$ = OMe; $R^1 = R^2$ = OMe, $R^3 = R^4$ = H
$R^1 = R^2 = R^4$ = OMe, R^3 = H; $R^1 = R^2$ = OMe, $R^3 = NO_2$, R^4 = H



303 **304**

X = O, n = 0; X = N, n = 1
R^1, R^2, R^3, R^4 = H or OMe

Scheme 3.124



305 **306**

Scheme 3.125

Under similar conditions, the phenanthro-fused thiazoles **302,** isoxazoles **304** (X = O, $n = 0$) and pyrimidines **304** (X = N, $n = 1$) can be prepared by oxidative coupling of the respective phenol ethers **301** and **303** (Scheme 3.124) [368, 369].

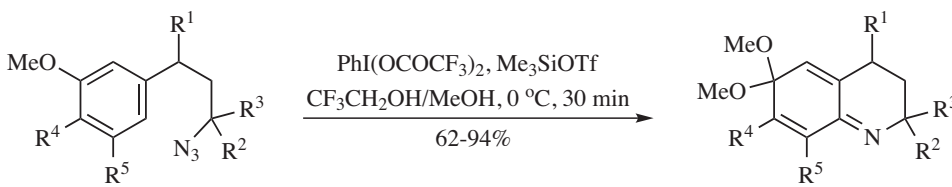
The hypervalent iodine-induced direct intramolecular cyclization of α-(aryl)alkyl-β-dicarbonyl derivatives **305** affords biologically important spirobenzannulated compounds **306** (Scheme 3.125) [366].

The oxidation of phenol ethers containing the azido group as an internal nitrogen nucleophile provides a useful methodology for the construction of nitrogen heterocycles [370–372]. Kita and coworkers have reported an efficient synthesis of quinone imine ketals **308** from the substituted phenol ethers **307** bearing an alkyl azido side chain (Scheme 3.126) [371].

A similar intramolecular cyclization of 3-(azidoethyl)indole derivatives **309** provides an efficient route to the pyrroloiminoquinone system **310** (Scheme 3.127), which is an essential component of several recently isolated marine alkaloids such as makaluvamines, isobatzelline C and discorhabdins, which possess potent biological activities [372].

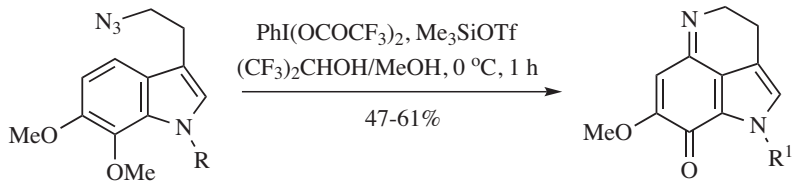
The oxidation of phenol ethers **311** bearing an alkyl sulfide side chain followed by treatment with aqueous methylamine selectively affords various dihydrobenzothiophenes **312** (Scheme 3.128) without yielding any sulfoxides as by-products [372]. This procedure has been applied in the total synthesis of the potent cytotoxic makaluvamine F, a sulfur-containing pyrroloiminoquinone marine product [373].

Additional examples of intramolecular oxidative coupling of phenolic ethers include the oxidative biaryl coupling of various N-substituted 1-benzyltetrahydroisoquinolines **313** to the corresponding aporphines **314** [374], the oxidative cyclization of 3,4-dimethoxyphenyl 3,4-dimethoxyphenylacetate (**315**) leading to the seven-membered lactone **316** [375] and the conversion of phenol ether derivatives **317** into the products of



307 R1, R2, R3 = H or Me; R4, R5 = H or OMe **308**

Scheme 3.126



309
R = Ts, Cbz, Ac, Bz

310
R1 = Ts, Cbz, or H

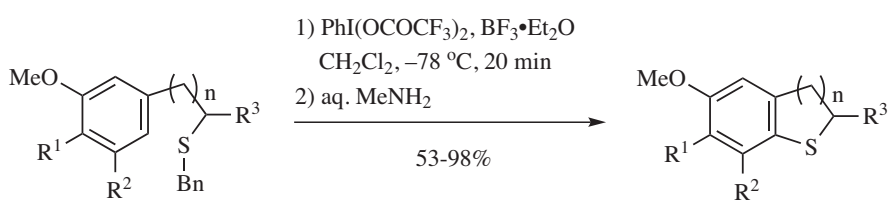
Scheme 3.127

intramolecular coupling **318** using a combination of [bis(trifluoroacetoxy)iodo]benzene and heteropoly acid (Scheme 3.129) [376]. A similar oxidative coupling reaction of benzyltetrahydroisoquinolines (laudanosine derivatives) using [bis(trifluoroacetoxy)iodo]benzene and heteropoly acid has been used in an efficient synthesis of morphinandienone alkaloids [377]. Catalytic versions of the oxidative coupling of phenolic ethers using iodoarenes as catalysts and *m*CPBA or hydrogen peroxide as stoichiometric oxidants have also been reported (Section 4.1).

Non-phenolic electron-rich aromatic substrates can also be oxidatively coupled using hypervalent iodine reagents (Schemes 3.130–3.133). Kita and coworkers reported a facile and efficient oxidative coupling reaction of alkylarenes **319** leading to alkylbiaryls **320** using a combination of [bis(trifluoroacetoxy)iodo]benzene and $BF_3{\cdot}OEt_2$ (Scheme 3.130) [378]. Similarly, multiply iodinated biaryls can be prepared in good yields by the [bis(trifluoroacetoxy)iodo]benzene-induced direct oxidative coupling reaction of the iodinated arenes [379].

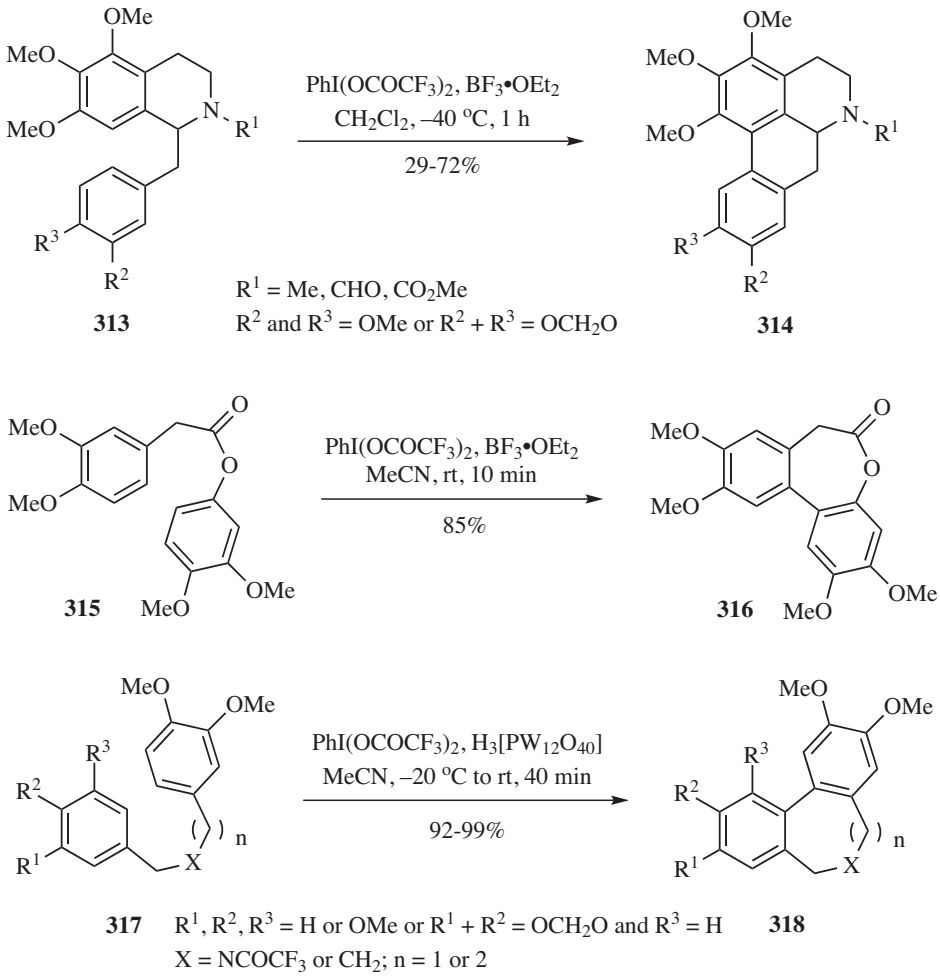
Oxidation of N-aromatic methanesulfonamides **321** with (diacetoxyiodo)benzene in the presence of thiophene in trifluoroethanol or hexafluoroisopropanol (HFIP) affords the respective coupling products **322** in good yield (Scheme 3.131) [380]. The head-to-tail thiophene dimers **324** can be selectively prepared by the hypervalent iodine oxidation of 3-substituted thiophenes **323** [381, 382] and bipyrroles **326** can be regioselectively synthesized by oxidative dimerization of pyrroles **325** with [bis(trifluoroacetoxy)iodo]benzene in the presence of bromotrimethylsilane [383]. Likewise, bithiophenes **328** have been synthesized from 3,4-disubstituted thiophenes **327** using [hydroxy(tosyloxy)iodo]benzene in the presence of bromotrimethylsilane in hexafluoroisopropanol [384].

A direct coupling reaction of cycloalkenylsilanes **329** with a silylated nucleobase **330** promoted by (diacetoxyiodo)benzene in the presence of trimethylsilyl triflate in dichloromethane at room temperature has been reported (Scheme 3.132) [385]. This procedure was applied in the synthesis of a novel carbocyclic cytidine derivative having bis(hydroxymethyl)cyclohexene as a pseudo-sugar moiety, which was designed as a potential anti-HIV agent.



311 R^1, R^2 = H or OMe; R^3 = H or Me; n = 1, 2, 3 **312**

Scheme 3.128

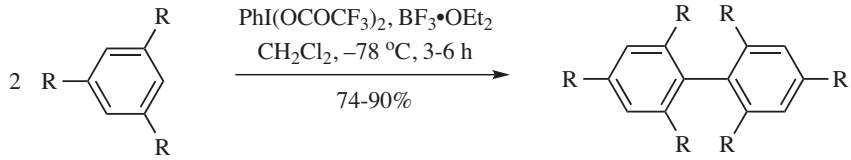


Scheme 3.129

[Bis(trifluoroacetoxy)iodo]benzene in conjunction with a Lewis acid promotes C—C coupling of Bodipy (4,4′-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene) monomers **331** leading to mixtures of dimers **332** (when X = I or *p*-tolyl) (Scheme 3.133) and higher oligomers when X = H [386]. Bodipy dyes have attracted significant interest in recent years due to their outstanding optical properties.

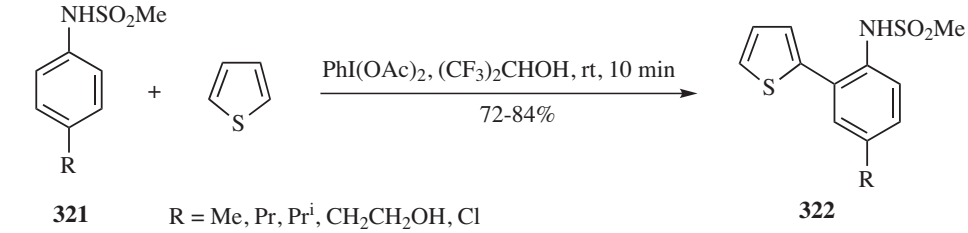
3.1.13 Oxidative Cationic Cyclizations, Rearrangements and Fragmentations

Hypervalent iodine(III) compounds, such as [bis(trifluoroacetoxy)iodo]benzene, (diacetoxyiodo)benzene and [hydroxy(tosyloxy)iodo]benzene, are commonly used as reagents in various cationic cyclizations, rearrangements and fragmentations. Numerous examples of such reactions have been reported in the literature and summarized in the reviews dedicated to synthetic applications of hypervalent iodine compounds [4, 7, 10, 11, 180, 191, 387].

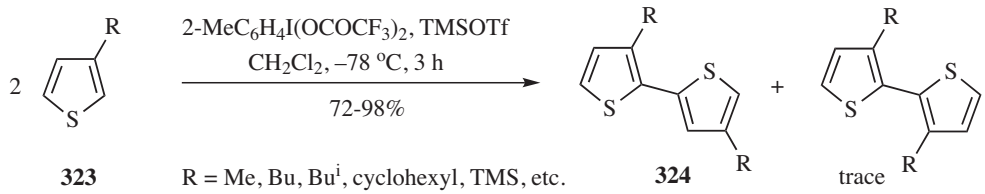


319 R = Me, Et or I **320**

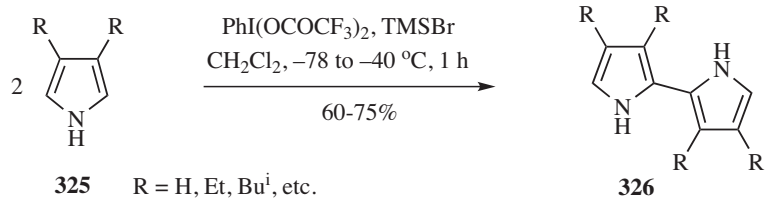
Scheme 3.130



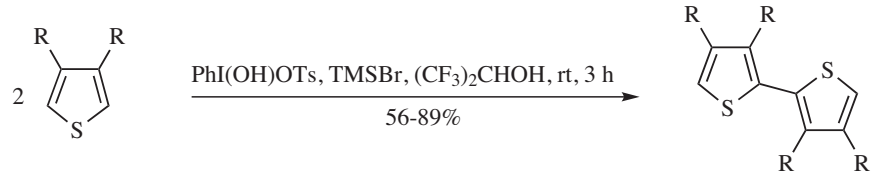
321 R = Me, Pr, Pr^{i}, CH_2CH_2OH, Cl **322**



323 R = Me, Bu, Bu^{i}, cyclohexyl, TMS, etc. **324** trace

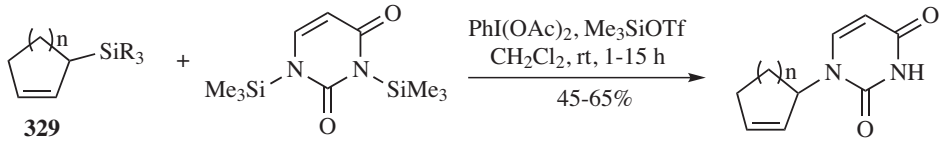


325 R = H, Et, Bu^{i}, etc. **326**



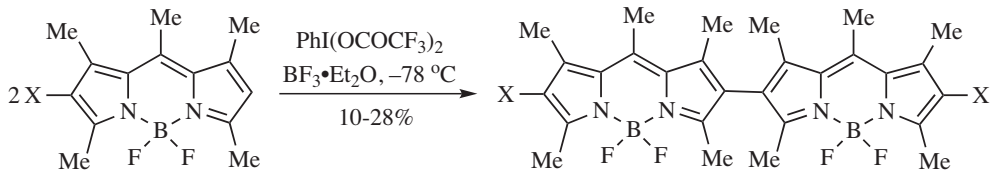
327 R = Me, Bu^{i}, *n*-C_6H_{13}, *n*-C_8H_{17}, OMe, OBu, 4-MeC_6H_4 or R + R = $O(CH_2)_2O$ **328**

Scheme 3.131



329 R = OEt or Me; n = 1 or 2 **330**

Scheme 3.132



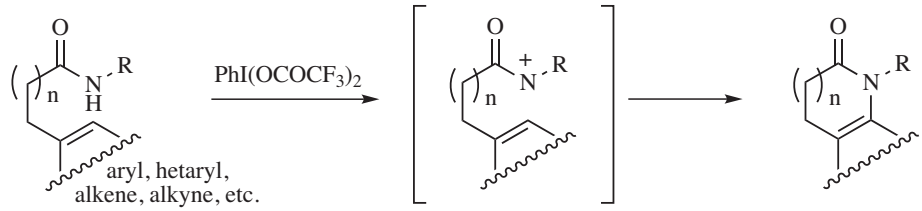
331 X = H, I, 4-MeC$_6$H$_4$ **332**

Scheme 3.133

3.1.13.1 Heterocyclizations

Cationic cyclizations, induced by hypervalent iodine reagents, are particularly useful in the synthesis of heterocycles. Tellitu and Dominguez have developed a series of [bis(trifluoroacetoxy)iodo]benzene-promoted intramolecular amidation reactions, generalized in Scheme 3.134, leading to various five, six and seven-membered heterocycles **335** [388, 389]. Experimental evidence supports the ionic mechanism of these reactions, involving *N*-acylnitrenium intermediates **334** generated in the initial reaction of the amide **333** with the hypervalent iodine reagent [390].

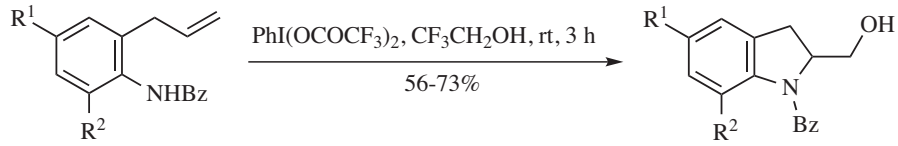
This methodology with some variations has been utilized in the synthesis of numerous heterocyclic systems, such as heterocycle-fused quinolinone derivatives [391], 1,4-benzodiazepin-2-ones [392], benzo-, naphtho- and heterocycle-fused pyrrolo[2,1-*c*][1,4]diazepines [393], quinolinone or pyrrolidinone derivatives [394], dibenzo[*a,c*]phenanthridines [395], thiazolo-fused quinolinones [396], isoindolinone and isoquinolin-2-one derivatives [397], indoline derivatives [398], 5-aroyl-pyrrolidinones [399, 400], indazolone derivatives [401, 402], substituted indolizidinones [403], 1-arylpyrrolopyrazinones [404], structurally diverse



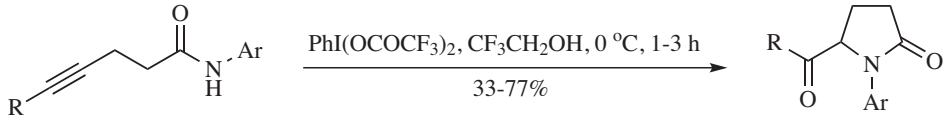
333 **334** **335**

R = OMe, alkyl, Bn, Ph, Ts, Bz, etc.
n = 0, 1, 2

Scheme 3.134

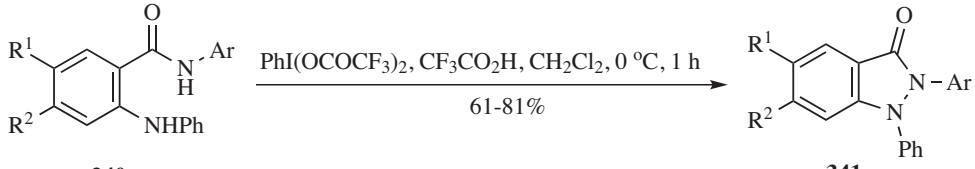


336 R^1 = OMe, Et, Br, or H; R^2 = H or Et **337**



338 **339**

R = Ph, 2-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-thienyl, PhCH=CH, etc.
Ar = 4-$MeOC_6H_4$



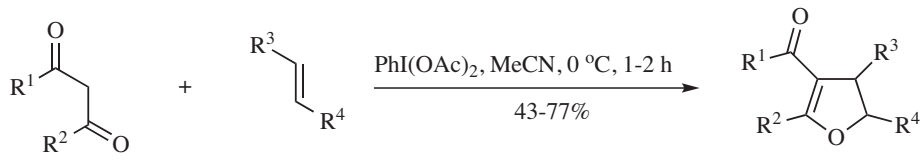
340 **341**

R^1 = H or F; R^2 = H or Cl
Ar = 4-$MeOC_6H_4$

Scheme 3.135

pyrrolo(benzo)diazepines [405] and furopyrimidinones [406]. Representative examples of these cyclizations are shown in Scheme 3.135 and include the preparation of indoline derivatives **337** from anilides **336** [398], pyrrolidinones **339** from alkynylamides **338** [399, 400] and indazol-3-ones **341** from anthranilamides **340** [401, 402].

Similar hypervalent iodine-induced heterocyclizations of the appropriate amide or amine precursors have been used in numerous useful synthetic transformations, such as the synthesis of 1-arylcarbazoles by metal-free electrocyclization [407], the synthesis of highly substituted pyrrolin-4-ones via $PhI(OCOCF_3)_2$-mediated cyclization of enaminones [408], the synthesis of 2-substituted-4-bromopyrrolidines via $PhI(OAc)_2$-induced intramolecular oxidative bromocyclization of homoallylic sulfonamides in the presence of KBr [409], the preparation of 1,2,4-thiadiazoles by the reaction of $PhI(OAc)_2$ or $PhI(OCOCF_3)_2$ with 1-monosubstituted thioureas [410, 411], the synthesis of azaspirocyclic synthetic intermediates via $PhI(OCOCF_3)_2$-induced nitrenium ion cyclizations [412–417], the preparation of lactams and spiro-fused lactams from the reaction of *N*-acylaminophthalimides and $PhI(OCOCF_3)_2$ [418], the synthesis of various substituted 1,2,4-triazolo[4,3-*a*]pyrimidines by $PhI(OAc)_2$-promoted oxidation of the appropriate 2,4-pyrimidinylhydrazones [419–421], the synthesis of pyrrolidino[60]fullerene from the $PhI(OAc)_2$-promoted reaction between C_{60} and amino acid esters [422], the synthesis of 1,3,4-oxadiazoles from acylhydrazones by $PhI(OCOCF_3)_2$ oxidation [423–425], the synthesis of 1-aryl-4-methyl-1,2,4-triazolo[4,3-*a*]quinoxalines from arenecarboxaldehyde-3-methyl-2-quinoxalinylhydrazones [426, 427], the synthesis of various N-substituted indole derivatives via $PhI(OCOCF_3)_2$-mediated intramolecular cyclization of enamines [428] and the synthesis of enantiomerically



342 **343** **344**

R^1 = Me, R^2 = Me
R^1 = Me, R^2 = OEt
$R^1 + R^2 = CH_2CMe_2CH_2$

R^3 and R^4 = H, alkyl, Ph, CH_2OAc, CH_2Cl, etc.

Scheme 3.136

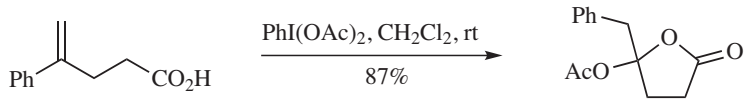
pure 2-arylproline derivatives by intramolecular oxyamination of alkenes with ureas employing chiral lactic acid-based hypervalent iodine reagents [429].

Numerous hypervalent iodine-promoted cyclizations of non-amine substrates have also been reported. Several examples of oxidative cyclizations leading to the formation of oxygen heterocycles are shown in Schemes 3.136–3.138. In particular, the (diacetoxyiodo)benzene-mediated oxidative addition of 1,3-dicarbonyl compounds **342** to alkenes **343** allows an efficient one-pot synthesis of 2,3-dihydrofuran derivatives **344** (Scheme 3.136) [430]. Various alkenes and cycloalkenes bearing electron-withdrawing or electron-donating substituents can be used in this cyclization. A similar intramolecular cycloaddition/cycloisomerization of 2-propargyl-1,3-dicarbonyl compounds upon treatment with $PhI(OCOCF_3)_2$ in hexafluoroisopropanol affords 4,5-disubstituted furfuryl alcohols in high yields [431].

The lactonization of 4-phenyl-4-pentenoic acid (**345**) upon treatment with $PhI(OAc)_2$ has been reported (Scheme 3.137) [432]. The mechanism of this reaction includes electrophilic lactonization induced by the addition of the iodine(III) electrophile to the double bond of substrate **345** followed by 1,2-phenyl migration leading to the final rearranged lactone **346.**

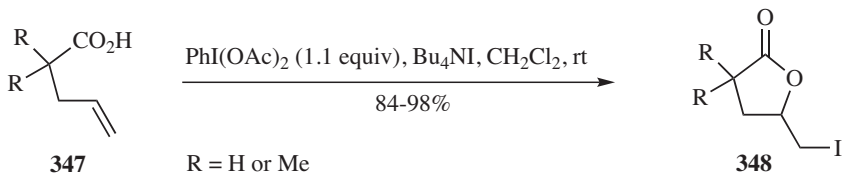
The (diacetoxyiodo)benzene-promoted oxidative iodolactonization of pentenoic acids **347** in the presence of tetrabutylammonium iodide proceeds smoothly at room temperature to afford lactones **348** in high yields (Scheme 3.138) [433]. A catalytic version of this iodolactonization using iodobenzene as a catalyst and sodium perborate monohydrate as the stoichiometric oxidant has also been reported (Section 4.1).

Additional examples of synthetic applications of hypervalent iodine-induced heterocyclizations include the following: the metal-free one-pot synthesis of 2-acylbenzothiazoles by oxidative cyclization of multiform substrates [434], iodine(III)-mediated tandem oxidative cyclization for construction of 2-nitrobenzo[*b*]furans [435], hypervalent iodine mediated oxidative cyclization of *o*-hydroxystilbenes into benzo- and naphthofurans [436], $PhI(OCOCF_3)_2$-mediated synthesis of 3-hydroxy-2-oxindoles and spirooxindoles from anilides [437], synthesis of isoxazoles by hypervalent iodine-induced cycloaddition of nitrile oxides to alkynes [438],



345 **346**

Scheme 3.137



347 R = H or Me **348**

Scheme 3.138

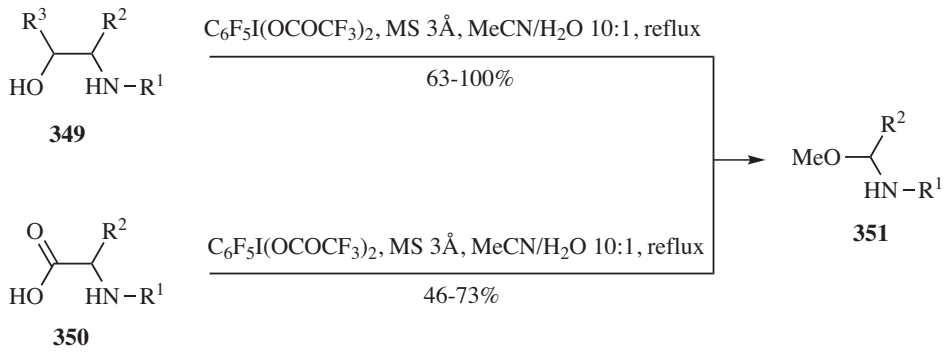
metal-free synthesis of polysubstituted pyrroles by (diacetoxyiodo)benzene-mediated cascade reaction of 3-alkynyl amines [439], highly efficient synthesis of multisubstituted 2-acyl furans via $PhI(OCOCF_3)_2/I_2$-mediated oxidative cycloisomerization of *cis*-2-en-4-yn-1-ols [440], synthesis of carbazoles by intramolecular oxidative C–N bond formation [441], one-pot synthesis of [1,2,4]triazolo[4,3-*a*][1,4]benzodiazepine derivatives by oxidative cyclization reaction of 2-hydrazino-1,4-benzodiazepines with various aldehydes in presence of (diacetoxyiodo)benzene [442], preparation of benzopyrano- and furopyrano-2-isoxazoline derivatives from 2-allyloxybenzaldoximes by $PhI(OAc)_2$ oxidation [443], preparation of 2-(*N*-acylaminal) substituted tetrahydropyrans by $PhI(OAc)_2$-induced oxidative cyclization of hydroxy-substituted *N*-acyl enamines [444], synthesis of 2-substituted benzothiazoles via the oxidative cyclization of thiobenzamides [445], preparation of 2,3-diphenylquinoxaline-1-oxide from benzil-α-arylimino oximes using $PhI(OAc)_2$ [446], synthesis of 2,5-disubstituted-1,3,4-oxadiazoles via $PhI(OCOCF_3)_2$-mediated oxidative cyclization of aldazines [447], preparation of 2-substituted oxazolines from aldehydes and 2-amino alcohols using $PhI(OAc)_2$ as an oxidant [448], synthesis of 3,4-bis(1-phenyl-3-arylpyrazolyl)-1,2,5-oxadiazole-*N*-oxides by the $PhI(OAc)_2$ oxidation of pyrazole-4-carboxaldehyde oximes [449], synthesis of 2-arylbenzimidazoles from phenylenediamines and aldehydes via a one-step process using $PhI(OAc)_2$ as an oxidant [450], $PhI(OAc)_2$-mediated efficient synthesis of imidazoles from α-hydroxy ketones, aldehydes and ammonium acetate [451], preparation of dihydrooxazole derivatives by $PhI(OAc)_2$-promoted 1,3-dipolar cycloaddition reactions of phthalhydrazide [452], synthesis of 2,3-diarylbenzo[*b*]furans by $PhI(OCOCF_3)_2$-mediated oxidative coupling sequence [453] and the synthesis of *seco*-psymberin/irciniastatin A via a $PhI(OAc)_2$-mediated cascade cyclization reaction [454]. Some of these heterocyclizations can be performed under catalytic conditions in the presence of an iodoarene catalyst and peracids as stoichiometric oxidants (Section 4.1).

3.1.13.2 Fragmentations and Rearrangements

Numerous examples of hypervalent iodine-promoted fragmentations or rearrangements at electron-deficient centers have been reported. Several examples of oxidative fragmentations are shown below in Schemes 3.139–3.142. A mild and efficient fragmentation reaction of β-amino alcohols **349** and α-amino acids **350** upon treatment with [bis(trifluoroacetoxy)iodo]pentafluorobenzene leading to N,O-acetals **351** has been developed (Scheme 3.139). This method has been utilized in an improved synthesis of the key intermediate of discorhabdins [455, 456].

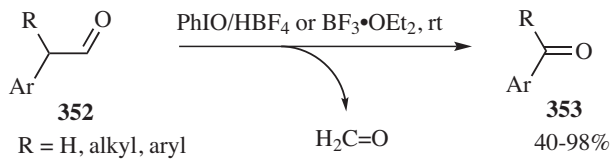
Aryl-substituted aldehydes **352** can be cleaved to chain-shortened carbonyl compounds **353** and formaldehyde by iodosylbenzene in the presence of acids or Lewis acids (Scheme 3.140). Formaldehyde is further oxidized to CO and CO_2 under the reaction conditions [457]. Oxidative decarboxylation of 2-aryl-substituted carboxylic acids **354** into corresponding aldehydes, ketones (e.g., **355**) and nitriles at room temperature can be achieved by treatment with (diacetoxyiodo)benzene and a catalytic amount of sodium azide in acetonitrile (Scheme 3.141) [458].

A synthetically useful oxidative fragmentation of tertiary cyclopropyl alcohols (e.g., **356**) with [bis(trifluoroacetoxy)iodo]benzene, which produces alkenoic acids or esters, has been reported [459, 460].



R^1 = Cbz or Fmoc; R^2 = H, Me, CO_2Me, etc; R^3 = H or Me

Scheme 3.139

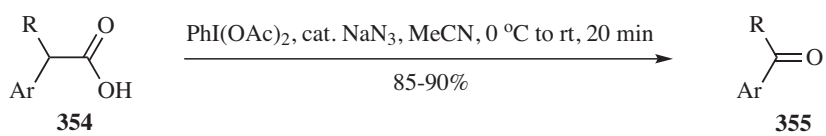


Scheme 3.140

This fragmentation has been successfully employed for the preparation of product **357** (Scheme 3.142), which is the key precursor in an efficient asymmetric synthesis of the alkaloid (–)-pinidine [460].

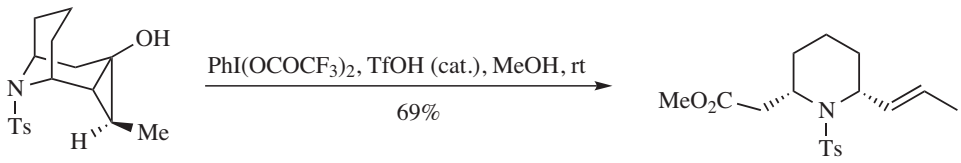
Hypervalent-iodine-promoted rearrangements have been utilized in various ring-expansion reactions (Schemes 3.143–3.146 below). A (diacetoxyiodo)benzene-promoted oxidative rearrangement of *cis*- and *trans*-1,5-diazadecalins to macrocyclic lactams has been reported [461]. In a specific example, upon treatment with (diacetoxyiodo)benzene in aqueous NaOH, 1,5-diaza-*trans*-decalin (**358**) undergoes oxidation along with C—C bond cleavage to yield the ring-expanded bislactam **359** (Scheme 3.143) [461].

A stereoselective synthesis of five- to seven-membered cyclic ethers has been achieved by de-iodonative ring-enlargement of cyclic ethers having an iodoalkyl substituent. For example, the reaction of tetrahydrofuran derivative **360** with (diacetoxyiodo)toluene proceeds under mild conditions to afford ring-expanded product **361** (Scheme 3.144). The use of hexafluoroisopropanol (HFIP) as solvent in this reaction is critical [462].



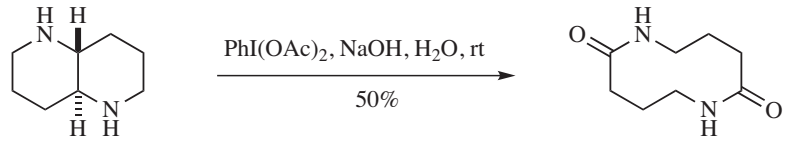
R = H or Me
Ar = Ph, 4-$MeOC_6H_4$, 2,5-$(MeO)_2C_6H_3$, 2-ClC_6H_4, 4-ClC_6H_4, 4-$EtOCOC_6H_4$, 4-$NO_2C_6H_4$, etc.

Scheme 3.141



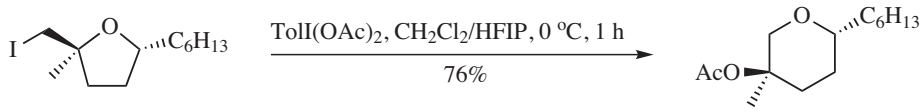
356 **357**

Scheme 3.142



358 **359**

Scheme 3.143

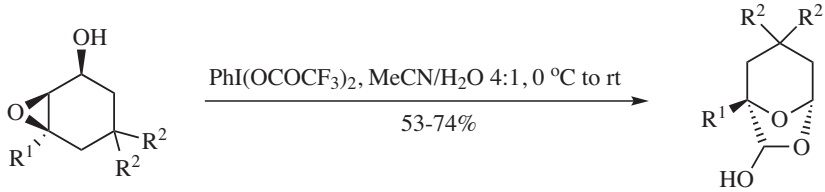


360 **361**

Scheme 3.144

A facile and efficient synthesis of lactols **363** via an oxidative rearrangement reaction of 2,3-epoxy alcohols **362** with [bis(trifluoroacetoxy)iodo]benzene has been reported (Scheme 3.145) [463–465]. This hypervalent-iodine-induced oxidative transformation has been utilized in the synthesis of several lactones and in the asymmetric synthesis of the marine γ-lactone metabolite (+)-tanikolide [463, 464].

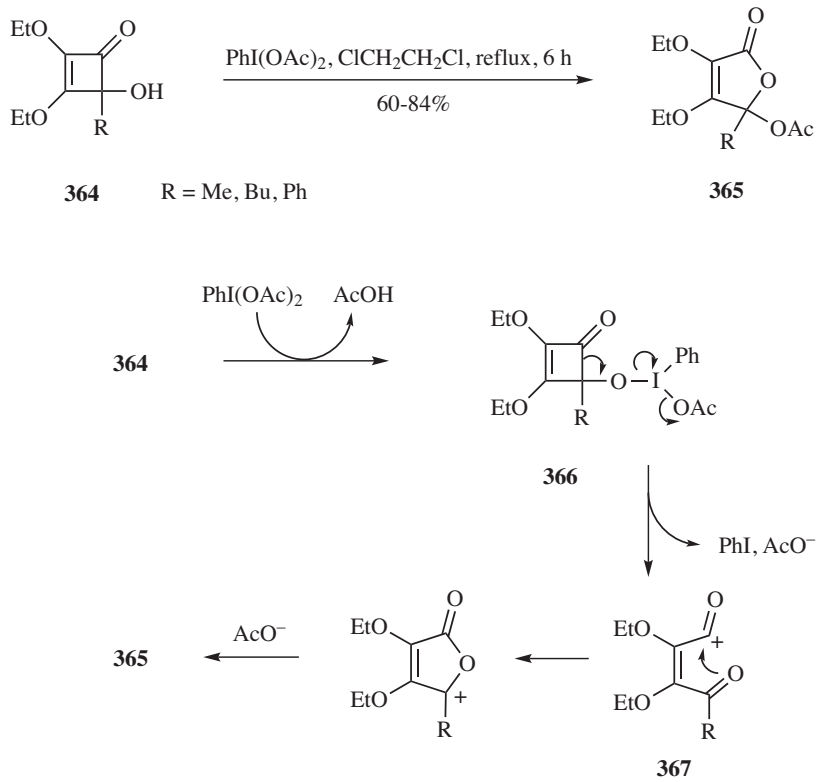
Reactions of 4-hydroxy-2-cyclobutenones **364** with (diacetoxyiodo)benzene in 1,2-dichloroethane at reflux afford 5-acetoxy-2(5*H*)-furanones **365** as rearranged products (Scheme 3.146) [466]. The formation of these products is explained by ring cleavage in the hypervalent iodine intermediate **366** followed by recyclization of the resulting acyl cation **367** with the carbonyl oxygen (Scheme 3.146). In a similar procedure,



362 R^1 = Me, Et, *n*-$C_{11}H_{23}$, $CH_2CH(CH_3)_2$, CH_2Ph
R^2 = H or Me

363

Scheme 3.145

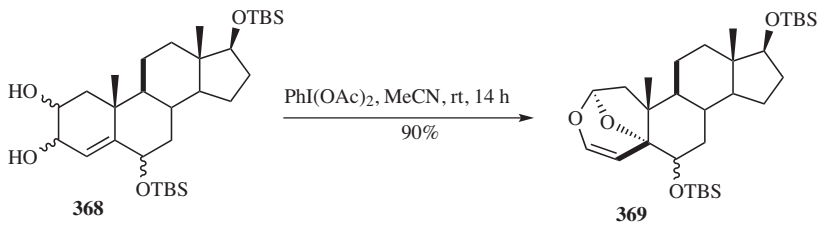


Scheme 3.146

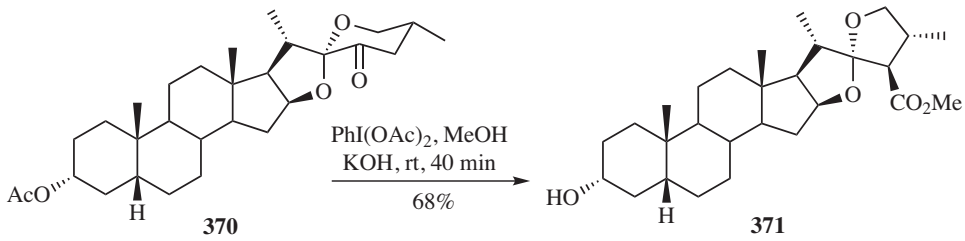
5-methoxy-2(5*H*)-furanones are obtained in good yields by using methanol as both a solvent and a nucleophile [466].

A (diacetoxyiodo)benzene-induced domino reaction of the vicinal unsaturated diol **368** affords cyclic ene-acetal **369** (Scheme 3.147), which has been further utilized in the synthesis of a norsesquiterpene spirolactone/testosterone hybrid [467].

Iglesias-Arteaga and coworkers have reported several (diacetoxyiodo)benzene-promoted oxidative transformations of steroidal substrates (Schemes 3.148 and 3.149) [468–471]. In particular, the treatment of (25*R*)-3α-acetoxy-5β-spirostan-23-one (**370**) with (diacetoxyiodo)benzene in basic methanol leads to F-ring contraction via Favorskii rearrangement to afford product **371** (Scheme 3.148) [468].



Scheme 3.147



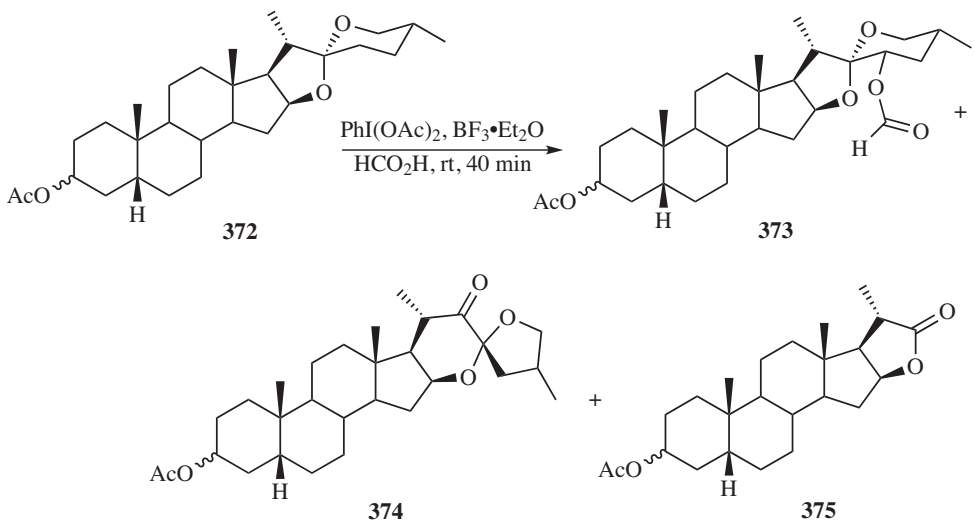
Scheme 3.148

Treatment of steroidal substrate **372** with (diacetoxyiodo)benzene and boron trifluoride etherate in acetic acid leads to the introduction of an axial acetoxy group at position C23 of the side chain [469], while a similar reaction of the same substrate **372** with (diacetoxyiodo)benzene and $BF_3{\cdot}OEt_2$ in formic acid unexpectedly produced the equatorial formate **373** mixed with products of rearrangement (**374** and **375**) (Scheme 3.149) [470].

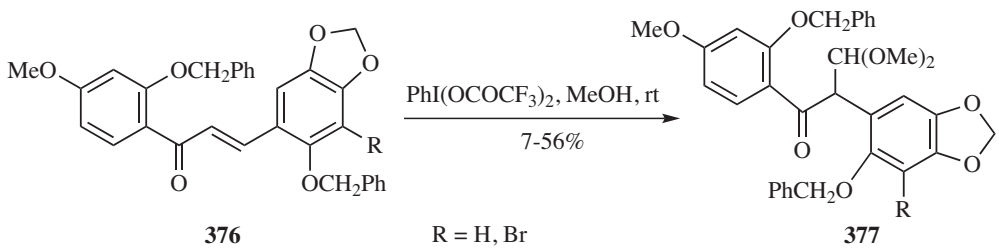
Reactions of [bis(acyloxy)iodo]arenes with alkenes in some cases can give products of an oxidative, carbocationic rearrangement. Such a rearrangement of pentaalkoxychalcones **376** upon treatment with [bis(trifluoroacetoxy)iodo]benzene has been applied toward the preparation of the rearranged chalcones **377** (Scheme 3.150), which are key precursors in the synthesis of pterocarpins [472].

[Hydroxy(tosyloxy)iodo]benzene (HTIB) has also been used in oxidative rearrangements of alkenes. Justik and Koser have reported a study of an oxidative rearrangement that occurs upon treatment of arylalkenes **378** with HTIB in aqueous methanol to afford the corresponding α-aryl ketones **379** in generally high yields (Scheme 3.151). This oxidative rearrangement is general for acyclic and cyclic arylalkenes and permits the regioselective syntheses of isomeric α-phenyl ketone pairs [473].

A similar HTIB-induced oxidative rearrangement has been utilized in the regioselective synthesis of 6-prenylpolyhydroxyisoflavone (wighteone) [474] and in a diastereoselective total synthesis of (±)-indatraline

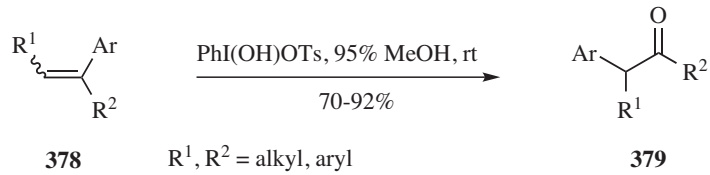


Scheme 3.149



376 R = H, Br **377**

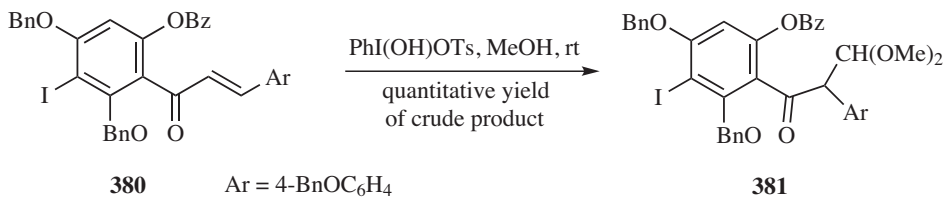
Scheme 3.150



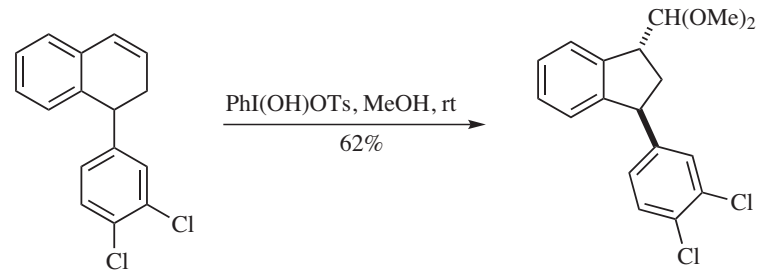
378 R^1, R^2 = alkyl, aryl **379**

Scheme 3.151

[475]. In particular, the key intermediate product **381** in the synthesis of wighteone was prepared by the oxidative rearrangement of 3′-iodotetraalkoxychalcone **380** [474] and the key step in the synthesis of (±)-indatraline involved the HTIB-promoted diastereoselective ring contraction of a 1,2-dihydronaphthalene **382** to construct the indane ring system **383** (Scheme 3.152) [475]. A similar oxidative rearrangement of 3-cinnamoyl-4-hydroxy-6-methyl-2*H*-pyran-2-ones with HTIB in dichloromethane followed by cyclization was used by Prakash and coworkers for the direct conversion of *o*-hydroxychalcones into isoflavone derivatives [476].

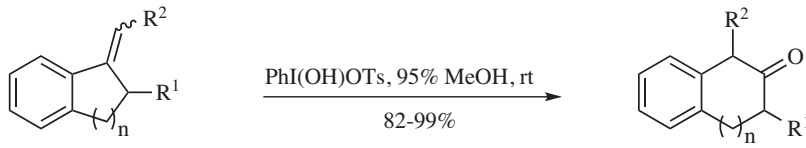


380 Ar = 4-$BnOC_6H_4$ **381**



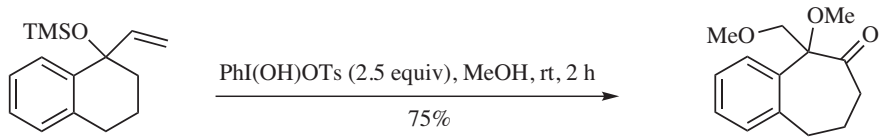
382 **383**

Scheme 3.152



384 R^1, R^2 = H or Me; n = 1-3 **385**

Scheme 3.153



386 **387**

Scheme 3.154

The HTIB-induced oxidative rearrangement of alkenes has been effectively used in ring expansion reactions (Schemes 3.153 and 3.154). Justik and Koser have investigated the oxidative ring expansions of alkylidenebenzocycloalkenes **384** to β-benzocycloalkenones **385** using HTIB in methanol (Scheme 3.153) [477]. This reaction allows the efficient conversion of alkenes **384,** which can be conveniently prepared from the respective α-benzocycloalkenones by Wittig olefination, into the homologous β-benzocycloalkenones **385** containing six-, seven- and eight-membered rings.

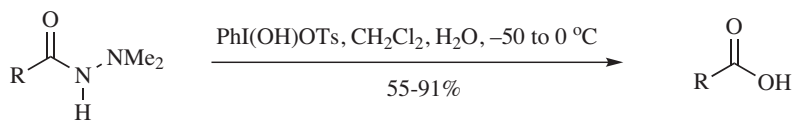
A similar HTIB-promoted ring expansion of 1-vinylcycloalkanol derivatives leading to seven- or eight-membered rings has been reported. In a specific example, the reaction of the unsaturated trimethylsilyl ether **386** with excess HTIB affords benzocycloheptanone derivative **387** in high yield (Scheme 3.154) [478].

HTIB can also be used in the oxidative rearrangements and fragmentations of various nitrogen-containing compounds [479–482]. *N*,*N*-Dimethylhydrazides **388** are efficiently cleaved to give the carboxylic acid **389** upon treatment with HTIB in water or aqueous dichloromethane (Scheme 3.155) [480].

Aromatic hydrazones **390** are converted into the corresponding tosylates **391** in high yield upon reaction with [methoxy(tosyloxy)iodo]benzene (MTIB) in dichloromethane (Scheme 3.156) [482].

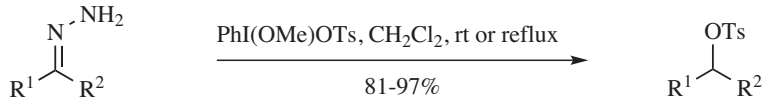
N-Substituted amidines react with MTIB to furnish cyclization products or the products of oxidative rearrangement. *C*-Alkyl-*N*-arylamidine **392** cyclizes to give benzimidazole **393** in high yield, while *C,N*-diarylamidine **394** rearranges to give product **395** (Scheme 3.157) derived from an intermediate carbodiimide [479].

Ketoximes generally react with HTIB to afford the corresponding ketones as deoximation products [481]. However, the treatment of oximes of *o*-allyloxyacetophenones **396** with HTIB gives tricyclic products **397**



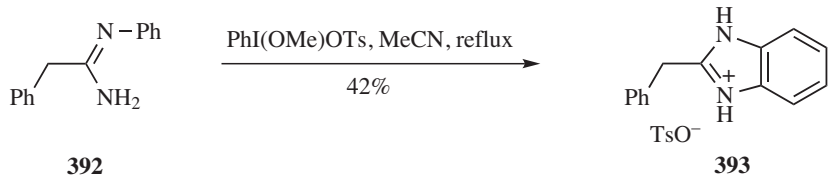
388 R = aryl, alkyl, alkenyl, etc. **389**

Scheme 3.155



390 R^1 = Ph, 3-$NO_2C_6H_4$, 4-CNC_6H_4, 4-$NO_2C_6H_4$
R^2 = H, Me, PhCO **391**

Scheme 3.156



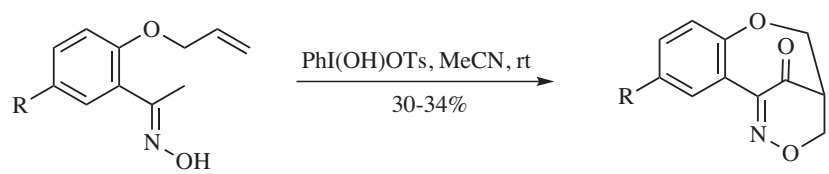
392 **393** **394** **395**

Scheme 3.157

(Scheme 3.158) resulting from the intramolecular cyclization of an intermediate nitrosoalkene generated from the oxime and HTIB [481].

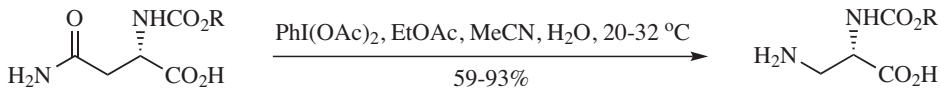
3.1.13.3 Hofmann Rearrangement

Organohypervalent iodine(III) compounds are particularly useful as the oxidants in the Hofmann-type degradation of aliphatic or aromatic carboxamides to the respective amines [483]. The most common reagents for Hofmann-type rearrangements include (diacetoxyiodo)benzene [484–488], [bis(trifluoroacetoxy)-iodo]benzene [489–494], [hydroxy(tosyloxy)]iodobenzene [495–499] and their recyclable analogs (Chapter 5). The catalytic version of the Hofmann rearrangement using aryl iodides and *m*-chloroperoxybenzoic acid as terminal oxidant has also been reported (Section 4.1).



396 R = H, Me, Cl **397**

Scheme 3.158



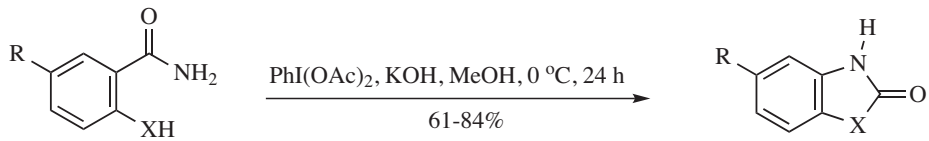
398 R = Bu, Bu^t, CH_2Ph, Et, etc. **399**

Scheme 3.159

(Diacetoxyiodo)benzene is a preferred reagent for performing the Hofmann rearrangement on a large scale. A comparative study of various oxidants (hypochlorite, hypobromide, *N*-bromosuccinimide, etc.) has demonstrated that (diacetoxyiodo)benzene is a superior reagent for the preparation of N-protected β-amino-L-alanine derivatives **399** from *N*-protected asparagines **398** (Scheme 3.159) [500]. This procedure has been used for the preparation of optically pure N_α-*n*-Boc-L-α,β-diaminopropionic acid **399** (R = CO_2Bu) from the respective *N*-Boc-protected asparagine in hundred kilogram quantities [485].

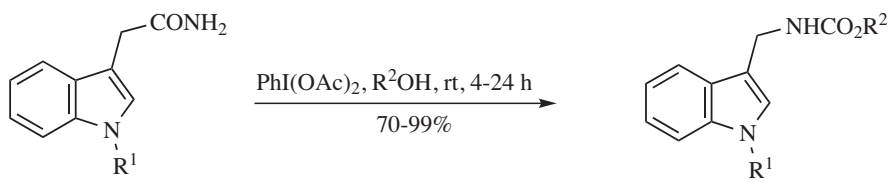
Moriarty and coworkers have developed a convenient synthetic approach to 2-benzimidazolones, 2-benzoxazolones and related compounds based on the Hofmann-type rearrangement in the reaction of anthranilamides, salicylamides and some β-substituted amides with (diacetoxyiodo)benzene [501]. For example, various 2-benzimidazolones (**401,** X = NR) and 2-benzoxazolones (**401,** X = O) were prepared by the treatment of amides **400** with (diacetoxyiodo)benzene in a basic methanolic solution (Scheme 3.160). This reaction probably occurs via initial Hofmann-type rearrangement followed by intramolecular cyclization of the intermediate isocyanate [501].

A series of alkyl carbamates of 1-protected indole-3-methylamines **403** have been prepared from the corresponding acetamides **402** in good to excellent yields via (diacetoxyiodo)benzene-promoted Hofmann rearrangement (Scheme 3.161). This procedure has been further extended to the preparation of alkyl carbamates of thiophenylmethylamines and pyrrolylmethylamines [502].



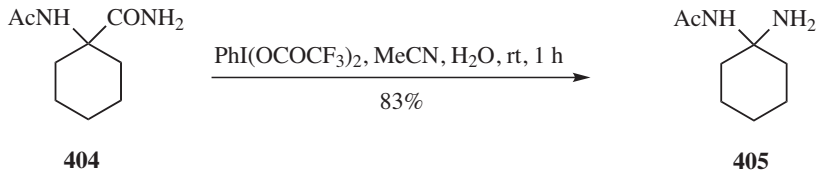
400 R = H or Cl
X = NH, NMe, NEt, NPr, NPr^i, NBu, or O **401**

Scheme 3.160



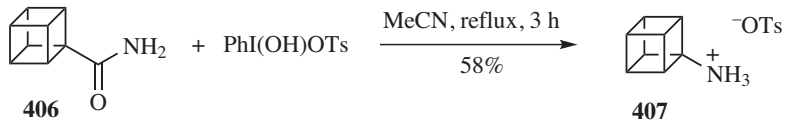
402 R^1 = Boc or Ts
R^2 = Me, Et, Pr^i, Bu^t, Bn **403**

Scheme 3.161



404 **405**

Scheme 3.162



406 **407**

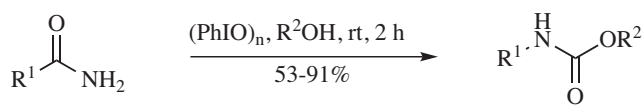
Scheme 3.163

[Bis(trifluoroacetoxy)iodo]benzene has also been used as a reagent for the Hofmann rearrangement, as illustrated by the conversion of amide **404** into the respective amine **405** (Scheme 3.162) [503]. A similar [bis(trifluoroacetoxy)iodo]benzene-induced Hofmann rearrangement has been used for the preparation of both enantiomers of *trans*-2-aminocyclohexanecarboxylic acid from *trans*-cyclohexane-1,2-dicarboxylic acid [492].

Similar to [bis(acyloxy)iodo]arenes, HTIB can serve as an efficient oxidant in Hofmann-type degradation of carboxamides to the respective amines [495–499]. In a representative example, HTIB has been used for the preparation of cubyl ammonium salt **407** from the respective carboxamide derivative **406** under mild reaction conditions (Scheme 3.163) [504].

An efficient method for the synthesis of 1,3-disubstituted ureas and carbamates from carboxamides by using iodosylbenzene as the oxidant in the presence of amines or alcohols has been described [505]. For example, carbamates **408** have been prepared by this procedure in high yields (Scheme 3.164). Various symmetric and asymmetric ureas and ureidopeptides can also be prepared in good yields by this method [505].

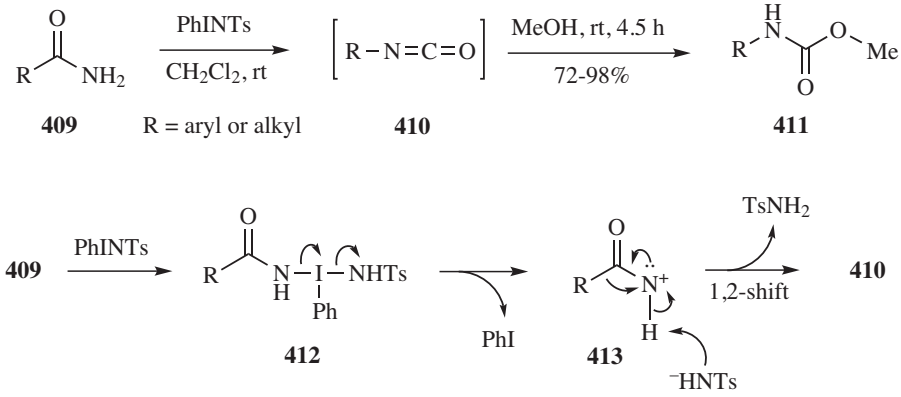
A very mild procedure for the Hofmann rearrangement of aromatic and aliphatic carboxamides **409** is based on the use of (tosylimino)phenyl-λ^3-iodane, PhINTs, as the oxidant (Scheme 3.165) [506]. Owing to the mild reaction conditions, this method is particularly useful for the Hofmann rearrangement of substituted benzamides **409** (R = aryl), which usually afford complex reaction mixtures with other hypervalent iodine oxidants. The mild reaction conditions and high selectivity in the reaction of carboxamides with PhINTs allow the isolation of the initially formed labile isocyanates **410,** or their subsequent conversion into stable carbamates **411** by treatment with alcohols. Based on the previously reported mechanistic studies of the Hofmann rearrangement using other hypervalent iodine reagents [489, 490, 496], it is assumed that the reaction



R^1 = Ph, $PhCH_2$, $PhCH_2CH_2$, Pr^i, cyclohexyl
R^2 = Me or $HC{\equiv}CCH_2$

408

Scheme 3.164



Scheme 3.165

starts from the formation of amidoiodane **412** (Scheme 3.165). Subsequently, the reductive elimination of iodobenzene and the 1,2-alkyl or -aryl shift to the electron-deficient nitrenium nitrogen atom in the intermediate **413** afford isocyanate **410.** Subsequent addition of an alcohol to isocyanate **410** gives the final carbamate **411** [506].

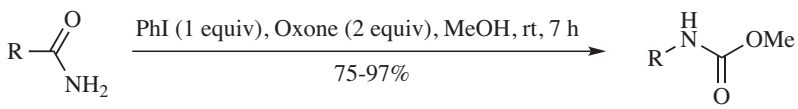
Alkylcarboxamides can be converted into the respective amines by Hofmann rearrangement using hypervalent iodine species generated *in situ* from iodobenzene and a terminal oxidant, such as Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) or *m*-chloroperoxybenzoic acid (*m*CPBA). In particular, a convenient experimental procedure for the preparation of alkylcarbamates using Oxone as the oxidant in the presence of iodobenzene in methanol (Scheme 3.166) has been developed [359].

Likewise, the Hofmann-type rearrangement of substituted phthalimides **414** or succinimides **416** using a hypervalent iodine(III) reagent generated *in situ* from iodobenzene and *m*CPBA in alcohol in the presence of a base affords anthranilic acid derivatives **415** or amino acid derivatives **417,** respectively (Scheme 3.167) [507].

3.1.14 Oxidations at Nitrogen, Sulfur and other Heteroatoms

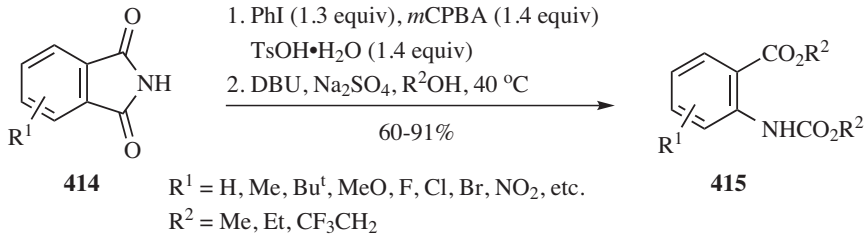
Hypervalent iodine(III) compounds have found wide application for the oxidation of organic derivatives of nitrogen, sulfur, selenium, tellurium and other elements. Reactions of λ^3-iodanes with organonitrogen compounds leading to the electron-deficient nitrenium intermediates and followed by cyclizations and rearrangements (e.g., Hofmann rearrangement) are discussed in Section 3.1.13. Several other examples of oxidations at a nitrogen center are shown below in Schemes 3.168–3.170.

Primary aliphatic amines or benzylamines can be dehydrogenated by iodosylbenzene to nitriles **418** in dry dichloromethane at room temperature (Scheme 3.168) [508].

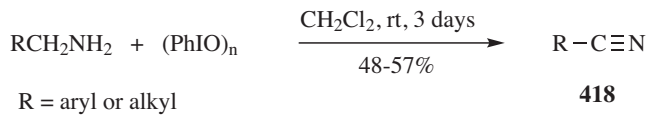


R = alkyl, cycloalkyl, $ArCH_2$, etc.

Scheme 3.166



Scheme 3.167

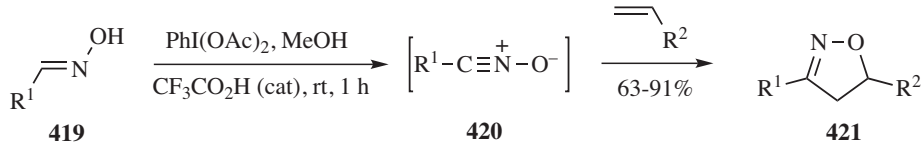


Scheme 3.168

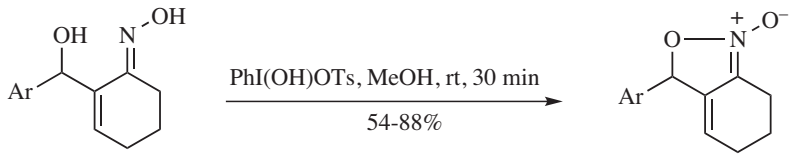
Aldoximes **419** are selectively oxidized by (diacetoxyiodo)benzene in methanol containing a catalytic amount of trifluoroacetic acid to give nitrile oxides **420,** which can be trapped *in situ* with olefins in a bimolecular or an intramolecular mode to give the synthetically valuable isoxazoline products **421** (Scheme 3.169) [509]. A similar reaction of α-oxo-aldoximes with $PhI(OAc)_2$ affords α-oxo-nitrile oxides, which can be further trapped with norbornene or styrene [510].

Various isoxazoline N-oxide derivatives **423** can be synthesized by the oxidation of β-hydroxyketoximes **422** using [hydroxy(tosyloxy)iodo]benzene in methanol or water (Scheme 3.170) [511].

Additional examples of oxidations at a nitrogen center include the following: the $PhI(OAc)_2$-induced oxidation of aromatic amines to imines applied for deprotection of protected amino diols [512], N-acylation of 1,3-disubstituted thioureas using $PhI(OAc)_2$ [513], $PhI(OAc)_2$-promoted oxidation of 1,2-dicarbethoxyhydrazine to diethyl azodicarboxylate as a key step in an organocatalytic Mitsunobu



Scheme 3.169



422 Ar = Ph, 2-$NO_2C_6H_4$, 2-BrC_6H_4, 2,4-$Cl_2C_6H_3$, etc. **423**

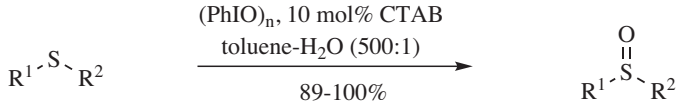
Scheme 3.170

reaction [514], $PhI(OCOCF_3)_2$-induced oxidations of phenylhydrazones leading to regeneration of the carbonyl function [515], low-temperature generation of diazo compounds by the reaction of $PhI(OCOCF_3)_2$ with hydrazones [516], preparation of *N*-aroyl-*N'*-arylsulfonylhydrazines by oxidation of aromatic aldehyde *N*-arylsulfonylhydrazones with $PhI(OCOCF_3)_2$ [517] and conversion of oximes into nitroso compounds using *p*-bromo(diacetoxyiodo)benzene [518].

Hypervalent iodine reagents are commonly used for the oxidation of organosulfur compounds. Applications of hypervalent iodine reagents for the preparation of sulfoxides, including enantioselective oxidations of organic sulfides, have been summarized in reviews [519, 520].

The oxidation of various sulfides **424** with iodosylbenzene in the presence of catalytic amounts of quaternary ammonium bromides affords the respective sulfoxides **425** in high yields (Scheme 3.171) [521]. The best catalytic effect in this reaction is observed when oxidation is carried out in a nonpolar solvent (toluene, hexane, dichloromethane) in the presence of trace amounts of water and 10 mol% of cetyltrimethylammonium bromide (CTAB). Iodosylbenzene can also be activated in the solid state by pulverization with natural clays or silica gels [522, 523]. The oxidation of various alkyl aryl sulfides with $(PhIO)_n$ supported on natural (montmorillonite, KSF and bentonite clays) as well as cation-exchanged K10-montmorillonite clays affords sulfoxides in excellent yields. A mechanism involving depolymerization of $(PhIO)_n$ by the acidic SiOH sites on the clay is proposed for this reaction [522]. Organic sulfides are also selectively oxidized to sulfoxides by the solid reagent system $PhI(OAc)_2$–alumina [524], or by $PhI(OAc)_2$ in water in the presence of KBr [525].

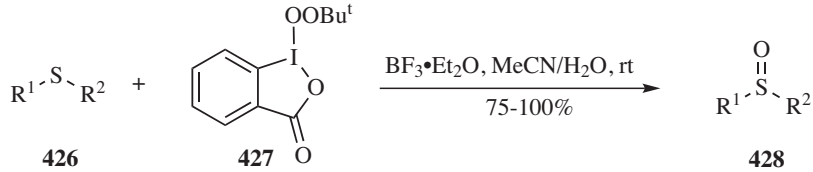
Oligomeric iodosylbenzene sulfate, $(PhIO)_3 \cdot SO_3$, which can be formally considered as a partially depolymerized activated iodosylbenzene (Section 2.1.4), is a readily available, stable and water-soluble hypervalent iodine reagent that is useful for the oxidation of sulfides to sulfoxides. Furthermore, it can be conveniently generated *in situ* from $PhI(OAc)_2$ and $NaHSO_4$ and can be used without isolation for oxidations in aqueous solution or under solvent-free conditions. The reaction of $(PhIO)_3 \cdot SO_3$ with organic sulfides at room temperature affords sulfoxides in high yields without overoxidation to sulfones and this reaction is compatible with the presence in the substrate molecule of hydroxy groups, double bonds, benzylic carbon atoms, carboxylate groups and various substituted aromatic rings [526].



424 **425**

R^1, R^2 = Ph, 2-MeC_6H_4, 2-$MeOC_6H_4$, $PhCH_2$, Me, Et

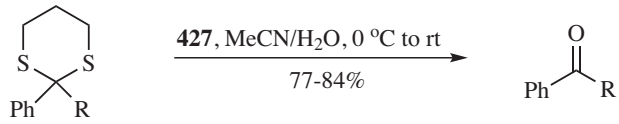
Scheme 3.171



426 **427** **428**

R^1 = Bu, Bu^i, Bu^s, $PhCH_2$, $Me(CH_2)_4$, $CH_2{=}CHCH_2$, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, Ph

R^2 = $PhCH_2$, Ph, Me, $CH_2P(O)(OEt)_2$



429 R = Me, C_5H_{11} **430**

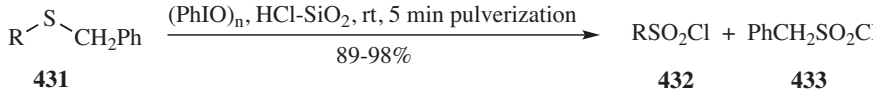
Scheme 3.172

Alkylperoxybenziodoxoles (Section 2.1.8.1.4) are useful oxidizing reagents toward organic sulfides, selenides and phosphines [527–529]. Sulfides **426** can be oxidized with peroxybenziodoxole **427** under mild conditions to afford sulfoxides **428** in high yields (Scheme 3.172) [511]. A similar oxidation of dithioacetals **429** leads to regeneration of the parent carbonyl compound **430** and thus can be useful as a method for selective deprotection [511].

Organic sulfides are oxidized to sulfonyl chlorides by iodosylbenzene, activated by crushing and grinding with a HCl-treated silica gel [522,523]. Sulfides **431** with benzylic substituents, such as dibenzyl, alkyl benzyl and benzyl phenyl sulfides, are converted by this reaction into the corresponding sulfonyl chlorides **432** and **433** in high yields (Scheme 3.173). Other types of sulfides, such as dialkyl and alkyl phenyl sulfides, give sulfonyl chlorides only in moderate yield.

The reaction of diaryl disulfides **434** or thiophenols with $PhI(OCOCF_3)_2$ affords the corresponding thiosulfonic S-esters **435** in good yields under mild conditions (Scheme 3.174) [530]. A similar reaction of diaryl disulfides **434** with $PhI(OCOCF_3)_2$ in the presence of alcohols affords the respective arylsulfinic esters **436** [531]. Diselenides **437** in the presence of sodium organosulfinates are oxidized by $PhI(OCOCF_3)_2$ to the respective selenosulfonates **438** [532]. The oxidation of ditellurides **439** by $PhI(OCOCF_3)_2$ under similar conditions affords arenetellurinic mixed anhydrides **440** [533].

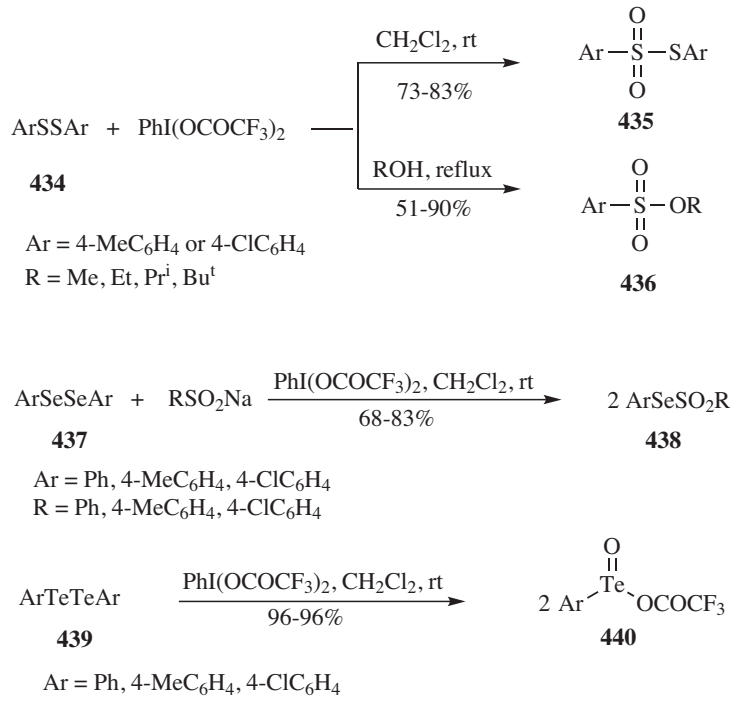
A similar oxidation of disulfides **441** with $PhI(OCOCF_3)_2$ in the presence of sodium trifluoromethanesulfinate provides a convenient synthetic approach to trifluoromethanethiosulfonates **442** (Scheme 3.175) [534].



431 **432** **433**

R = $PhCH_2$, $PhCH_2CH_2$, Ph, CH_3, C_4H_9, C_8H_{17}, etc.

Scheme 3.173

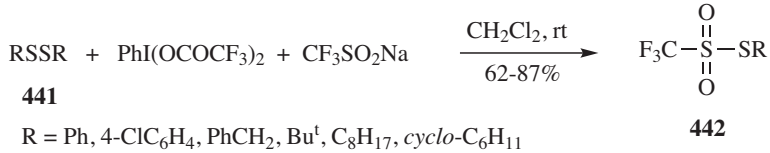


Scheme 3.174

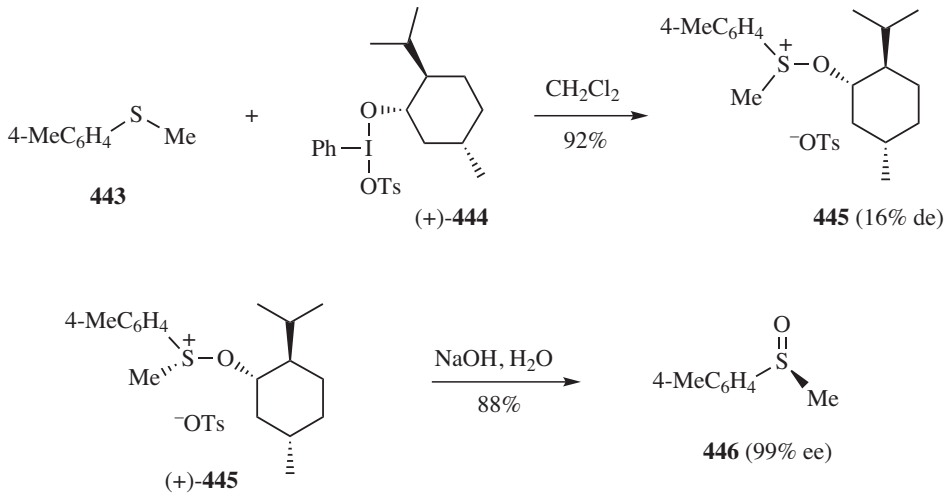
The analogous reaction of diselenides can be used for the preparation of trifluoromethaneselenosulfonates [534].

Enantioselective oxidation of sulfides **443** has been achieved by using chiral, non-racemic [menthyloxy(tosyloxy)iodo]benzenes derived from (1*S*,2*R*,5*S*)-(+)-menthol (structure **444**) and (1*R*,2*S*,5*R*)-(–)-menthol. Reaction of organic sulfides with these reagents in dichloromethane gives optically active (menthyloxy)sulfonium tosylates (e.g., **445**). For example, the treatment of methyl *p*-tolyl sulfide with (+)-**444** gave (+)-menthyloxylmethyl-*p*-tolylsulfonium tosylate **445** in 92% yield as a mixture (ca. 16% de) of diastereomers. The major diastereomer (+)-**445** was separated with 49% efficiency by recrystallization of the mixture from CH_2Cl_2/Et_2O and hydrolyzed in aqueous NaOH to optically pure (*S*)-(–)-methyl *p*-tolyl sulfoxide **446** (Scheme 3.176) [535].

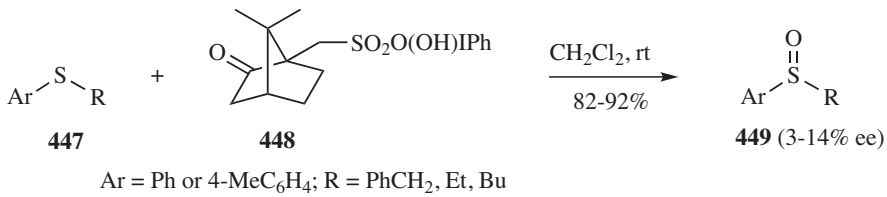
The oxidation of alkyl and aryl sulfides **447** with [hydroxy((+)-10-camphorosulfonyloxy)iodo]benzene **448** as chiral oxidant has been reported (Scheme 3.177). This reaction affords the corresponding sulfoxides **449** in good yields but with low enantioselectivity [536].



Scheme 3.175



Scheme 3.176

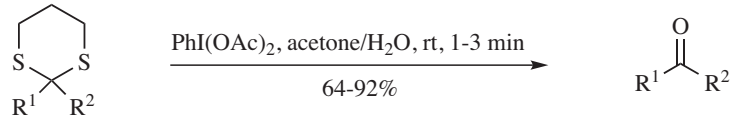


Scheme 3.177

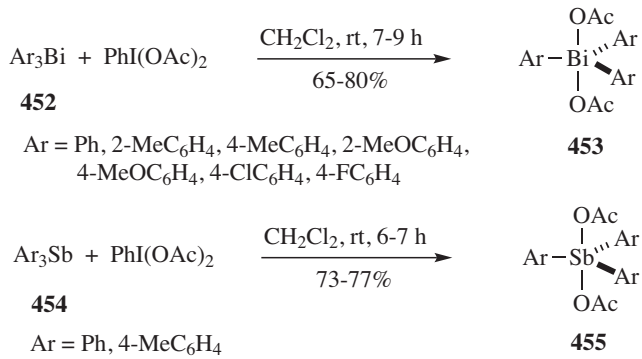
For the enantioselective oxidations of organic sulfides to chiral sulfoxides using iodine(V) reagents, also see Section 3.2.

Thioacetals and thioketals **450** are efficiently cleaved to carbonyl compounds **451** with $PhI(OCOCF_3)_2$ or $PhI(OAc)_2$ under mild conditions (Scheme 3.178). This reaction is especially useful for the selective deprotection of either thioacetals or thioketals and is compatible with various other functional groups [537–541].

Hypervalent iodine compounds can serve as effective oxidants of trivalent phosphorus compounds. In particular, various organic phosphines are selectively oxidized by iodosylbenzene to the respective phosphine oxides in quantitative yield [542].



Scheme 3.178



Scheme 3.179

[Bis(acyloxy)iodo]arenes are useful for the oxidation of organic derivatives of bismuth and antimony [543, 544]. Triarylbismuthanes **452** react with (diacetoxyiodo)benzene in dichloromethane under mild, neutral conditions to afford pentavalent triarylbismuth diacetates **453,** which can be isolated in good yields (Scheme 3.179) [543]. Triarylstibines **454** react with $PhI(OAc)_2$ under similar conditions to afford triarylantimony(V) diacetates **455** [544].

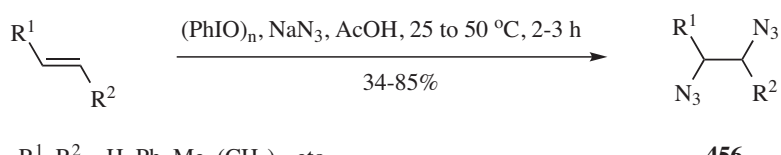
3.1.15 Azidations

Azidoidanes generated *in situ* from a hypervalent iodine reagent [e.g., iodosylbenzene or $PhI(OAc)_2$] and a source of azide anion (Section 2.1.12.1) are commonly used as efficient reagents for introduction of the azido function into organic molecules. Zbiral and coworkers in the early 1970s first investigated reactions of the $PhI(OAc)_2/TMSN_3$ system with alkenes leading to diazides, α-azido ketones, or nitriles [545–547]. Later, in the 1980s, Moriarty and coworkers developed a convenient experimental procedure for the preparation of vicinal diazides **456** from alkenes by reaction with iodosylbenzene/NaN_3 in acetic acid (Scheme 3.180) [548].

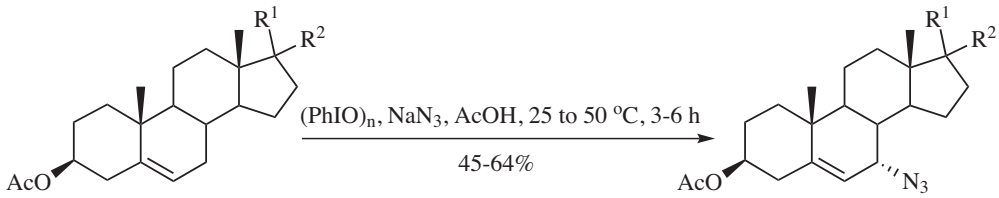
This reaction (Scheme 3.180) is predominantly *anti* stereoselective; in several cases α-azido ketones has been isolated as by-products [548]. Steroids **457** under the same conditions give exclusively allylic azides **458** (Scheme 3.181) [549].

Ochiai and coworkers have developed a simple method for the synthesis of allyl azides **460** from allyltrimethylsilanes **459** using the iodosylbenzene/$TMSN_3/BF_3{\cdot}Et_2O$ combination (Scheme 3.182) [550].

Treatment of β-dicarbonyl compounds **461** with iodosylbenzene/$TMSN_3$ in chloroform at reflux affords azides **462** in moderate to good yield (Scheme 3.183) [551]. Under similar conditions, 2-(trimethylsiloxy)furan (**463**) gives azidofuranone **464** as the main product [552].

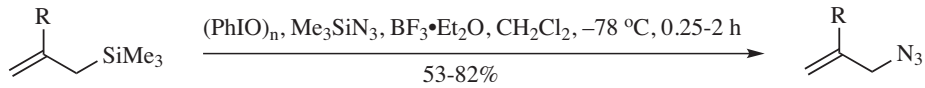


Scheme 3.180



457 $R^1, R^2 = H, C_8H_{17}, COCH_3, OAc$ **458**

Scheme 3.181



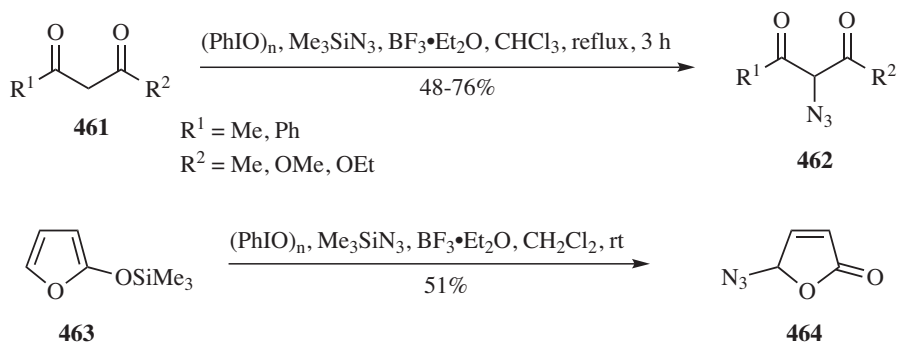
459 R = alkyl, cycloalkyl **460**

Scheme 3.182

Aromatic compounds, such as anisoles and alkylbenzenes, can be azidated in the ring by treatment with $PhI(OCOCF_3)_2/TMSN_3$ in hexafluoroisopropanol (HFIP) [553]. It is assumed that this reaction does not involve azidoiodanes as reactive intermediates, but proceeds via cation–radicals generated by SET from the aromatic substrate to $PhI(OCOCF_3)_2$ (Section 3.1.12) [362]. It is possible, however, to change the course of this reaction by using acetonitrile instead of HFIP as the solvent. Treatment of *p*-alkylanisols **465** with $PhI(OCOCF_3)_2/TMSN_3$ under these conditions affords arylalkyl azides **466** in moderate yields (Scheme 3.184) [554].

A radical mechanism for this reaction (Scheme 3.184) involving the initial formation of azidoiodane **467** and its subsequent homolytic decomposition has been proposed (Scheme 3.185) [554]. Experimental evidence supporting the generation of azide radicals in the thermal decomposition of azidoiodanes formed from $PhI(OAc)_2/NaN_3$ has been reported by Fontana and coworkers [555].

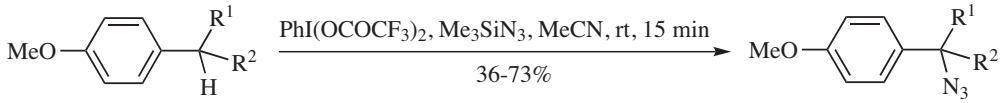
Magnus and coworkers have reported several synthetically important azidations using the iodosylbenzene/$TMSN_3$ combination, which serves as the source of non-isolable azidoiodanes $PhI(N_3)_2$



461 R^1 = Me, Ph; R^2 = Me, OMe, OEt **462**

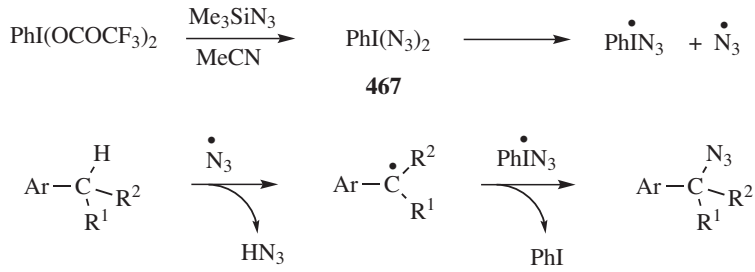
463 **464**

Scheme 3.183



465 R^1, R^2 = H, alkyl, cycloalkyl, CN, SMe, CO_2Me, etc. **466**

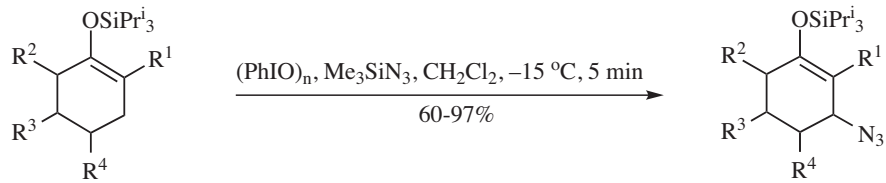
Scheme 3.184



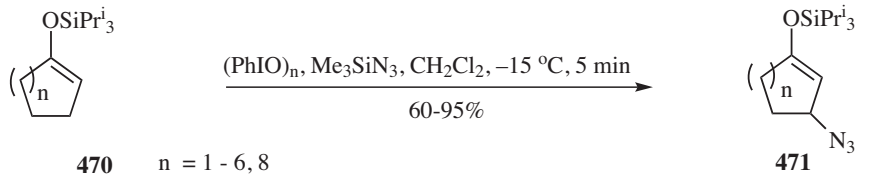
Scheme 3.185

or PhI(N_3)OTMS [556–568]. In particular, various triisopropylsilyl (TIPS) enol ethers **468** and **470** react with this reagent at –15 to –18 °C to give the β-azido adducts **469** and **471,** respectively, in excellent yields (Scheme 3.186) [562].

A similar reaction of silyl ether **472** with iodosylbenzene/$TMSN_3$ at lower temperatures and in the presence of catalytic amounts of the stable radical TEMPO stereoselectively affords vicinal *trans*-diazides **473** as the major products (Scheme 3.187) [562]. The effect of TEMPO on the outcome of this reaction has been explained by a change of mechanism from ionic dehydrogenation to a radical addition process in the presence of TEMPO [562].

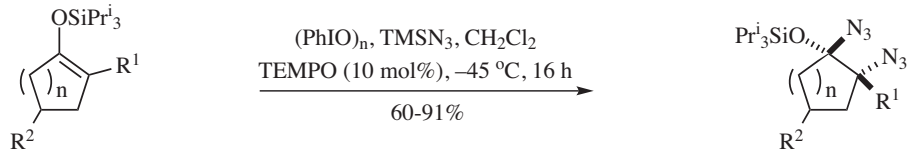


468 R^1, R^2 = H or Me; R^3 = H, Pr^i or 2-propenyl; R^4 = H, Me, Et, Pr^i, Bu^t, etc. **469**



470 n = 1 - 6, 8 **471**

Scheme 3.186



472 n = 1 or 2; R^1 = H or Ph; R^2 = H, Bu^t, etc. **473**

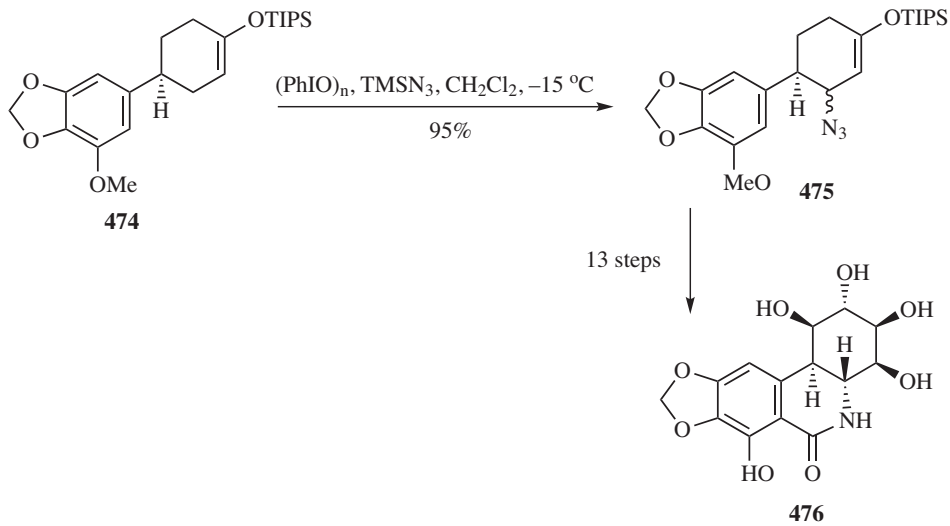
TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl

Scheme 3.187

The β-azidation reaction of triisopropylsilyl enol ethers (Schemes 3.186 and 3.187) has been effectively utilized in organic synthesis [563–565]. Magnus and coworkers have developed a mechanistically different enone synthesis that involves treatment of β-azido TIPS enol ethers **469** and **471** with fluoride anion to effect desilylation and concomitant β-elimination to give an α,β-enone [563]. Alternatively, the β-azido group in **469** or **471** can be ionized with Me_3Al or Me_2AlCl and the intermediate enonium ion trapped by various nucleophiles, such as an allylstannane, electron-rich aromatics and trimethylsilyl enol ethers, to give various β-substituted TIPS enol ethers. Reduction of the β-azido TIPS enol ether provides access to the synthetically useful β-amino TIPS enol ethers [563].

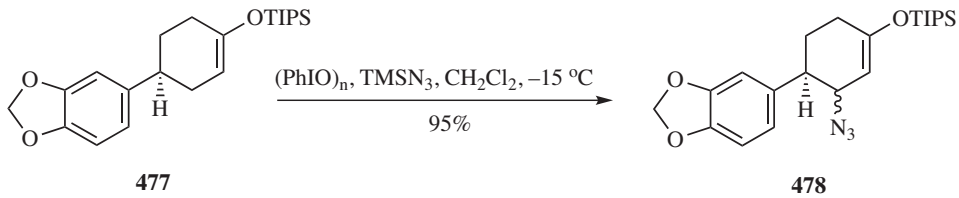
The β-azidation of the TIPS derivative **474** has been utilized in the total synthesis of the antitumor alkaloid (+)-pancratistatin (**476**). Azide **475,** the key intermediate product in this synthetic scheme, was obtained in high yield as a mixture of *trans*- and *cis*-diastereomers (3.5 : 1 ratio) and was further converted into pancratistatin (**476**) in 13 steps (Scheme 3.188) [564, 565].

Likewise, the β-azidation reaction has been applied to the enantioselective synthesis of the core structure of lycorane Amaryllidaceae alkaloids. The key intermediate **478** in this synthesis was obtained by β-azidation of the TIPS derivative **477** as a mixture of *trans*- and *cis*-diastereomers (3.5 : 1 ratio) (Scheme 3.189) [566].



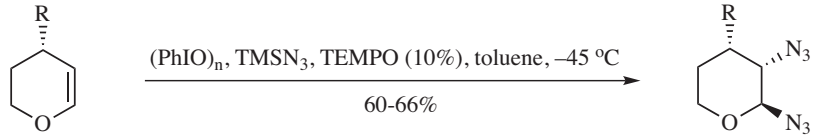
474 **475** **476**

Scheme 3.188



477 **478**

Scheme 3.189



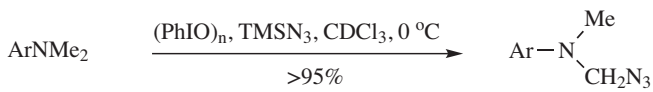
479 R = H or $NHCO_2Ad$ **480**

Scheme 3.190

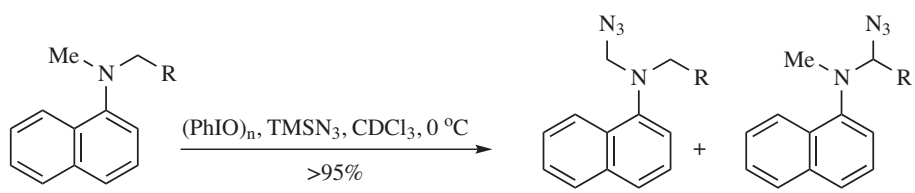
The diazidation reaction leading to vicinal *trans*-diazides (Scheme 3.187) has also been utilized in organic synthesis [567]. Dihydropyrans **479** react with the $(PhIO)_n/TMSN_3$/TEMPO system to give 2,3-bis-azido adducts **480** (Scheme 3.190), which can be further elaborated into amino-pyrans [567].

Treatment of *N*,*N*-dimethylarylamines **481** with the iodosylbenzene/$TMSN_3$ reagent system results in the functionalization of one of the methyl groups to give *N*-azidomethyl derivatives **482** (Scheme 3.191). The reaction with an excess of the iodosylbenzene/$TMSN_3$ reagent (2.6–4 equiv) affords the respective bis(*N*,*N*-azidomethyl) derivatives. The azidation of unsymmetrical substrates **483** gives a mixture of products **484** and **485** [568].

Amides, carbamates and ureas can also be α-azidated under similar conditions; however, the yields of azides in this case are generally lower [557, 561]. For example, the piperidine derivatives **486** are converted

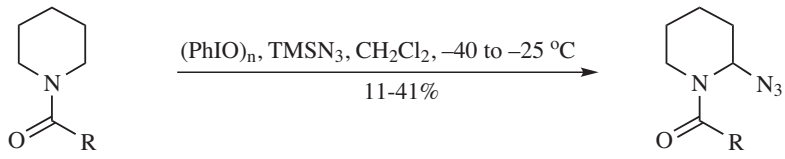


481 Ar = Ph, 4-pyridyl, 3-$MeOC_6H_4$, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, 4-$Me_2NC_6H_4$, etc. **482**



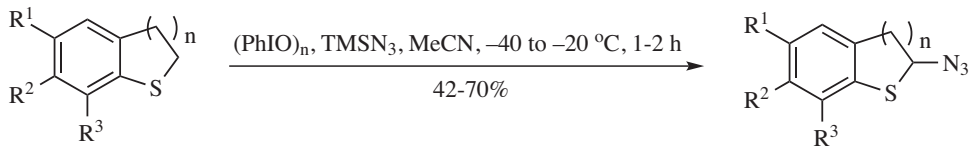
483 R = H or Ph **484** 2:1 (R = H) 1:1.8 (R = Ph) **485**

Scheme 3.191



486 R = Me, Bu^{t}O, Ph, Ph_2N, PhO, 4-$NO_2C_6H_4$, etc. **487**

Scheme 3.192



488 R^1, R^2 = H, OMe, OAc
R^3 = H or OMe; n = 1, 2

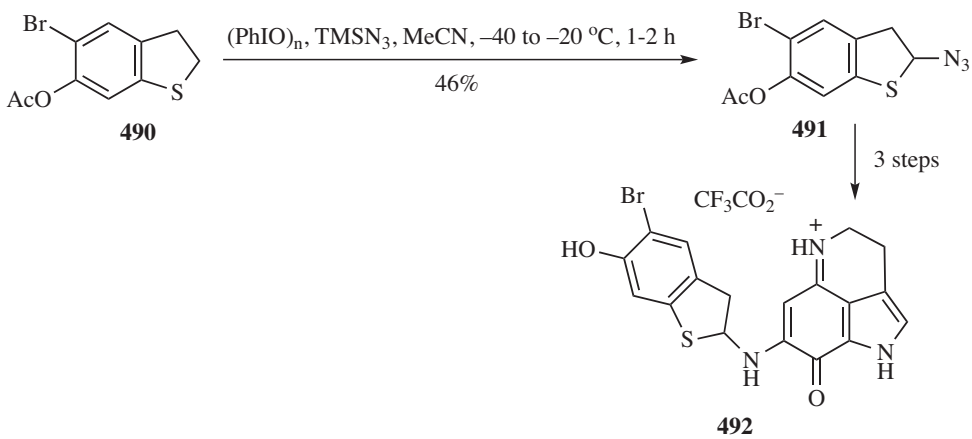
489

Scheme 3.193

into azides **487** in moderate yield (Scheme 3.192) with some starting material remaining in the reaction mixture.

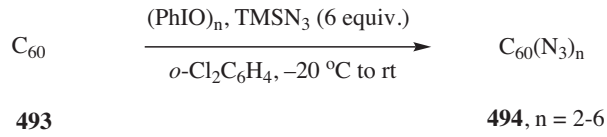
Kita and coworkers have reported the direct α-azidation of cyclic sulfides using the iodosylbenzene/$TMSN_3$ reagent system [569]. This method is applicable to substrates that are easily aromatized under oxidative conditions, such as monocyclic and bicyclic sulfides **488,** to give the corresponding α-azido sulfides **489** in moderate to good yields (Scheme 3.193).

A similar α-azidation of cyclic sulfide **490** leading to the α-azido sulfide **491** has been applied in the total synthesis of the strongly cytotoxic marine alkaloid (±)-makaluvamine F (**492**) (Scheme 3.194) [373, 570].



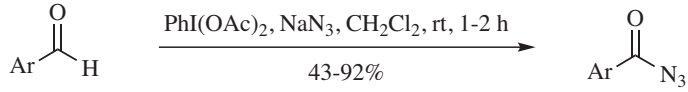
490 **491** **492**

Scheme 3.194



493 **494**, n = 2-6

Scheme 3.195



495 Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$Bu^tC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 3-BrC_6H_4, 4-$NO_2C_6H_4$ **496**

Scheme 3.196

Fullerene C_{60} (**493**) smoothly reacts with the iodosylbenzene/$TMSN_3$ reagent system under typical azidation conditions to form explosive polyazidofullerenes **494** (Scheme 3.195) [571].

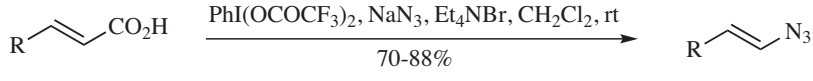
Polystyrene can be directly azidated in 1,2-dichloroethane or chlorobenzene using the $PhI(OAc)_2$/$TMSN_3$ reagent combination at 0 °C for 4 h followed by heating to 50 °C for 2 h. The 2D NMR HMBC spectra indicate that the azido groups are attached to the polymer backbone and also possibly to the aromatic rings. The amount of introduced azido groups is approximately one in every eleven styrene units according to semiquantitative IR spectroscopy and elemental analysis [572].

The combination of (diacetoxyiodo)benzene and sodium azide, which presumably generates (diazidoiodo)benzene as the principal reagent, readily reacts with aryl aldehydes **495** to afford aroyl azides **496** in generally high yields (Scheme 3.196) [573].

Vinyl azides **498** can be prepared directly from α,β-unsaturated carboxylic acids **497** by treatment with [bis(trifluoroacetoxy)iodo]benzene and sodium azide in dichloromethane under phase-transfer conditions (Scheme 3.197) [574]. This method is also useful for the preparation of acyl azides [574].

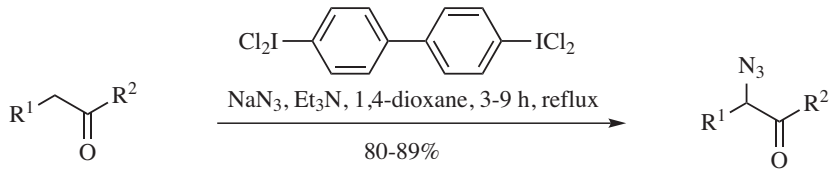
A simple method for the preparation of α-azido ketones and esters **500** in good yields by direct azidation of carbonyl derivatives **499** at the α-carbon using 4,4′-bis-(dichloroiodo)biphenyl and sodium azide has been reported (Scheme 3.198) [575]. The hypervalent iodine reagent, 4,4′-bis-(dichloroiodo)biphenyl, can be easily recycled from the reaction mixture.

Azidobenziodoxoles (Section 2.1.8.1.5) can be used as efficient azidating reagents toward various organic substrates (Scheme 3.199). For example, reagent **501** reacts with *N,N*-dimethylanilines in dichloromethane at reflux in 30 min to afford the respective *N*-azidomethyl-*N*-methylanilines **502** in excellent yields [576]. The main advantage of reagent **501** over the unstable $(PhIO)_n$/$TMSN_3$ reagent combination is its high thermal stability, which allows its use at higher temperatures. Azidobenziodoxole **501** can even be used for direct



497 R = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, Pr^i, CO_2Me **498**

Scheme 3.197

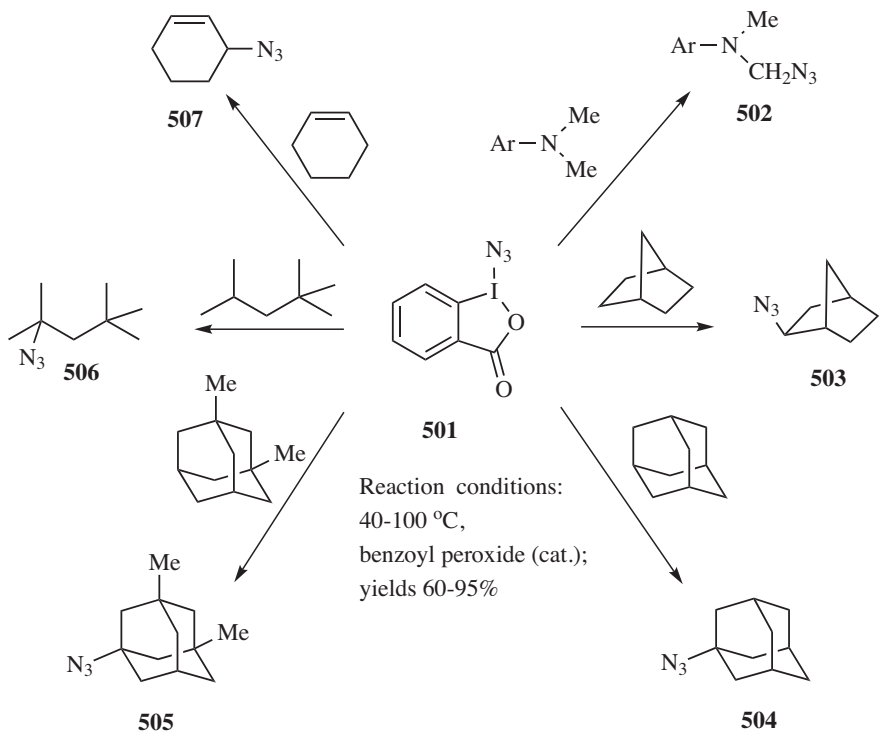


499 R^1 = H, Me, Et, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, etc. **500**
R^2 = OMe, OEt, OBn, Ph, Me
or $R^1 + R^2 = (CH_2)_4$

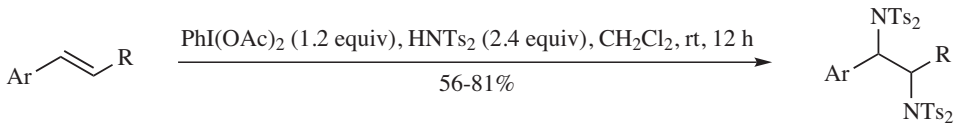
Scheme 3.198

azidation of hydrocarbons at higher temperatures and in the presence of radical initiators (Scheme 3.199). Reagent **501** selectively reacts with isooctane upon reflux in 1,2-dichloroethane in the presence of catalytic amounts of benzoyl peroxide to afford tertiary azide **506.** Under similar conditions, reactions of azidobenziodoxole **501** with bicyclic and tricyclic hydrocarbons afford the respective alkyl azides **503–505.** Cyclohexene is azidated at the allylic position to form 3-azidocyclohexene **507** [576].

Azidations with azidobenziodoxoles can be effectively catalyzed by iron salts, such as iron(II) propionate, $Fe(O_2CEt)_2$. In the presence of chiral oxazoline ligands (boxmi ligands), the Fe-catalyzed azidations of



Scheme 3.199



Ar = Ph, 4-$NO_2C_6H_4$, 4-BrC_6H_4, 4-ClC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$, 3-$NO_2C_6H_4$, 3-$PhOC_6H_4$, 3-$MeOC_6H_4$, etc.
R = H, Me, Ph

508

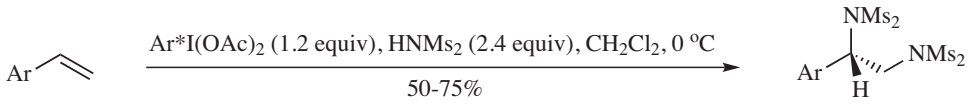
Scheme 3.200

β-keto esters and oxindoles afford the respective α-azido-β-keto esters and 3-azidooxindoles with high enantioselectivity (up to 94% ee) [577].

3.1.16 Aminations

Direct introduction of the amino or amido functional group is an important synthetic goal that can be effectively achieved by using hypervalent iodine amides and imides (Section 2.1.12) as reagents. The amides, for example, $ArI(OAc)NTs_2$ or $ArI(NTs_2)_2$, can be conveniently generated *in situ* from [bis(acyloxy)iodo]arenes and ditosylamine $HNTs_2$ and used without isolation in reactions with alkenes [578, 579]. For example, numerous vicinal diamines **508** have been prepared by direct diamination of alkenes by the action of (diacetoxyiodo)benzene and bis-sulfonimides as nitrogen sources (Scheme 3.200) [578]. The reaction is characterized by its robustness and its wide substrate scope; it proceeds selectively with both terminal and internal alkenes and tolerates a range of functional groups.

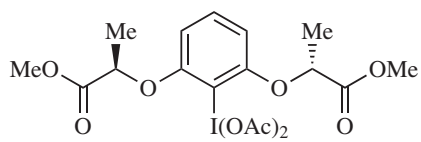
Furthermore, alkenes can be directly diaminated in enantioselective fashion by using chiral hypervalent iodine reagents. Styrenes have been converted into the corresponding (*S*)-diamine derivatives **509** with high enantioselectivity under metal-free conditions using chiral (diacetoxyiodo)arene **510** (Section 2.1.5) as the oxidant and Ms_2NH as nitrogen source (Scheme 3.201) [580]. Ditosylamine $HNTs_2$ has also been successfully used as a nitrogen source in this reaction.



Ar = 4-$Bu^tC_6H_4$, 4-BrC_6H_4, 4-ClC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$, 4-$AcOC_6H_4$, 4-$PhthNCH_2$, C_6H_4, 3-FC_6H_4, 3-$PhOC_6H_4$, 3-$CF_3C_6H_4$, 2-ClC_6H_4, 2-FC_6H_4, 3,5-$Me_2C_6H_3$, etc.

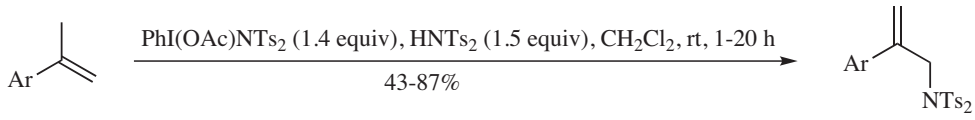
509
85-99% ee

Ar*I(OAc)$_2$ =



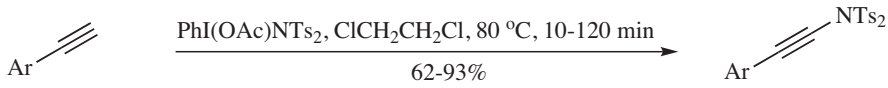
510

Scheme 3.201



511 Ar = Ph, 4-$NO_2C_6H_4$, 4-MeC_6H_4, 4-$Bu^tC_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$, 3-MeC_6H_4, 3-BrC_6H_4, etc. **512**

Scheme 3.202



513 Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-$Bu^tC_6H_4$, 4-BrC_6H_4, 2-MeC_6H_4, 3-$MeOC_6H_4$, 3-ClC_6H_4, 2,4-$F_2C_6H_3$, 1-naphthyl **514**

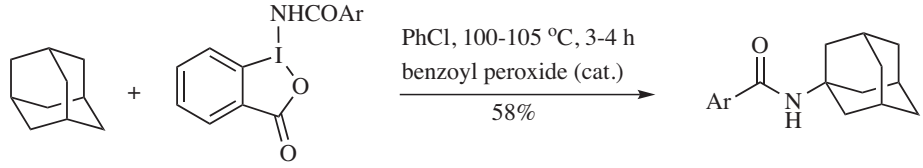
Scheme 3.203

Hypervalent iodine amides have been used for direct intermolecular allylic amination. α-Methyl styrenes **511** are selectively aminated by hypervalent iodine amide $PhI(OAc)NTs_2$ in the presence of ditosylamine as a nitrogen source to give allylic bistosylamides **512** in generally high yields (Scheme 3.202) [581].

A direct metal-free amination of arylethynes by the reaction of terminal alkynes **513** with hypervalent iodine imide allows a simple, one-step synthesis of an important class of ynamides **514** (Scheme 3.203) [582].

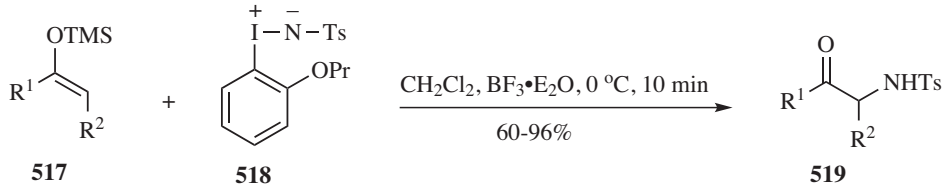
Amidobenziodoxoles (Section 2.1.8.1.6) have been used as the amidating reagents toward polycyclic alkanes under radical conditions. For example, reagent **515** reacts with adamantane in chlorobenzene at 100–105 °C in the presence of a catalytic amount of benzoyl peroxide to afford 1-amidoadamantane **516** in moderate yield (Scheme 3.204) [583].

Imidoiodanes, ArINTs (Section 2.1.12.4), can be used for various amidations under transition metal catalysis (Section 3.1.21) [584–586] or under metal-free conditions [587, 588]. In particular, *o*-alkoxyphenyliminoiodane **518** readily reacts with silyl enol ethers **517** in the presence of BF_3·etherate to give products of α-tosylamination **519** in good yields (Scheme 3.205) [588]. Furthermore, reagent **518** in the presence of catalytic amounts of iodine readily reacts with adamantane to give the product of tosylamination (**520**) in excellent yield under very mild conditions. For comparison, PhINTs reacts with adamantane and iodine (0.2 equiv) in dichloromethane at room temperature in 2 h to afford 1-tosylaminoadamantane **520** in only 63% yield [589].



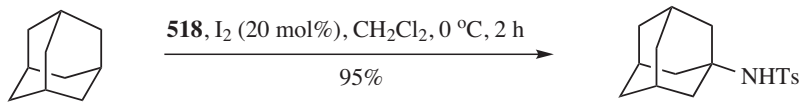
515 Ar = 4-ClC_6H_4 **516**

Scheme 3.204



517 **518** **519**

R^1 = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 2-ClC_6H_4 and R^2 = H;
or R^1 = Pr and R^2 = Et; or $R^1 + R^2 = (CH_2)_4$



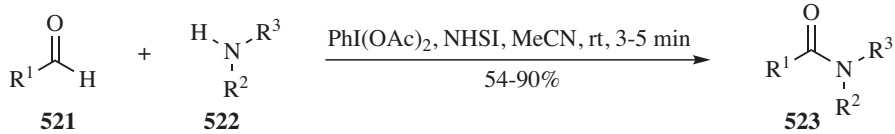
520

Scheme 3.205

An oxidative amination of aldehydes using amines, *N*-hydroxysuccinimide and (diacetoxyiodo)benzene has been developed [590]. The method allows the coupling of a wide range of aldehydes **521** with amines **522** under mild reaction conditions, providing amides **523** in good to excellent yield (Scheme 3.206). A radical mechanism was proposed for this reaction based on an ESR study [590]. A similar protocol has been reported for a one-pot synthesis of a series of glycosyl carboxamides in 78–96% yield by the coupling of aldehydes with secondary amines using (diacetoxyiodo)benzene in the presence of ionic liquid at room temperature [591].

3.1.17 Thiocyanations and Arylselenations

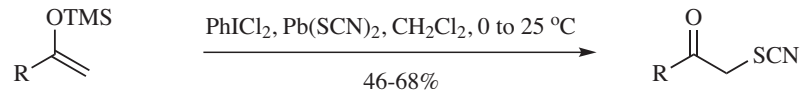
Hypervalent iodine reagents in combination with a source of appropriate nucleophiles are commonly used to prepare products with new C—S and C—Se bonds. Moriarty and coworkers have developed convenient procedures for the thiocyanation of organic substrates using the combination of $PhICl_2$ with $Pb(SCN)_2$ [592–594]. Various enol silyl ethers **524,** ketene silyl acetals **526** and **528** and β-dicarbonyl compounds **530** can be effectively thiocyanated with this combination of reagents to produce the respective thiocyanato



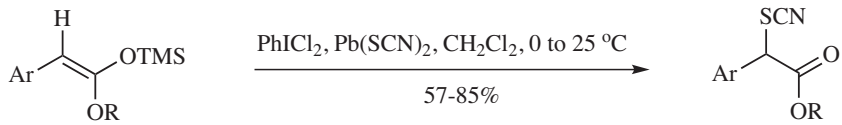
521 **522** **523**

R^1 = $PhCH_2CH_2$, (*E*)-PhCH=CH, Bu^t, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$
R^2 = $PhCH_2CH_2$, MeO, (*S*)-PhMeCH, (*S*)-$HOCH_2MeCH$, Ph, $HOCH_2CH_2$, etc.
R^3 = H, Me, or $R^2 + R^3 = (CH_2)_4$
NHSI = *N*-hydroxysuccinimide

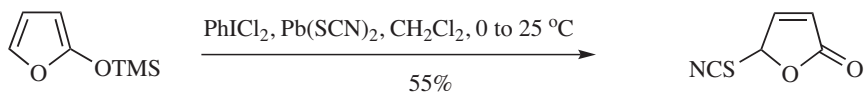
Scheme 3.206



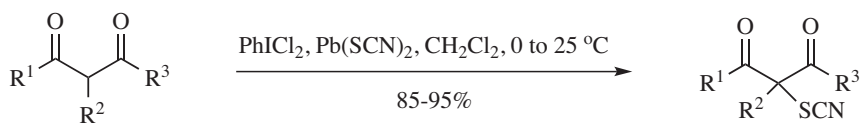
524 R = Ph, 2-furyl, 2-thienyl, 2-pyridyl, etc. **525**



526 Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$; R = Me, Et **527**



528 **529**

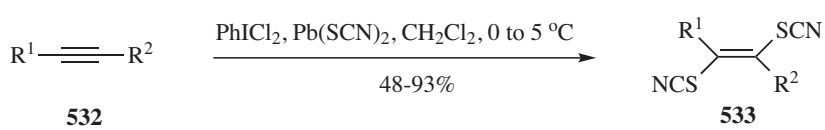


530 R^1, R^3 = Me or Ph; R^2 = H or Me **531**

Scheme 3.207

derivatives of carbonyl and β-dicarbonyl compounds **525, 527, 529** and **531,** respectively (Scheme 3.207) [592, 593]. The mechanism of these reactions presumably involves the intermediate formation of unstable iodine(III) thiocyanate, $PhI(SCN)_2$.

Under similar conditions, various alkynes **532** are stereoselectively converted into (*E*)-1,2-dithiocyanated alkenes **533** in generally good yield and with less than 5% of the corresponding (*Z*) isomers (Scheme 3.208) [594].

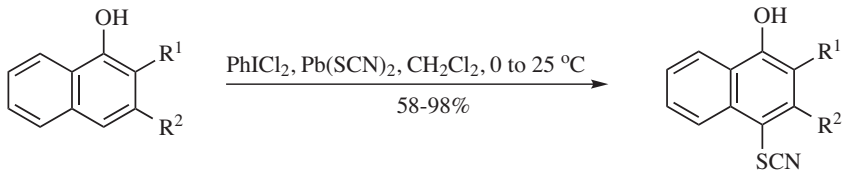


532 **533**

R^1 = Ph, 4-MeC_6H_4, Pr, $CH_3(CH_2)_3$, $CH_3(CH_2)_5$, $CH_3(CH_2)_7$, $HO(CH_2)_4$, 1-cyclohexenyl

R^2 = H, Me, Ph, TMS

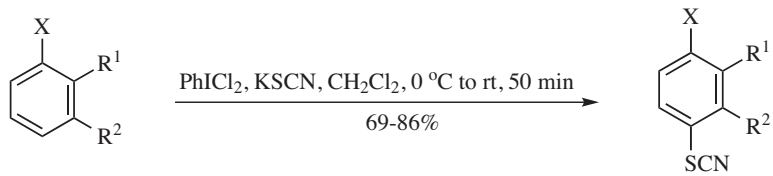
Scheme 3.208



534 R^1 = H, COMe, CO_2Et, $CONEt_2$
R^2 = H, Me, Ph, CH_2OCOMe, CO_2Et, $CONEt_2$

535

Scheme 3.209



536 X = OH or NH_2
R^1 = H, OH or CO_2H
R^2 = H or OH

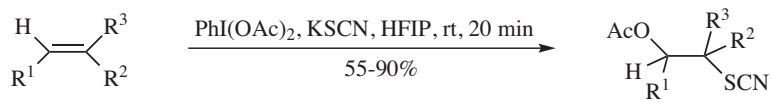
537

Scheme 3.210

The $PhICl_2/Pb(SCN)_2$ combination is an effective reagent for the regioselective thiocyanation of various types of *para*-unsubstituted phenols and naphthols to give the respective *para*-thiocyanatophenols and naphthols in good to quantitative yields [595]. Various functional groups, such as chloro, allyl, carbonyl, ester, amide and primary hydroxyl groups, have been shown to be compatible with this reaction. For example, the thiocyanation of naphthols **534** affords the respective thiocyanates **535** in generally high yield (Scheme 3.209) [595].

An improved method for the thiocyanation of 2-arylindan-1,3-diones, phenols and anilines employs a reagent combination of (dichloroiodo)benzene and potassium thiocyanate in dry dichloromethane [596]. For example, the *para*-unsubstituted phenols and anilines **536** are efficiently converted under these reaction conditions into the respective *p*-thiocyanato derivatives **537** in high yields (Scheme 3.210).

The combination of (diacetoxyiodo)benzene and thiocyanate anion in a polar, protic, non-nucleophilic solvent has been used for the oxidative functionalization of alkenes **538** to acetoxy thiocyanate derivatives **539** with *anti*-stereoselectivity and with good regioselectivity (Scheme 3.211) [597].

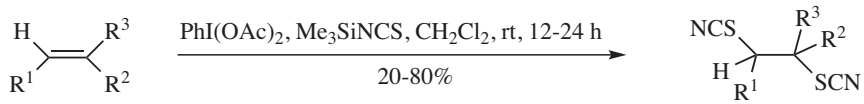


538

539

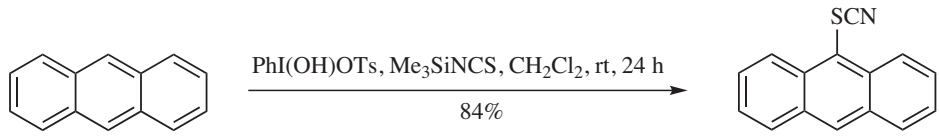
R^1 = C_4H_9, C_6H_{13}, C_8H_{17}, *cyclo*-C_6H_{11}; R^2 and R^3 = H
R^1 = C_5H_{11}, R^2 = H, R^3 = Me or $R^1 + R^2 = (CH_2)_4$, $(CH_2)_5$, R^3 = H
HFIP = 1,1,1,3,3,3-hexafluoroisopropanol

Scheme 3.211



R^1, R^2 and R^3 = H, alkyl, aryl, cycloalkyl, etc. **540**

Scheme 3.212



Scheme 3.213

A similar reaction of (diacetoxyiodo)benzene with alkenes and trimethylsilyl isothiocyanate in dichloromethane affords 1,2-dithiocyanates **540** in moderate yield (Scheme 3.212). Cyclic alkenes, such as cyclohexene and 1-methylcyclohexene, react with this reagent system stereoselectively with the formation of the respective *trans*-adduct [598, 599].

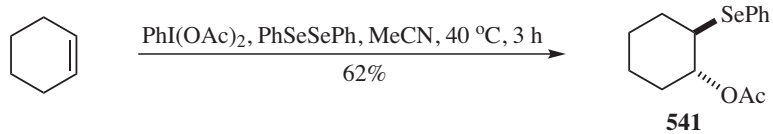
The reaction of polycyclic aromatic hydrocarbons with [hydroxy(tosyloxy)iodo]benzene in the presence of trimethylsilyl isothiocyanate leads to the regioselective thiocyanation of an arene nucleus, as illustrated by the reaction of anthracene shown in Scheme 3.213 [274].

In the 1990s, Tingoli and coworkers developed a general approach to various arylselenated products by the reaction of unsaturated compounds with diaryl diselenides and (diacetoxyiodo)benzene [600–603]. Various phenylselenated products are formed in good yields from the reaction of alkenes with diphenyl diselenide and (diacetoxyiodo)benzene in acetonitrile. In particular, cyclohexene under these conditions stereoselectively affords *trans*-1-acetoxy-2-(phenylseleno)cyclohexane (**541**) in good yield (Scheme 3.214) [603].

Cyclic phenylselenated products are obtained when this reaction is applied to alkenes containing hydroxy, benzamido, enolizable ketones and carboxylic acids as remote functional groups. For example, the alkenol derivative **542** reacts with diphenyl diselenide and (diacetoxyiodo)benzene in acetonitrile to furnish C-glycoside **543** in moderate yield (Scheme 3.215) [603].

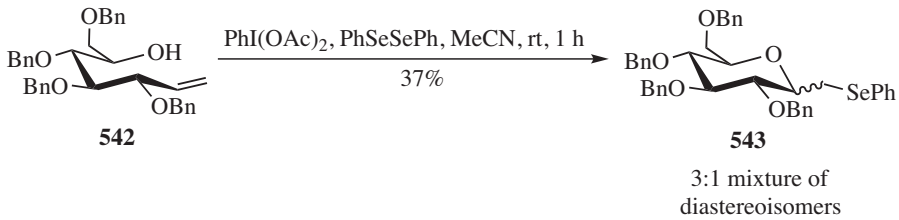
Several further modifications of this reaction have been reported more recently [250–252, 604]. In particular, a multicomponent reaction of allenes **544,** diaryl diselenides, (diacetoxyiodo)benzene and alcohols or acids affords 3-functionalized 2-arylselenyl-substituted allyl derivatives **545** in moderate yields (Scheme 3.216) [250].

Alkenes react with (diacetoxyiodo)benzene in the presence of diphenyl diselenide and sodium azide to produce vicinal azido selenides **546** in good yield (Scheme 3.217) [600]. This azidophenylselenation reaction



541

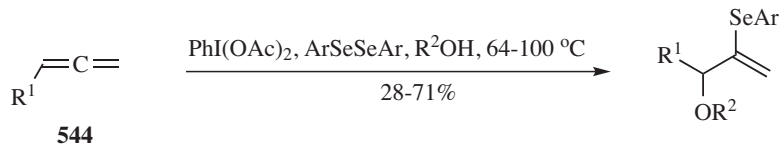
Scheme 3.214



542 **543**

3:1 mixture of diastereoisomers

Scheme 3.215



544 **545**

R^1 = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, α-$C_{10}H_7$
Ar = Ph or 4-MeC_6H_4; R^2 = Me, Et, Pr^i, Bu^t, Ac, C_3H_7CO

Scheme 3.216

proceeds with complete *anti*-Markovnikov regioselectivity, which has been explained by a radical process initiated by the azido radicals.

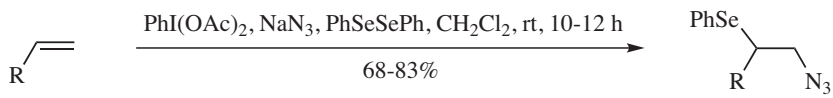
The *anti*-Markovnikov azidophenylselenation of protected galactals **547** under similar conditions proceeds as a stereospecific *anti*-addition to afford exclusively α-galacto isomer **548,** while the analogous glucals **549** give both *anti*- and *syn*-addition products **550** and **551** (Scheme 3.218) [605].

Nifantiev and coworkers have reported an improved preparative method for homogeneous azidophenylselenylation of glycols by the reaction with (diacetoxyiodo)benzene, diphenyldiselenide and trimethylsilyl azide [251]. In a representative example, the reaction of tri-*O*-benzyl-galactal **552** with $PhI(OAc)_2/Ph_2Se_2/TMSN_3$ in dichloromethane under mild conditions affords the corresponding selenoglycoside **553** in moderate yield (Scheme 3.219) [251]. Non-carbohydrate alkenes, such as styrene and substituted cyclopentenes, can also be azidophenylselenated under these conditions.

The selenodecarboxylation of cinnamic acid derivatives **554** with diaryldiselenides promoted by (diacetoxyiodo)benzene in acetonitrile affords vinyl selenides **555** in moderate yields (Scheme 3.220). A similar reaction of arylpropiolic acids gives the respective alkynyl selenides in 60–90% yields [604].

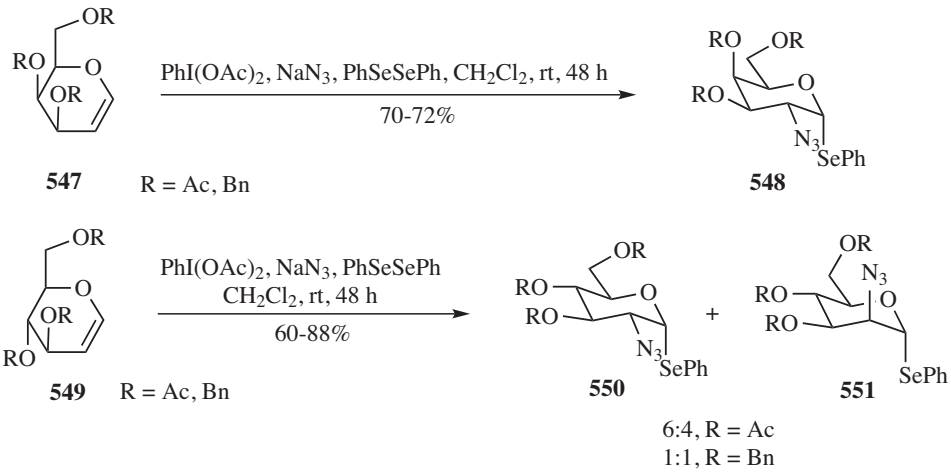
3.1.18 Radical Fragmentations, Rearrangements and Cyclizations

[Bis(acyloxy)iodo]arenes are commonly used as efficient initiators of radical processes. Under photochemical conditions or heating these reagents undergo decarboxylative decomposition generating alkyl

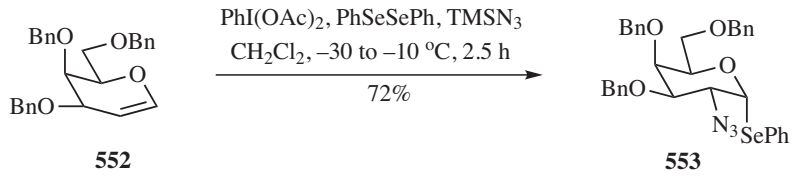


R = alkyl, aryl, cycloalkyl, etc. **546**

Scheme 3.217

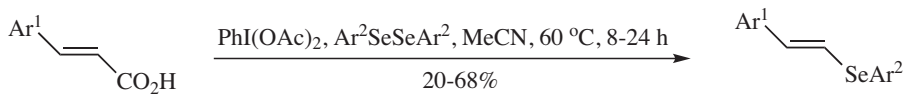


Scheme 3.218



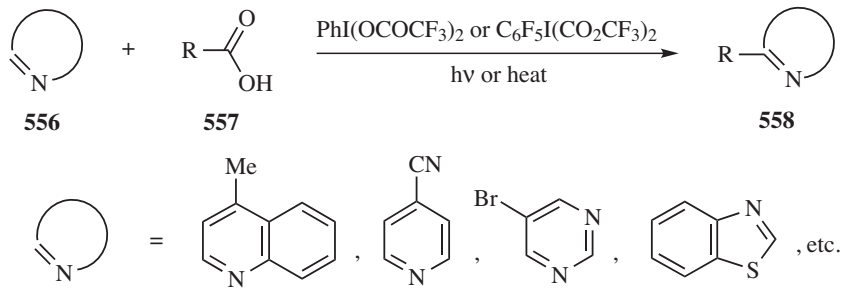
Scheme 3.219

radicals, which can be effectively trapped with various heteroaromatic bases or electron-deficient alkenes [606–611]. In particular, a convenient experimental procedure for radical alkylation of nitrogen heterocycles **556** to products **558** using carboxylic acids **557** in the presence of [bis(trifluoroacetoxy)iodo]benzene or [bis(trifluoroacetoxy)iodo]pentafluorobenzene has been developed (Scheme 3.221) [606, 608]. This reaction has been used for the preparation of C-nucleosides and their analogs [609]. This procedure has been further modified to allow the use of alcohols as the source of alkyl radicals. In this case, alcohols are first converted into the oxalic acid monoalkyl esters **559,** which are used as reagents in the radical alkylation of heteroaromatic bases as exemplified in Scheme 3.221 [607–609].

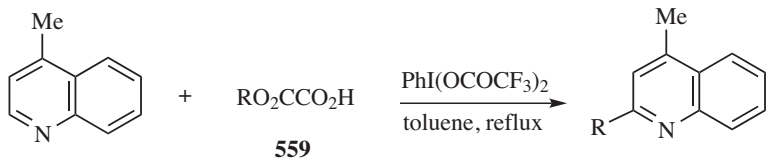


Ar^1 = 3,4-$(OCH_2O)C_6H_3$, 4-$MeOC_6H_4$, 3,4,5-$(MeO)_3C_6H_2$
Ar^2 = Ph or 4-MeC_6H_4

Scheme 3.220



R = 1-adamantyl, cyclohexyl, 2-$PhCH_2CH_2$, $PhOCH_2$, PhC(O), C-nucleosides, etc.



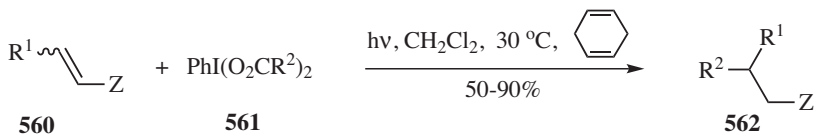
R = 1-adamantyl, cyclohexyl, 1-methylcyclohexyl, (–)-menthyl, etc.

Scheme 3.221

Electron-deficient alkenes can be alkylated under similar conditions. In this procedure, a mixture of alkene **560** and [bis(acyloxy)iodo]arenes **561** [prepared from $PhI(OAc)_2$ and the respective carboxylic acid or monoalkyl esters of oxalic acid] is irradiated with a high-pressure mercury lamp in dichloromethane in the presence of 1,4-cyclohexadiene to give a reductive addition product (**562**) (Scheme 3.222) [610, 611].

Conjugate addition of radicals generated by decarboxylative fragmentation of (diacyloxyiodo)benzene **564** to dehydroamino acid derivatives **563** has been used in the synthesis of diaminopimelic acid analogues **565** (Scheme 3.223) [612].

Several useful synthetic methodologies are based on the generation of the oxygen-centered radicals from carboxylic acids and the (diacetoxyiodo)benzene–iodine system [613–617]. In particular, a direct conversion of 2-substituted benzoic acids **566** into lactones **567** via oxidative cyclization induced by [bis(acyloxy)iodo]arene/iodine has been reported (Scheme 3.224) [613, 614].

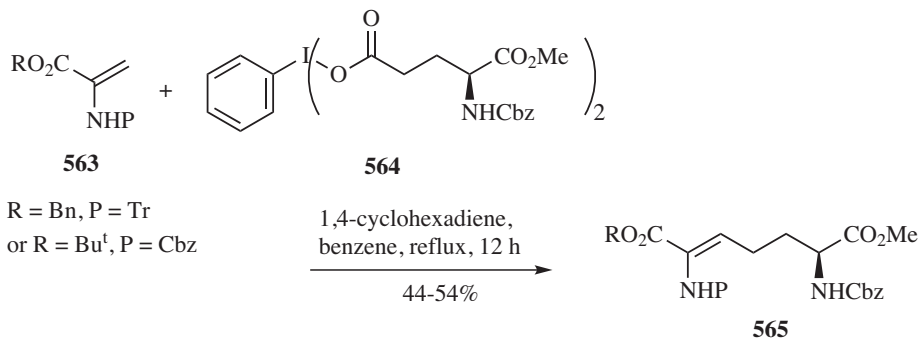


Z = SO_2Ph, SOPh, CO_2Me, P(O)$(OEt)_2$

R^1 = H, Me

R^2 = 1-adamantyl, cycloalkyl, 2-$PhCH_2CH_2$, C-nucleosides, etc.

Scheme 3.222



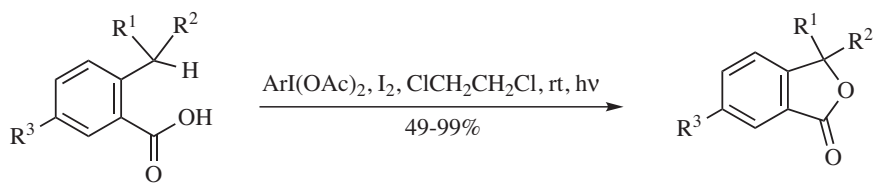
Scheme 3.223

The reaction of carboxylic acids with the $PhI(OAc)_2$–iodine system may result in a decarboxylation leading to the intermediate formation of a carbon-centered radical, which can be further oxidized to a carbocation and trapped by a nucleophile. This process has been utilized in several syntheses [97, 615,616, 617]. In a typical example, the oxidative decarboxylation of uronic acid derivatives **568** in acetonitrile under mild conditions affords acetates **569** in good yields (Scheme 3.225) [615]. A similar oxidative decarboxylation has been be used for the synthesis of 2-substituted pyrrolidines **571** from the cyclic amino acid derivatives **570** [616,617].

Kita and coworkers have developed a simple and reliable method for the direct construction of biologically important aryl lactones **573** from carboxylic acids **572** using a combination of $PhI(OAc)_2$ with NaBr (Scheme 3.226). The mechanism of this reaction includes initial generation of carbonyloxy radical followed by intramolecular benzylic hydrogen abstraction and cyclization [618].

Adamantyl sulfides **576** have been prepared by radical decarboxylation of [bis(1-adamantanecarboxy)iodo]benzene **575** (Ar = Ph) in the presence of disulfides **574** (Scheme 3.227). A study of the reactivity of various [bis(1-adamantanecarboxy)iodo]arenes **575** in this reaction has shown that the introduction of strong electron-withdrawing groups, such as nitro and perfluoro, into the aromatic ring of **575** leads to a significant reduction of the yield of product **576,** which is explained by the lower reactivity of *p*-nitro and perfluorophenyl derivatives **575** in radical reactions due to the increased I—O bond strength in these compounds [619].

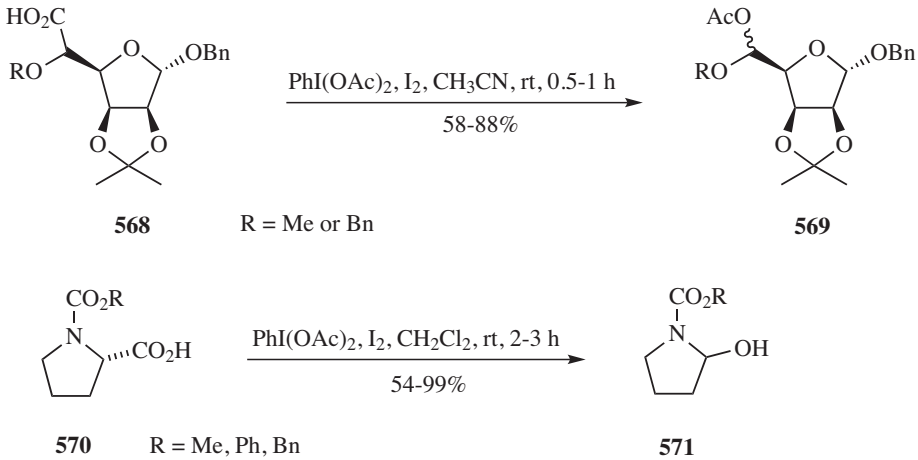
Useful synthetic methodologies are based on the cyclization, rearrangement, or fragmentation of the alkoxy radicals generated in the reaction of alcohols with [bis(acyloxy)iodo]arenes in the presence of iodine under photochemical conditions or in the absence of irradiation. Photolysis of $PhI(OAc)_2$ with cyclic alcohols in the presence of iodine leads to the generation of the respective alkoxy radical, which can undergo various



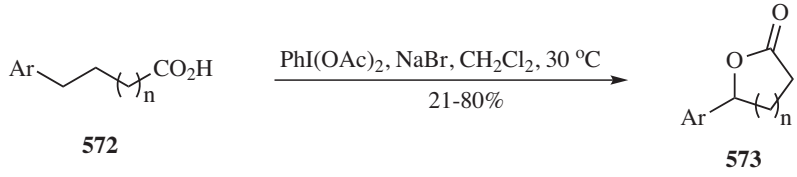
566 R^1 = H, Me; R^2 = Me, Ph; R^3 = H, Pr^i **567**

Ar = Ph, 2-MeC_6H_4, 2-$MeOC_6H_4$, 2-ClC_6H_4

Scheme 3.224



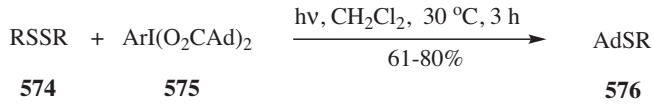
Scheme 3.225



Scheme 3.226

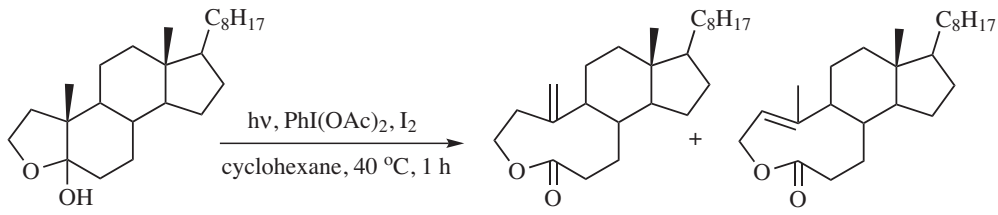
sequential reactions. This methodology has been utilized in several syntheses. Suarez and coworkers applied a sequential alkoxy radical fragmentation for the preparation of highly functionalized macrocycles and some steroidal derivatives [620–625]. For example, photolysis of steroidal hemiacetals, such as **577,** with stoichiometric amounts of $PhI(OAc)_2$ and iodine in the absence of oxygen affords medium-sized lactones in good yield as a result of alkoxy radical fragmentation (Scheme 3.228) [621].

When the reaction of cyclic alcohols **578** is conducted under an oxygen atmosphere, the initially produced C-radical traps a molecule of O_2, yielding peroxide **579** according to Scheme 3.229 [622]. This and similar sequential alkoxy radical fragmentations can be applied to the preparation of various synthetically interesting medium-sized ketones and lactones.



R = 4-$MeOC_6H_4$, 4-MeC_6H_4, Ph, 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$, Bu, *n*-$C_{12}H_{25}$
Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4, Ph, 4-ClC_6H_4, 4-$NO_2C_6H_4$, C_6F_5

Scheme 3.227



577

Scheme 3.228

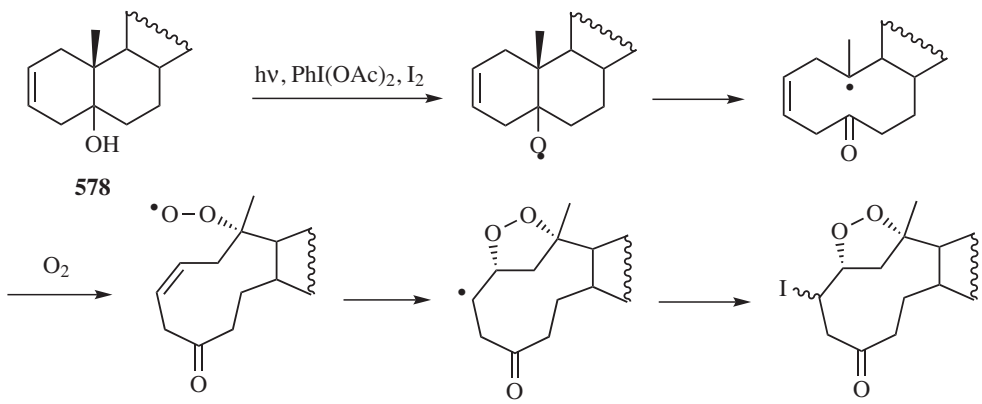
Treatment of bicyclic dienol **580** with $PhI(OAc)_2/I_2$ in degassed cyclohexane under irradiation and reflux results in a cascade radical fragmentation–transannulation–cyclization sequence leading to ketone **581** in high yield (Scheme 3.230) [626].

Additional examples of this methodology include the synthesis of 1,1-difluoro-1-iodo alditols **583** [627], 2-azido-1,2-dideoxy-1-iodo-alditols **585** [628, 629] and chiral vinyl sulfones **587** [630] by fragmentation of carbohydrate anomeric alkoxy radicals generated from the respective carbohydrates **582, 584** and **586** (Scheme 3.231).

The methodology, based on generation of the alkoxy radicals, has also been used for the oxidative cyclization of various alcohols. For example, the irradiation of alcohols **588** with (diacetoxyiodo)benzene and iodine affords the chroman derivatives **589** in moderate to good yields (Scheme 3.232) [631].

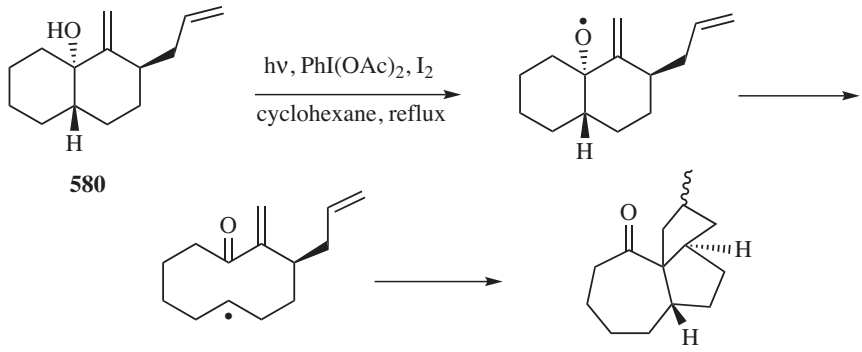
Photolysis of $PhI(OAc)_2$ with tertiary allylic alcohols **590** in the presence of iodine affords α-iodoepoxides **591** (50–72% yield) as a result of alkoxy radical rearrangement (Scheme 3.233) [632].

Fragmentation of anomeric alkoxy radicals, generated from appropriate carbohydrates by a similar method, provides a convenient entry into useful chiral synthetic intermediates [633, 634]. Suarez and coworkers have reported the $PhI(OAc)_2$-initiated radical fragmentation of protected furanoses **592** leading to four-carbon chiral building blocks of the erythrose type **593** in good yield (Scheme 3.234) [633]. A similar fragmentation of pyranose derivatives **594** to the product **595** has also been reported. Interestingly, these reactions proceed smoothly at room temperature and do not require irradiation [634].



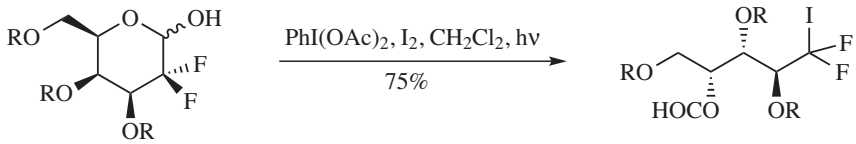
578 **579**

Scheme 3.229

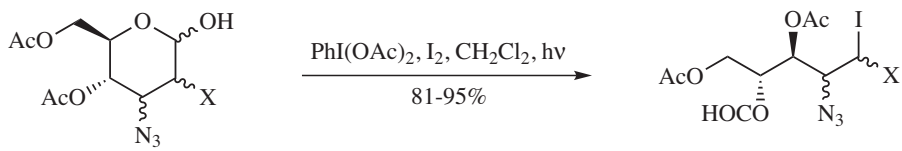


580 **581**

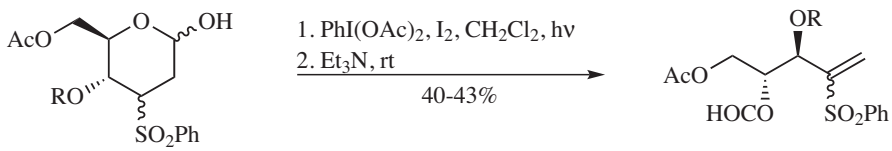
Scheme 3.230



582 R = OAc or OMe **583**

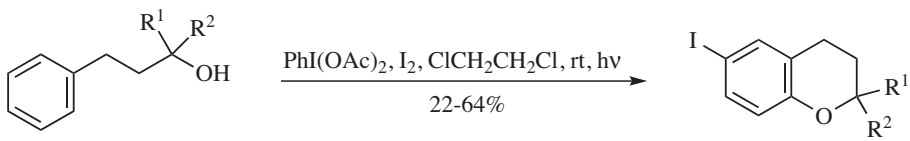


584 X = H, F, Cl, Br, I **585**



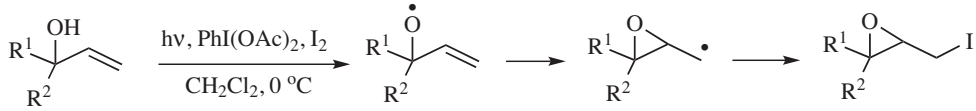
586 R = Ac or β-D-Gal **587**

Scheme 3.231



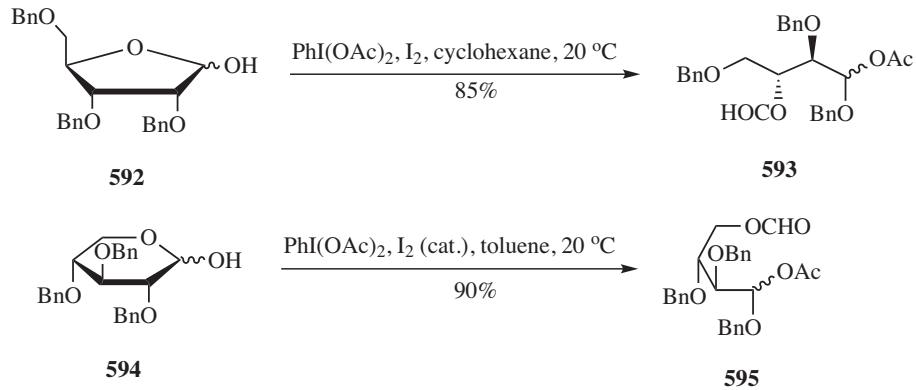
588 R^1 = H, Me, Bu, *n*-$C_{13}H_{27}$, Ph; R^2 = H or Me **589**

Scheme 3.232



590 R^1 = Et, *n*-C_5H_{11}; R^2 = Me, Et; or $R^1 + R^2 = (CH_2)_n$, n = 4, 5, 6, 7 **591**

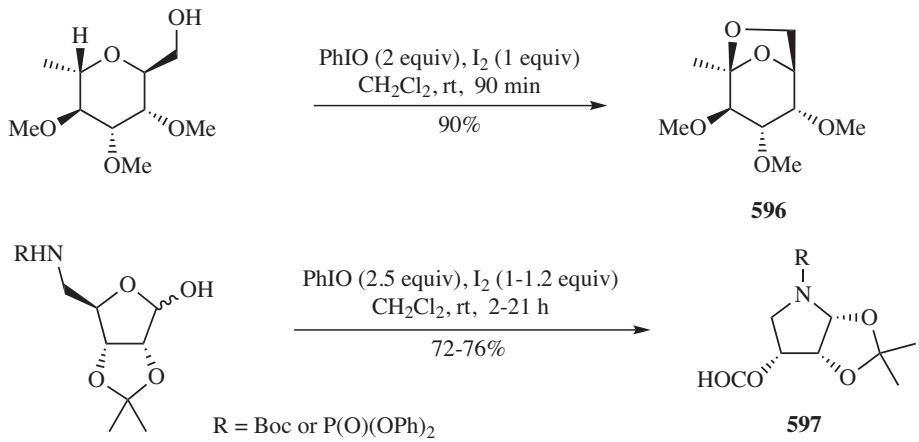
Scheme 3.233



592 **593** **594** **595**

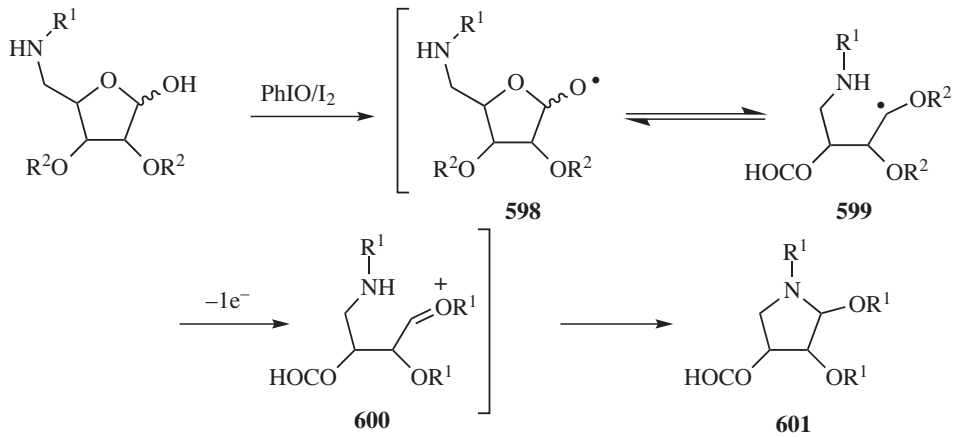
Scheme 3.234

Iodosylbenzene can also react with alcohols in the presence of iodine to form the respective alkoxy radicals, presumably through an alkyl hypoiodite intermediate [635]. Suarez and coworkers have developed a valuable synthetic methodology based on a sequential fragmentation of alkoxy radicals generated from alcohols, iodosylbenzene and iodine. This methodology has been applied in the synthesis of carbohydrate derivatives **596** and imino sugars **597** (Scheme 3.235) [636, 637].



596 **597**

Scheme 3.235



R^1 = Boc, Cbz, $P(O)(OPh)_2$; R^2 = protective group

Scheme 3.236

The proposed mechanism for this reaction involves a β-fragmentation of the initially formed alkoxy radical **598,** leading to a carbon-centered radical **599,** which is further oxidized by an excess of the reagent to the oxycarbenium ion **600** (Scheme 3.236). Intramolecular nucleophilic cyclization of **600** affords the final sugar derivative **601** [636].

A similar methodology has been applied in the synthesis of various useful chiral synthetic intermediates. Representative examples include the syntheses of alduronic acid lactone **603** [637, 638], chiral dispiroacetals **605** and **606** [639] and α-iodoalkyl ester **608** from respective carbohydrate derivatives **602, 604** and **607** (Scheme 3.237) [640].

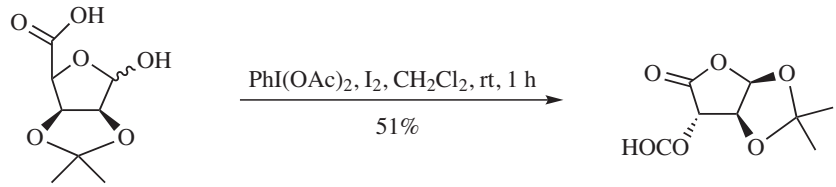
The oxidative cyclization of steroidal bromohydrins **609** selectively affords products **610** in high yields (Scheme 3.238) [641]. This reaction can be promoted by either photolysis or ultrasonic irradiation. The yields of products **610** are significantly better under the ultrasound-assisted conditions.

A similar oxidative cyclization initiated by the irradiation of a substrate in the presence of (diacetoxyiodo)benzene and iodine can be used for the deprotection of benzyl ethers (e.g., **611**) situated next to the hydroxyl in the α, β, or γ-position [642]. Depending on the substrate, the corresponding cyclic ethers of diols (such as **612**) can be isolated (Scheme 3.239).

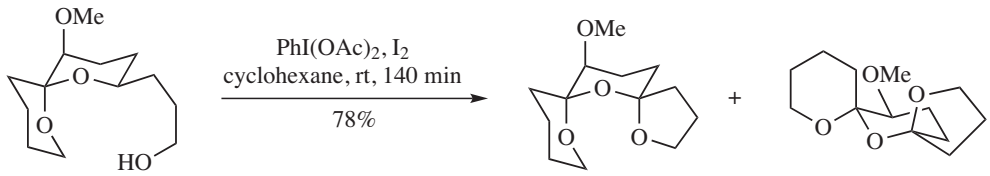
The intramolecular hydrogen abstraction reactions promoted by alkoxy radicals in carbohydrates are particularly useful for the stereoselective synthesis of various polycyclic oxygen-containing ring systems [643–647]. This reaction can be illustrated by the intramolecular 1,8-hydrogen abstraction between glucopyranose units in disaccharide **613** promoted by alkoxy radicals and leading to the 1,3,5-trioxocane derivative **614** (Scheme 3.240) [644].

Boto and Hernandez have reported a short, efficient synthesis of chiral furyl carbinols from carbohydrates, such as **615,** based on the alkoxy radicals fragmentation reaction leading to the intermediate product **616** (Scheme 3.241) [648]. The same authors have developed an efficient procedure for the selective removal from carbohydrate substrates of methoxy protecting groups next to hydroxy groups by treatment with the $PhI(OAc)_2$–I_2 system [649].

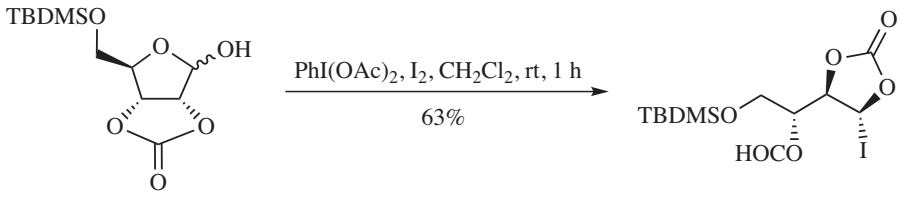
A mild and highly efficient one-pot synthesis of aryl glycines **618** from readily available serine derivatives **617** has been reported (Scheme 3.242) [650]. This method is based on the β-fragmentation of a primary alkoxy radical, generated on treatment of the serine derivative with $PhI(OAc)_2$–I_2, immediately followed by



602 **603**

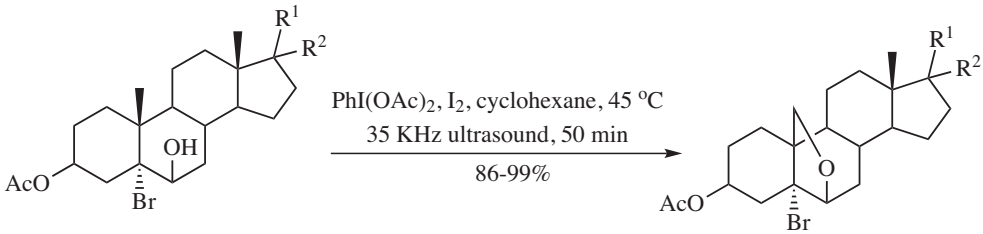


604 **605** **606**



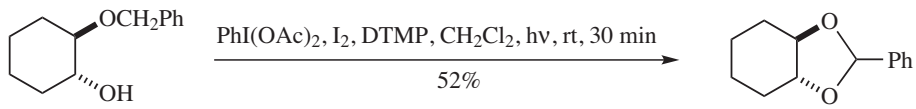
607 **608**

Scheme 3.237



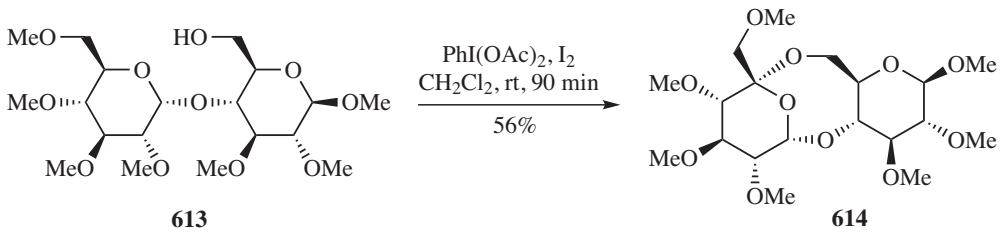
609 $R^1 = n\text{-}C_8H_{17}$, COMe, $COCH_2OAc$; $R^2 = H$ or $R^1 + R^2 = O$ **610**

Scheme 3.238



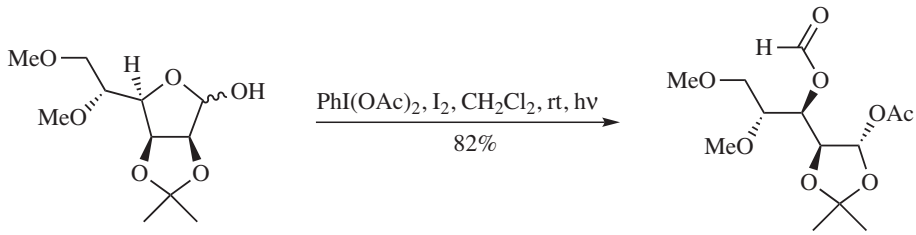
611 DTMP = 2,6-di-*tert*-butyl-4-methylpyridine **612**

Scheme 3.239



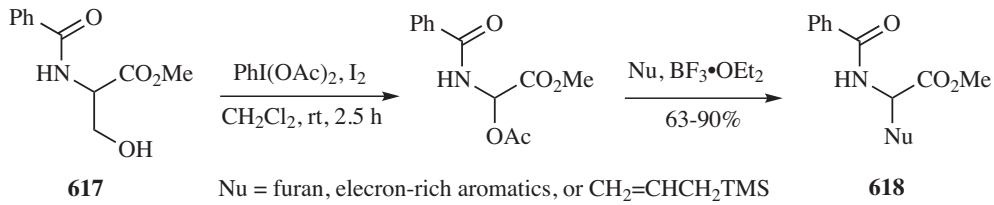
613 **614**

Scheme 3.240



615 **616**

Scheme 3.241

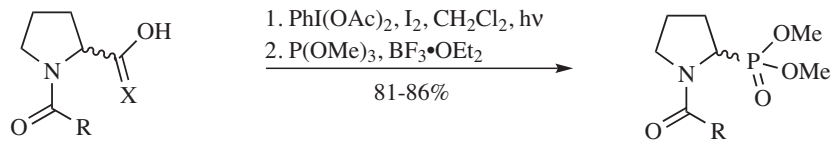


617 Nu = furan, elecron-rich aromatics, or CH_2=$CHCH_2TMS$ **618**

Scheme 3.242

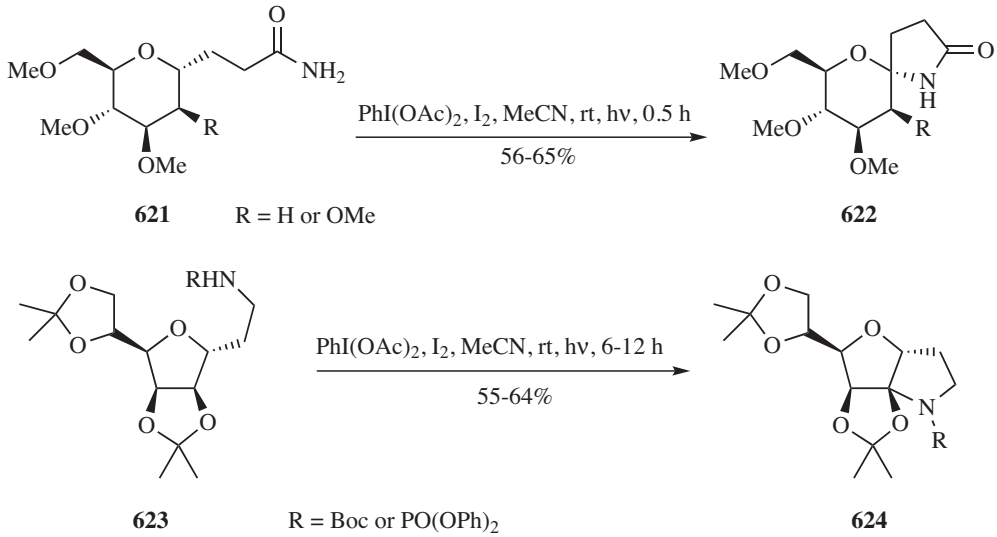
the addition of the nucleophile Nu. This procedure is also applicable to the synthesis of other uncommon amino acids [650].

The one-pot radical fragmentation–phosphorylation reaction of α-amino acids or β-amino alcohols (e.g., **619**) affords α-amino phosphonates **620** in good yields (Scheme 3.243). This reaction has been applied to the synthesis of biologically active phosphonates [651].



619 R = Ph or OMe; X = 2H or O **620**

Scheme 3.243

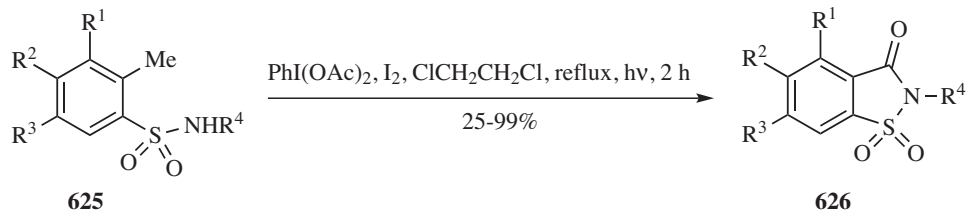


Scheme 3.244

Useful synthetic methodologies are based on the cyclization or rearrangement of the nitrogen-centered radicals generated in the reaction of the appropriate amides with (diacetoxyiodo)benzene in the presence of iodine [652–655]. Specific examples are illustrated by the synthesis of bicyclic spirolactams **622** from amides **621** [653] and preparation of the oxa-azabicyclic systems (e.g., **624**) by the intramolecular hydrogen atom transfer reaction promoted by carbamoyl and phosphoramidyl radicals generated from the appropriately substituted carbohydrates **623** (Scheme 3.244) [654].

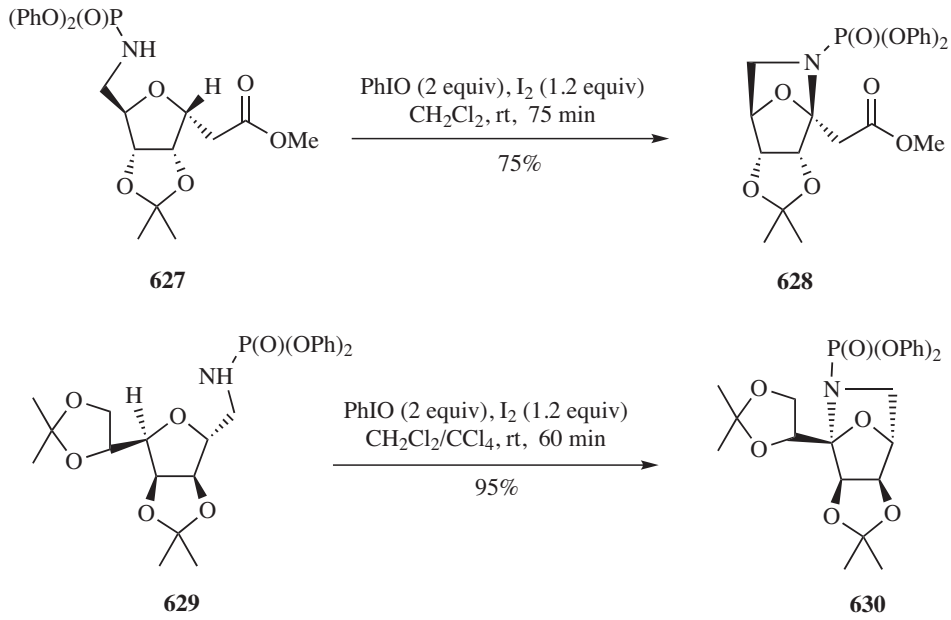
Togo, Yokoyama and coworkers have developed a useful synthetic procedure for the preparation of nitrogen heterocycles based on the N-radical cyclization onto an aromatic ring [247, 656–658]. For example, various *N*-alkylsaccharins **626** can be conveniently prepared in moderate to good yields by the reaction of arenesulfonamides **625** with (diacetoxyiodo)benzene in the presence of iodine under irradiation with a tungsten lamp (Scheme 3.245) [656]. A similar procedure has been applied to the synthesis of 1,2,3,4-tetrahydroquinoline derivatives [247, 657] and 3,4-dihydro-2,1-benzothiazine 2,2-dioxides [658].

The methodology based on the generation of N-centered radicals from the reaction of amides with iodosylbenzene and iodine has been utilized in the synthesis of homochiral 7-oxa-2-azabicyclo[2.2.1]heptane



R^1, R^2 = H or Me; R^3 = H, Me, Br, Bu^t, $CONEt_2$, NO_2, SO_2CH_3; R^4 = H, Me, Et, Pr, Bu, CH_2Ph

Scheme 3.245



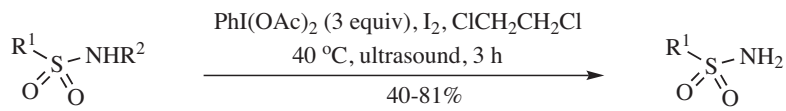
Scheme 3.246

derivatives **628** and **630** from the respective phosphoramidate derivatives of carbohydrates **627** and **629** (Scheme 3.246) [659].

Under conditions of ultrasonic irradiation in the presence of (diacetoxyiodo)benzene and iodine, *N*-alkylsulfonamides **631** are dealkylated to afford sulfonamides **632** in moderate to good yields (Scheme 3.247) [660].

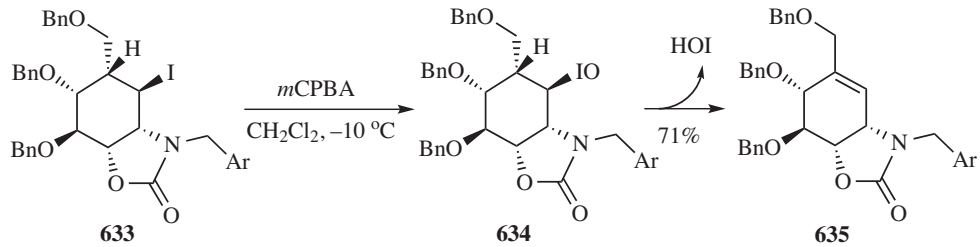
3.1.19 Reactions via Alkyliodine(III) Intermediates

Alkyliodides can be readily oxidized with various oxidizing agents to afford either products of elimination or the products of oxidatively assisted nucleophilic substitution of iodine. Both pathways involve alkyliodine(III) derivatives as reactive intermediates. The elimination pathway generally occurs in reactions of alkyliodides with peracids in a non-nucleophilic solvent, such as dichloromethane [661–663]. Reich and Peake first demonstrated that the elimination proceeds with *syn*-stereochemistry and also proposed iodosylalkanes as reactive intermediates in this reaction [661]. The Reich iodosyl *syn*-elimination has been utilized in several syntheses as a very mild and selective elimination method alternative to the standard selenoxide and sulfoxide protocols.



631 R^1 = alkyl, aryl; R^2 = Et, Pr, Bu, etc. **632**

Scheme 3.247



Scheme 3.248

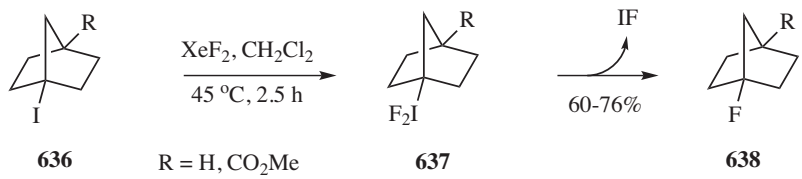
The iodosyl elimination has been used in the preparation of unsaturated oxazolidinone **635** (Scheme 3.248), the key intermediate in the synthesis of valienamine [662]. This reaction proceeds via oxidation of iodide **633** to the intermediate iodosyl compound **634,** which spontaneously eliminates HOI to afford product **635.** The Reich iodosyl *syn*-elimination has also been used for the preparation of intermediate steroidal units of cephalostatin 7 [663].

The second pathway of oxidative deiodination of alkyliodides involves nucleophilic substitution of the oxidized iodine moiety. In fact, functionalities containing hypervalent iodine (e.g., $-IX_2$) belong to the best leaving groups [664]. For example, the normally unreactive 1-iodonorbornane can be readily transformed into 1-bromonorbornane by reaction with bromine via the intermediate $RIBr_2$ [664]. Likewise, the bridgehead 1-fluoronorbornanes **638** have been prepared by the analogous fluorodeiodination of 1-iodonorbornanes **636** by reaction with xenon difluoride (Scheme 3.249) [665]. The mechanism of this reaction involves initial formation of unstable difluoroiodides **637** and their subsequent decomposition with elimination of the IF fragment.

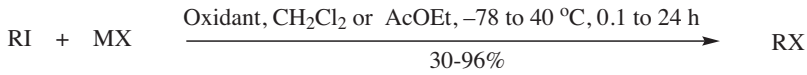
Even extremely weak nucleophiles, such as perchlorate and triflate anions, can participate in the oxidatively assisted nucleophilic substitution of iodine [666–668]. The oxidation of alkyliodides in the presence of lithium perchlorate or appropriate tetrabutylammonium salts in non-nucleophilic solvents affords the respective alkyl perchlorates or alkylsulfonates **639** as principal products (Scheme 3.250) [669].

The oxidatively assisted nucleophilic substitution of iodine with perchlorate anion in primary and secondary substrates proceeds according to an S_N2 mechanism as indicated by the stereochemistry of this reaction in the polycyclic substrates **640** leading to products **641** with inverted configuration (Scheme 3.251) [668].

Treatment of alkyliodides with peracids in the presence of water results in oxidatively assisted hydrolysis and the formation of alcohols [661]. This reaction can be used as a synthetic method for the mild hydrolysis of iodides; for example, iodide **642** undergoes facile stereoselective hydrolysis to the protected amino alcohol **643** under neutral conditions upon exposure to ten equivalents of buffered peroxytrifluoroacetic acid (Scheme 3.252) [670]. The oxidatively assisted hydrolysis of iodide **642** results in a complete inversion of configuration, which is consistent with the S_N2 mechanism of substitution in the hypervalent iodine intermediate [670].



Scheme 3.249

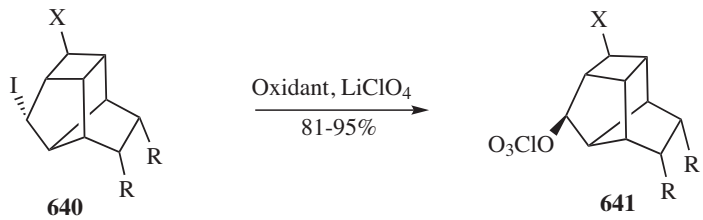


RI = MeI, $C_6H_{13}I$, Pr^iI, CH_2I_2, $I(CH_2)_6I$, $PhCOCH_2I$, ICH_2CO_2H, ICH_2CO_2Me, *cyclo*-$C_6H_{11}I$ **639**

MX = $LiOClO_3$, Bu_4NOClO_3, Bu_4NOTf, Bu_4NOTs, Bu_4NOSO_2Me, Bu_4NOSO_2F

Oxidant = Cl_2, Br_2, H_5IO_6, NO_2BF_4, *m*CPBA, $PhI(OCOCF_3)_2$, PhI(OH)OTs

Scheme 3.250



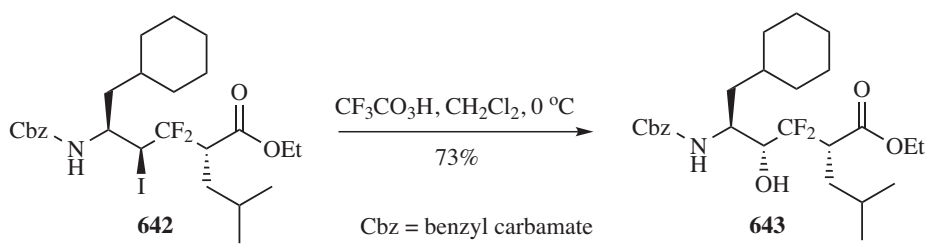
X = Br, 2,4-$(NO_2)_2C_6H_3S$, 2,4-$(NO_2)_2C_6H_3SO_2$, 2,4-$(NO_2)_2C_6H_3SO$
R = Me, CO_2Me
Oxidant = Cl_2, NO_2BF_4, $PhI(OCOCF_3)_2$

Scheme 3.251

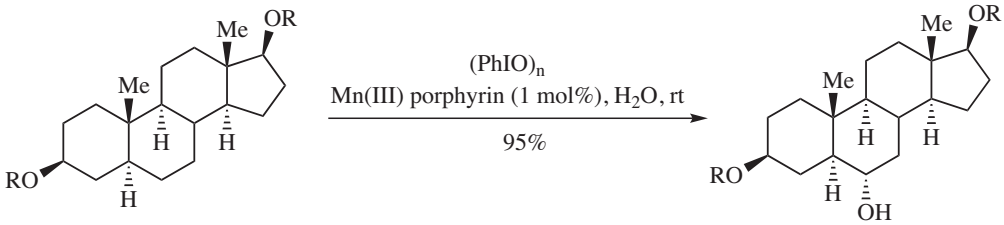
3.1.20 Transition Metal Catalyzed Oxidations

Transition metals have a strong catalytic effect on oxidations with hypervalent iodine reagents. In 1979 Groves and coworkers found that iodosylbenzene is the most efficient source of oxygen in the oxygenation of hydrocarbons in the presence of iron(III) porphyrin complexes [671] and since then iodosylarenes and other hypervalent iodine reagents have been widely used as stoichiometric oxidants in reactions mimicking natural oxidations performed by the heme-containing cytochrome P-450 class of enzymes [672–686].

Iodosylbenzene has been used as an effective oxidant in hydrocarbon hydroxylation catalyzed by metalloporphyrins [687–696]. In particular, various iron(III) and manganese(III) porphyrins can be used as catalysts in hydroxylations of cyclohexane, cyclohexene, adamantane and aromatic hydrocarbons [687, 688, 692]. Breslow and coworkers have reported regioselective hydroxylations of several steroidal derivatives catalyzed by metalloporphyrins [689–691]. In a specific example androstanediol derivative **644** was



Scheme 3.252



644 R = protective group

Scheme 3.253

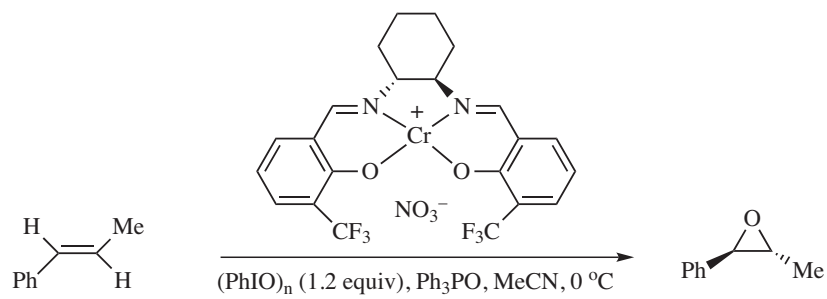
hydroxylated at the 6α carbon with complete positional selectivity in the presence of a manganese(III) porphyrin catalyst (Scheme 3.253) [689]. Presumably, this selective hydroxylation is directed by the geometry of the catalyst–substrate complex, as in the enzyme.

Transition metal complexes can effectively catalyze the epoxidation of alkenes using iodosylarenes as the source of oxygen atom [266, 697–701]. In particular, a highly enantioselective alkene epoxidation catalyzed by chiral non-racemic chromium salen complexes has been reported [701–703]. Iodosylbenzene was found to be the only applicable oxidant in these reactions and the highest ee (92%) was achieved in the epoxidation of (*E*)-β-methylstyrene **645** mediated by a chromium salen complex in stoichiometric mode and in the presence of Ph_3PO as a donor ligand (Scheme 3.254) [701]. Carrying out this reaction in catalytic mode (5–10 mol% of chromium complex), or the use of other substituted salen ligands, results in a slightly lower enantioselectivity.

Epoxidation of alkenes with iodosylbenzene can be effectively catalyzed by the analogous salen or chiral Schiff base complexes of manganese(III), ruthenium(II), or ruthenium(III). For example, the oxidation of indene with iodosylbenzene in the presence of (*R,S*)-Mn-salen complexes as catalysts affords the respective (1*S*,2*R*)-epoxyindane in good yield with 91–96% ee [704]. Additional examples include epoxidation of alkenes with iodosylbenzene catalyzed by various metalloporphyrins [705–709], corrole metal complexes, ruthenium-pyridinedicarboxylate complexes of terpyridine and chiral bis(oxazolinyl)pyridine [710, 711].

Iodosylbenzene in the presence of transition metal catalysts can effectively oxidize alcohols to carbonyl compounds [712–714] and organic sulfides to sulfoxides [715–717].

Iodosylarenes other than iodosylbenzene have also been used in the transition metal catalyzed oxidation reactions. The soluble *o*-(*tert*-butylsulfonyl)iodosylbenzene (Section 2.1.4) can serve as an alternative to iodosylbenzene in (porphyrin)manganese(III)-catalyzed alkene epoxidation reactions [718]. A convenient recyclable reagent, *m*-iodosylbenzoic acid, can selectively oxidize primary and secondary alcohols to the



645 92% ee

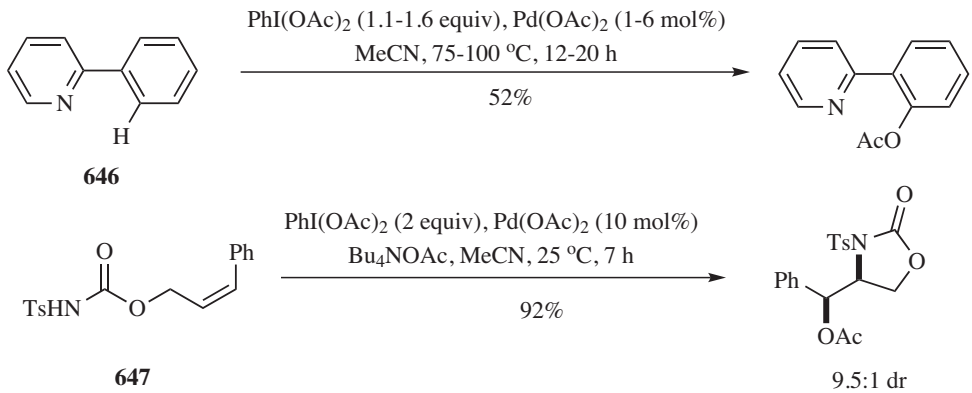
Scheme 3.254

respective carbonyl compounds in the presence of $RuCl_3$ (0.5 mol%) at room temperature in aqueous acetonitrile [719]. Oligomeric iodosylbenzene sulfate can serve as an effective terminal oxidant in the binuclear iron(III) phthalocyanine(μ-oxodimer)-catalyzed oxygenation of aromatic hydrocarbons [720,721].

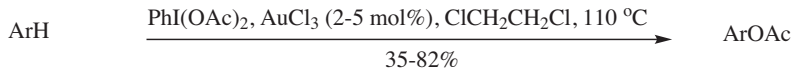
It is generally agreed that the intermediate high valent metal oxo-complexes are responsible for the oxygen transfer from iodosylarenes to the organic substrate. However, the details of the initial interaction of iodine(III) species with metal complex are still unclear. In particular, it has been shown that iodosylbenzene reacts with metalloporphyrins with the formation of unstable adducts, which can serve as the actual oxidants in catalytic oxygenations and thus explain the unusual reactivity of hypervalent iodine reagents as terminal oxidants [717, 722–725].

Various oxidations with [bis(acyloxy)iodo]arenes are also effectively catalyzed by transition metal salts and complexes [726]. (Diacetoxyiodo)benzene is occasionally used instead of iodosylbenzene as the terminal oxidant in biomimetic oxygenations catalyzed by metalloporphyrins and other transition metal complexes [727–729]. Primary and secondary alcohols can be selectively oxidized to the corresponding carbonyl compounds by $PhI(OAc)_2$ in the presence of transition metal catalysts, such as $RuCl_3$ [730–732], Ru(Pybox)(Pydic) complex [733], polymer-micelle incarcerated ruthenium catalysts [734], chiral-Mn(salen)-complexes [735,736], Mn(TPP)CN/Im catalytic system [737] and (salen)Cr(III) complexes [738]. The epoxidation of alkenes, such as stilbenes, indene and 1-methylcyclohexene, using (diacetoxyiodo)benzene in the presence of chiral binaphthyl ruthenium(III) catalysts (5 mol%) has also been reported; however, the enantioselectivity of this reaction was low (4% ee) [739].

The mechanisms and applications of palladium-catalyzed reactions of (diacetoxyiodo)benzene and other hypervalent iodine reagents in synthetically useful organic transformations have been reviewed by Deprez and Sanford [740]. Particularly useful are the Pd-catalyzed oxidation reactions, including the oxidative functionalization of C—H bonds and the 1,2-aminooxygenation of olefinic substrates [740–756]. Representative examples of these catalytic oxidations are illustrated by the selective acetoxylation of C—H bonds adjacent to coordinating functional groups (e.g., pyridine in substrate **646**) [741] and by the $Pd(OAc)_2$-catalyzed intramolecular aminoacetoxylation in the reaction of γ-aminoolefins (e.g., cinnamyl alcohol derived tosyl carbamate **647**) with $PhI(OAc)_2$ (Scheme 3.255) [742]. A key mechanistic step in these catalytic transformations is the hypervalent iodine-promoted oxidation of Pd(II) to the Pd(IV) species, as proved by the isolation and X-ray structural identification of stable Pd(IV) complexes prepared by the reaction of $PhI(O_2CPh)_2$ with Pd(II) complexes containing chelating 2-phenylpyridine ligands [753]. Several examples of Pd-catalyzed chlorinations of organic substrates using (dichloroiodo)benzene have also been reported [754,755].



Scheme 3.255



648 ArH = 1,3,5-Me_3C_6H; 1,2,3,4,5-Me_5C_6H; 1,2,4,5-$Me_5C_6H_2$; $MeOC_6H_5$; 1,4-$(MeO)_2C_6H_4$; 2-Br,1,3-MeC_6H_3; 1-F,4-$MeOC_6H_4$, etc.

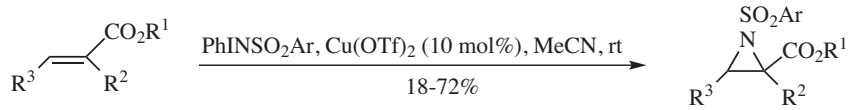
Scheme 3.256

Hypervalent iodine oxidations of organic substrates can be effectively catalyzed by salts and complexes of gold [757–760]. For example, direct acetoxylation of electron-rich aromatic compounds **648** can be performed with (diacetoxyiodo)benzene in the presence of catalytic amounts of $AuCl_3$ (Scheme 3.256) [757].

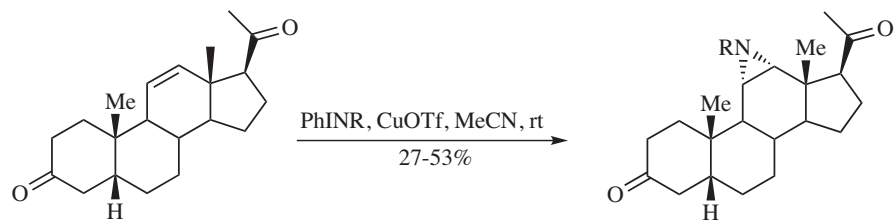
3.1.21 Transition Metal Catalyzed Aziridinations and Amidations

Imidoiodanes and especially *N*-tosyliminoiodanes, ArINTs (Section 2.1.12.4), have found broad synthetic application as useful nitrene precursors in transition metal catalyzed aziridination of alkenes and amidation of various organic substrates [584, 761]. Mansuy and coworkers in 1984 first reported the aziridination of alkenes with tosyliminoiodane PhINTs in the presence of iron- or manganese-porphyrins [762]. This reaction has a mechanism similar to the metal-catalyzed oxygen atom transfer reactions of iodosylbenzene (Section 3.1.20) and involves a metal–nitrene complex as the intermediate.

Significant recent interest in the transition metal catalyzed reactions of imidoiodanes was initiated in the 1990s by the pioneering works of Evans [586, 763, 764] and Jacobsen [765, 766] on the asymmetric aziridination of olefins using copper catalysts (2–10 mol%) with chiral dinitrogen ligands and PhINTs as the nitrene precursor. Since these initial publications, research activity in this area has surged and the copper-catalyzed aziridination of alkenes has been utilized in numerous syntheses. For example, Dodd and coworkers applied the Evans aziridination procedure to 2-substituted acrylates and cinnamates **649** [767] and to steroids **650** (Scheme 3.257) [768].

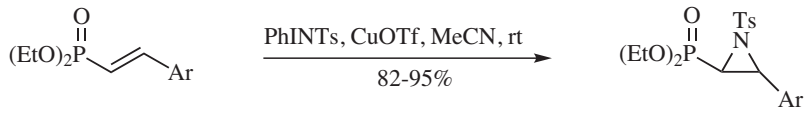


649 R^1 = Me, Et, Bu^t; R^2 and R^3 = H, Me, Ph
Ar = 4-MeC_6H_4, 4-$NO_2C_6H_4$



650 R = Ts, Ns, $Me_3SiCH_2CH_2SO_2$

Scheme 3.257



Ar = Ph, 4-ClC_6H_4, 1-naphthyl, 2-naphthyl

651

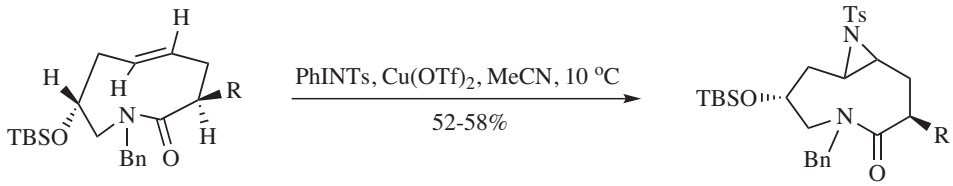
Scheme 3.258

The copper-catalyzed aziridination of the appropriate olefinic substrates has been employed in the preparation of various 2-acylaziridines [769, 770] and aziridinylphosphonates **651** (Scheme 3.258) [771].

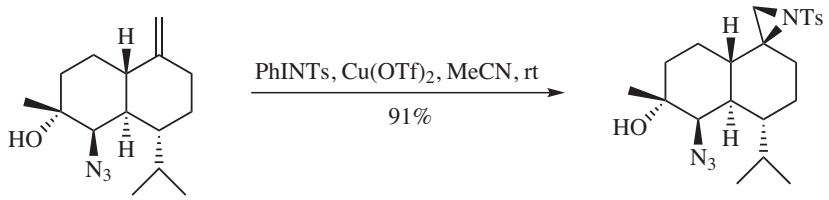
A similar catalytic aziridination has also been applied for the functionalization of the optically active azoninones **652** [772], in the preparation of a key intermediate **653** in the total synthesis of kalihinane diterpenoids [773], in the synthesis of α-methylserinal derivatives **654** (Scheme 3.259) [774], in the preparation of 2,4-disubstituted *N*-tosylpyrrolidines [775] and in the synthesis of nosylaziridines [776].

Particularly important are enantioselective aziridinations of alkenes using PhINTs and copper catalysts with chiral dinitrogen ligands [777–781]. In a representative example, the PhINTs-promoted asymmetric aziridination of alkene **655** affords chiral aziridine **656** with excellent enantioselectivity (Scheme 3.260) [777].

Various chiral ligands or counter-anions, or complexes of other than copper transition metals, have been evaluated in these reactions. High enantioselectivity in the copper-catalyzed aziridination of styrene derivatives was observed in the presence of chiral biaryldiamines [782], chiral C_2-symmetric bisferrocenyldiamines



652 R = Ph, Cl



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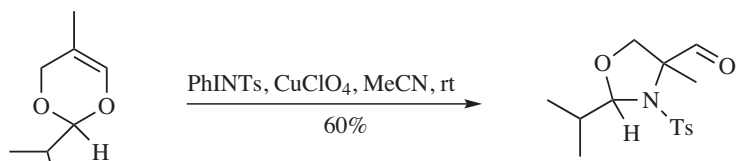
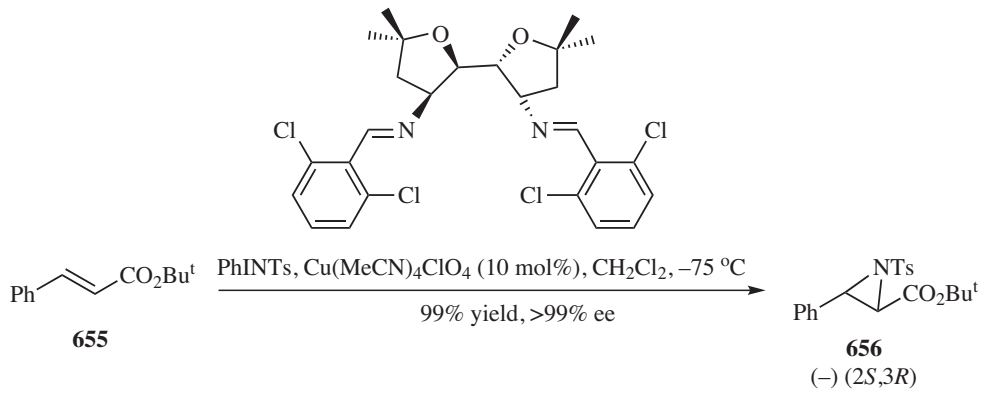


654

Scheme 3.259



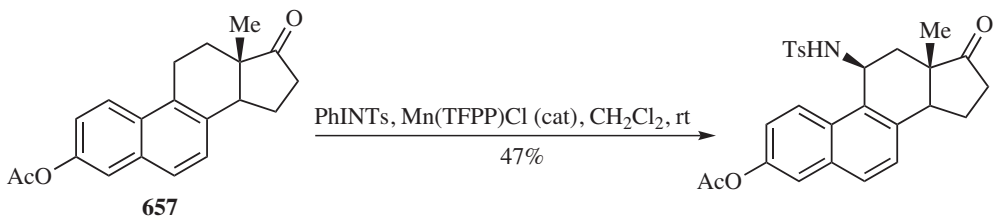
Scheme 3.260

[783], chiral borate counter-anion [784], a phosphoramidite derived from (–)-(a*R*)-[1,1′-binaphthalene]-8,8′-diol [785], bis(oxazolines) on zeolite Y [786, 787], chiral tartrate-derived bis-oxazoline ligands [788] and C_2-symmetric bis(aziridine) ligands [789]. The highly enantioselective catalytic aziridination of styrenes was realized by using (salen)manganese(III) complexes [790], manganese and iron tetramethylchiroporphyrins [791] and the chiral rhodium(II) complexes [792–794]. An enhanced reactivity of PhINTs in the olefin aziridination reaction under achiral conditions was observed in the presence of the copper(II) complexes of pyridyl-appended diazacycloalkanes [795, 796], poly(pyrazolyl)borate–copper complexes [797], the copper(II) complexes of 1,4,7-triisopropyl-1,4,7-triazacyclononane [798], a Cu(I) complex of ferrocenyldiimine [799], bis(tosyl)imidoruthenium(VI) porphyrin complexes [800] and methyltrioxorhenium [801].

Mechanistic studies of copper-catalyzed aziridinations have demonstrated that copper nitrene species are the key intermediates in this reaction [802–804].

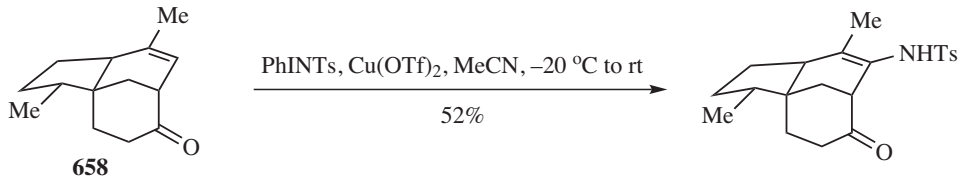
N-Tosyliminoiodanes, ArINTs, have found synthetic application as useful nitrene precursors in transition metal catalyzed amidation of saturated C—H bonds in various organic substrates. Breslow and coworkers have developed the regioselective amidation of steroidal derivatives catalyzed by metalloporphyrins [690, 691]. Specifically, the aromatic steroid equilenin acetate **657** undergoes regioselective and stereoselective amidation catalyzed by a manganese porphyrin using PhINTs as the nitrene donor (Scheme 3.261) [690].

Overman and Tomasi applied the copper-catalyzed amidation of compound **658** (Scheme 3.262) in the key step of the enantioselective total synthesis of the natural tetracyclic spermidine alkaloid (–)-hispidospermidin [805].



Mn(TFPP)Cl = chloro[5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato] manganese(III)

Scheme 3.261



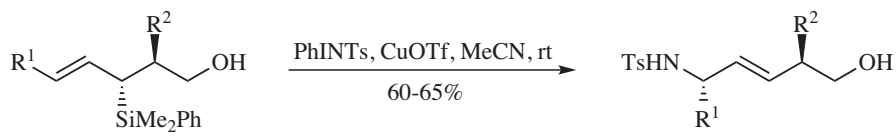
Scheme 3.262

Allylic silanes can be converted into allylic tosylamides by the reaction with PhINTs in the presence of copper salts. In particular, the copper(I)-catalyzed enantioselective amidation of the chiral (*E*)-crotylsilanes **659** (Scheme 3.263) has been used in the asymmetric synthesis of (*E*)-olefin dipeptide isosteres [806].

The amidation of saturated C—H bonds can be effectively catalyzed by ruthenium or manganese complexes. Unfunctionalized hydrocarbons, such as adamantane, cyclohexene, ethylbenzene, cumene, indane, tetralin, diphenylmethane and others, are selectively amidated with PhINTs in the presence of ruthenium or manganese porphyrins or the ruthenium cyclic amine complexes to afford N-substituted sulfonamides in 80–93% yields with high selectivity [807]. The enantioselective amidation of a C—H bond can be catalyzed by chiral (salen)manganese(III) complexes (e.g., **660**) [808], or by chiral ruthenium(II) and manganese(III) porphyrins (Scheme 3.264) [809].

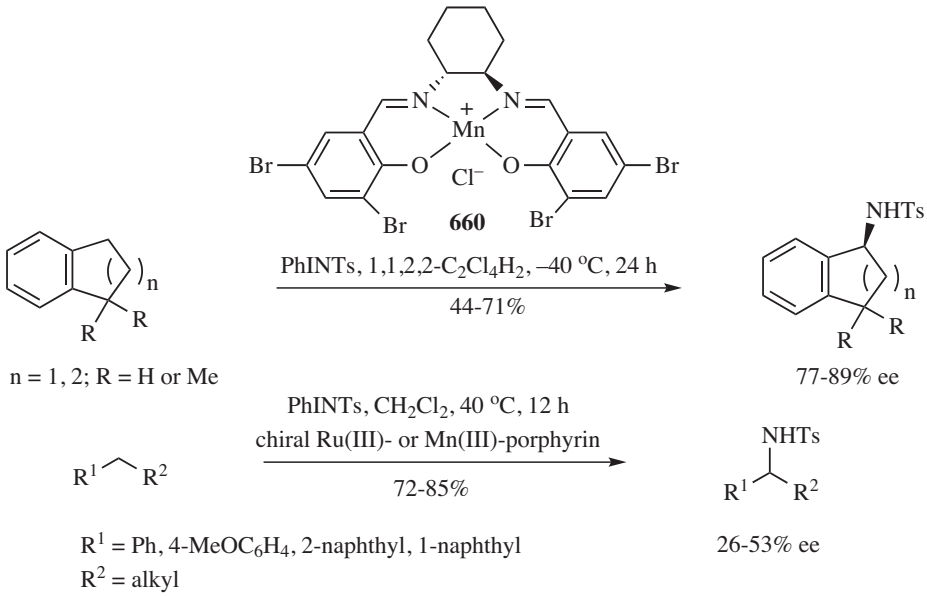
The aziridination and amidation reactions of imidoiodanes can be efficiently catalyzed by Rh(II) complexes [810–815]. Dirhodium(II) tetrakis[*N*-tetrafluorophthaloyl-(*S*)-*tert*-leucinate], Rh_2(*S*-TFPTTL)$_4$, has been found to be an exceptionally efficient catalyst for enantioselective aminations of silyl enol ethers **661** with imidoiodane **662** to afford α-amido ketones **663** in high yields and with enantioselectivities of up to 95% ee (Scheme 3.265). The effectiveness of this catalytic protocol has been demonstrated by an asymmetric formal synthesis of (–)-metazocine [810]. This catalyst has also been used for the asymmetric synthesis of phenylglycine derivatives by enantioselective amidation of silylketene acetals with PhINTs [811].

Additional examples of C—H amidations using PhINTs as the nitrene precursor are represented by the following publications: the highly efficient Ru(II) porphyrin catalyzed C—H bond amidation of aldehydes [816,817], aromatic C—H amidation mediated by a diiron complex [818], gold-catalyzed nitrene insertion into aromatic and benzylic C—H bonds [819, 820], silver-catalyzed intermolecular and intramolecular amidation of C—H bond in saturated hydrocarbons [821,822], α-amidation of cyclic ethers catalyzed by $Cu(OTf)_2$ [823], a mechanistic study of catalytic intermolecular amination of C—H bonds [824], nitrene insertion into the sp^3 C—H bonds of alkylarenes and cyclic ethers or the sp^2 C—H bonds of benzene using a copper homoscorpionate complex [825], Co(II)-catalyzed allylic amidation reactions [826], Ru(II) porphyrin-catalyzed amidation of aromatic heterocycles [827], non-heme iron-catalyzed amidation of aromatic substrates [828] and by the efficient stereoselective allylic C—H amination of terpenes and enol ethers involving the combination of a chiral aminating agent with a chiral rhodium catalyst [829].



659 R^1 = Me, Pr^i; R^2 = H, Me, OMe

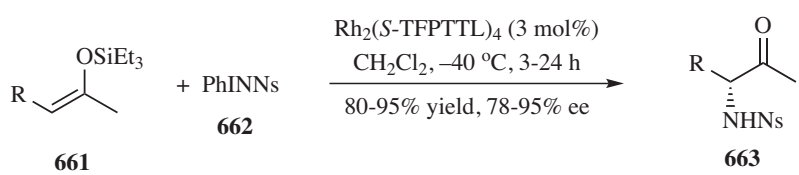
Scheme 3.263



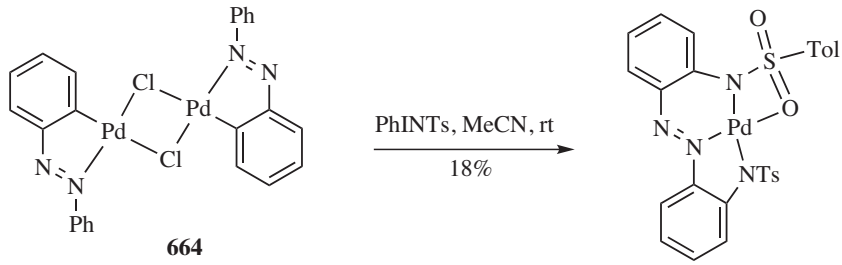
Scheme 3.264

Sanford and coworkers have investigated the carbon–nitrogen bond–forming reactions of palladacycles with aryliodonium imides [830]. In particular, palladium(II) complexes (e.g., **664**) containing bidentate cyclometalated chelating ligands react with PhINTs at room temperature to give products of insertion of the tosylimino group into the Pd—C bond (Scheme 3.266). This tosylimino insertion reaction has been applied to palladacycle complexes of azobenzene, benzo[*h*]quinoline and 8-ethylquinoline. The newly aminated organic ligands can be liberated from the metal center by protonolysis with a strong acid [830].

Imidoiodanes can be used to transfer the imido group to other elements under catalytic conditions. The imido group can be efficiently transferred to the sulfur atom in organic sulfides or sulfoxides [588, 831–835], or the nitrogen atom in aromatic nitrogen heterocycles using aryliodonium imides in the presence of copper, ruthenium, or iron complexes [836, 837]. Specific examples are illustrated by the selective N-imidation of aromatic nitrogen heterocycles (e.g., **665**) catalyzed by carbonyl[*meso*-tetrakis(*p*-tolyl)porphyrinato]ruthenium(II), [Ru(II)(TPP)(CO)] [836] and the iron-catalyzed imidation of sulfoxides (e.g., **666**) and sulfides using imidoiodane **662** (Scheme 3.267) [831].

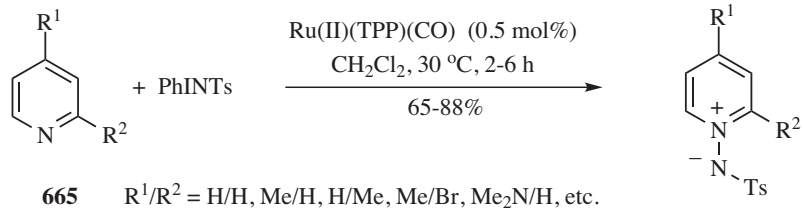


Scheme 3.265

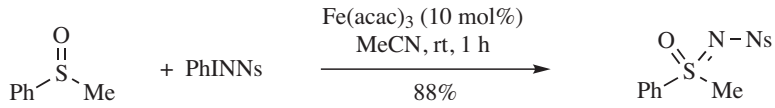


664

Scheme 3.266



665 R^1/R^2 = H/H, Me/H, H/Me, Me/Br, Me_2N/H, etc.



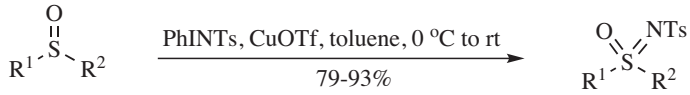
666 **662**

Ns = 4-$NO_2C_6H_4SO_2$

Scheme 3.267

Likewise, the reaction of PhINTs with sulfoxides **667** in the presence of catalytic amounts of copper(I) triflate affords the corresponding *N*-tosylsulfoximides **668** in high yield (Scheme 3.268) [835]. The imidation of enantiomerically pure sulfoxides **667** allows stereoselective access to *N*-tosylsulfoximides **668** with complete retention of configuration at sulfur. A similar imidation procedure has been used for the preparation of chiral ferrocenylsulfoximides [838, 839].

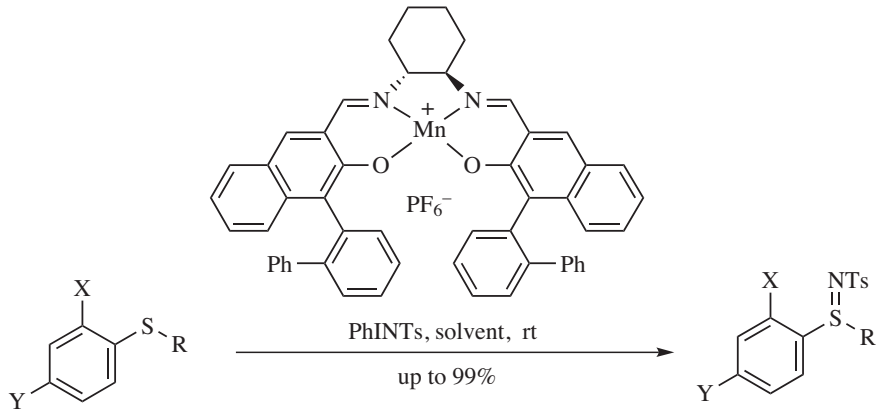
Enantioselective imidation of alkyl aryl sulfides **669** can be achieved by using the chiral manganese(salen) complex shown in Scheme 3.269 as a catalyst [840, 841].



667 **668**

R^1 = Ph, 4-MeC_6H_4; R^2 = Me, Et, Pr^i, vinyl, allyl, $PhCH_2$

Scheme 3.268



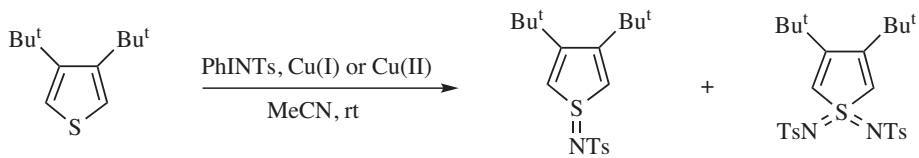
669 Solvent = PhCl, MeCN, PhCN
X = NO_2, H, Br; Y = H, NO_2; R = Me, Et, Bn

up to 97% ee

Scheme 3.269

Similarly, a direct catalytic sulfimidation of sulfides or 1,3-dithianes with PhINTs using a catalytic amount of copper(I) triflate and a chiral 4,4′-disubstituted bis(oxazoline) as ligand affords the respective chiral monosulfimides in good yield and with moderate enantioselectivity of up to 40–71% ee [842, 843]. Under same conditions, prochiral selenides react with PhINTs in the presence of CuOTf and the chiral 4,4′-disubstituted 2,2′-bis(oxazoline) ligands to give the corresponding chiral selenimides with up to 64% yield and 36% ee [844, 845].

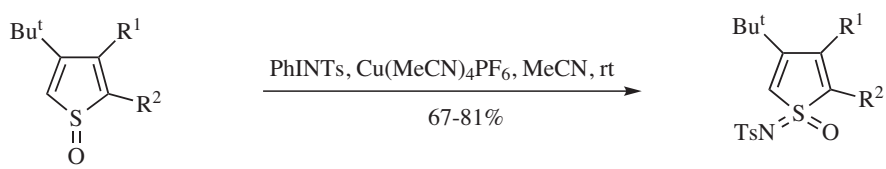
The reaction of 3,4-di-*tert*-butylthiophene (**670**) with PhINTs in the presence of copper(I) or copper(II) catalysts affords a mixture of imide **671** and diimide **672** as principal products (Scheme 3.270) [846–848].



670 Cu(I) = $Cu(MeCN)_4PF_6$
Cu(II) = $Cu(OTf)_2$

671 (23-61%)

672 (7-18%)



673 R^1 = Bu^t, R^2 = H or R^1 = H, R^2 = Bu^t

674

Scheme 3.270

Likewise, the imidation of thiophene 1-oxides **673** under similar conditions gives imides **674** in good yield [849].

The reaction of PhINTs with complexes of ruthenium(II) [800], osmium(II) [850, 851] and cobalt(III)[852] results in imidation at the metal center with the formation of the respective tosylimido-metal complexes. X-Ray structures have been determined for several bis(tosylimido)ruthenium(VI) and bis(tosylimido)-osmium(VI) porphyrin complexes [800, 850, 851].

3.1.22 Reactions of Iodonium Salts and C-Substituted Benziodoxoles

Aryliodonium salts, Ar(R)IX (R = aryl, alkenyl, alkynyl, alkyl, fluoroalkyl, or cyano ligands and X = triflate, tetrafluoroborate, or other anion) and C-substituted benziodoxoles (e.g., cyanobenziodoxoles, trifluoromethyl-benziodoxoles and alkynylbenziodoxoles) are particularly useful reagents for the electrophilic transfer of a carbon ligand to nucleophilic substrates. The high reactivity of aryliodonium derivatives in these reactions is explained by the "hyperleaving group ability" of the ArI group; for example, the leaving group ability of PhI is about a million times greater than that of triflate [853]. The chemistry of iodonium salts [854–856] and the atom-transfer reactions of benziodoxoles [857–859] have been summarized in several reviews.

3.1.22.1 Reactions of Diaryliodonium Salts

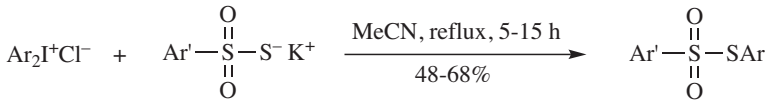
Diaryliodonium salts represent the most stable and well-investigated class of iodonium salts. Their chemistry was extensively covered in several reviews [854, 855, 860]. The most important and synthetically useful reactions of diaryliodonium salts include the following: the direct electrophilic arylation of various nucleophiles, transition metal mediated cross-coupling reactions and reactions involving generation and trapping of the benzyne intermediates.

Diaryliodonium salts have found synthetic application as arylating reagents in reactions with various organic substrates under polar, catalytic, or photochemical conditions. Typical examples of arylations of nucleophiles under polar, non-catalytic conditions are shown in Scheme 3.271 and include the reactions of diaryliodonium salts with thiosulfonate anions **675** [861], fluoride anion [862, 863], malonates **676** [864] and silyl enol ethers **677** [865].

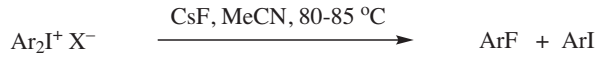
Additional examples include the electrophilic arylations of sodium arenesulfinates [866], potassium carbonotrithioates [867] and benzazoles [868] using diaryliodonium salts in ionic liquids and the arylations of anilines [869], sodium tetraphenylborate [870] and vinylindiums [871]. Particularly important are the reactions of diaryliodonium salts with fluoride anion as nucleophile. This reaction is widely applied for introduction of the radioactive ^{18}F isotope into different organic substrates to obtain labeled agents for positron emission tomography. This topic is covered separately in Chapter 7 due to its importance and wide usage.

The O-arylation of appropriate phenols using symmetrical iodonium salts has been employed in the synthesis of hydroxylated and methoxylated polybrominated diphenyl ethers, some of which are related to natural products [872, 873]. For example, several polybrominated diphenyl ethers **680** have been prepared by the reaction of iodonium salt **678** with phenols **679** in *N,N*-dimethylacetamide (DMAC) solution in the presence of base (Scheme 3.272) [872].

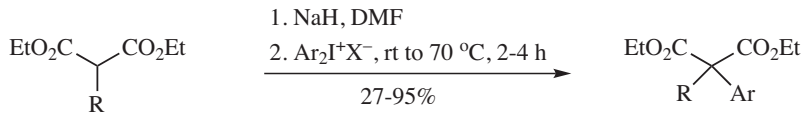
Olofsson and coworkers have developed a general and high-yielding synthesis of various diaryl ethers **681** using the reaction of diaryliodonium salts with phenols under basic conditions (Scheme 3.273) [874]. The scope of products includes bulky *ortho*-substituted diaryl ethers, which are difficult to obtain by metal-catalyzed protocols. A similar procedure has been used for the metal-free synthesis of aryl esters from carboxylic acids and diaryliodonium salts [875].



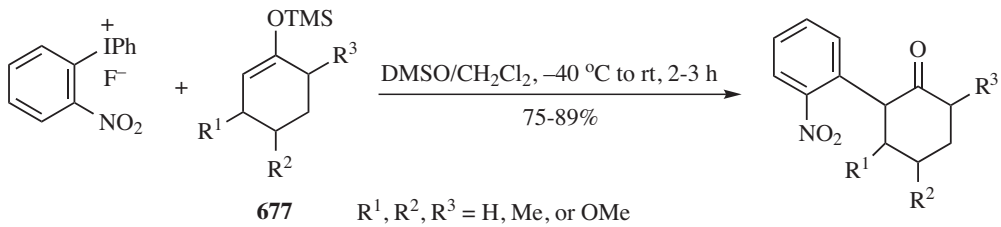
675 Ar = Ph, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 4-MeC_6H_4
Ar' = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-ClC_6H_4



Ar = Ph, 2-MeC_6H_4, 4-MeC_6H_4, 2-furyl, 2-thienyl, etc.
X = TfO, CF_3CO_2, TsO

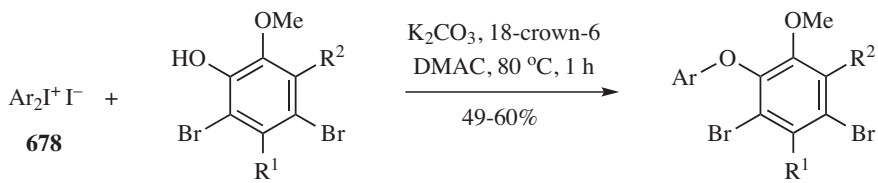


676 R = H, Me, $CH_2CH{=}CH_2$; Ar = Ph, 4-MeC_6H_4; X = BF_4, OTf



677 R^1, R^2, R^3 = H, Me, or OMe

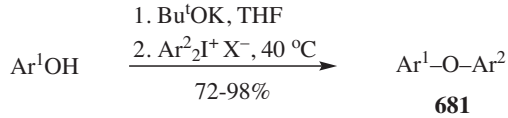
Scheme 3.271



Ar = 2,4-$Br_2C_6H_3$
R^1 = H, R^2 = H
R^1 = H, R^2 = Cl
R^1 = Br, R^2 = H
R^1 = Br, R^2 = Br

679 DMAC = *N*,*N*-dimethylacetamide **680**

Scheme 3.272



Ar^1 = Ph, 4-MeOC$_6$H$_4$, 4-Bu^{t}C$_6$H$_4$, 3-CNC$_6$H$_4$, etc.
Ar^2 = Ph, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 2,4-Bu$^t_2$C$_6$H$_3$, 2-FC$_6$H$_4$, etc.

Scheme 3.273

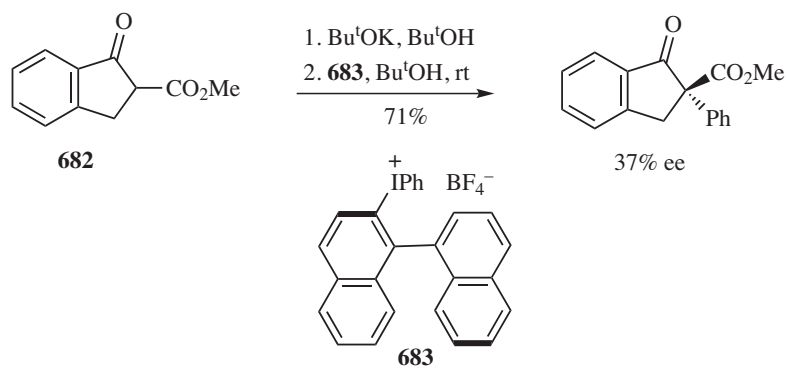
Thienyl(phenyl)iodonium salts and other heteroaryl(phenyl)iodonium salts can be used as the selective heteroaryl transfer agents in reactions with phenol ethers. These heteroarylations occur at room temperature in the hexafluoroisopropanol solution in the presence of trimethylsilyl triflate via a SET mechanism [876].

Several examples of S-arylation of sulfides and P-arylation of phosphines using diaryliodonium salts were reported in the older literature [877, 878]. These reactions generally proceed by a radical chain mechanism. The arylation of phosphines has been used to promote the photo-initiation of cationic polymerization [879]. More recently, the synthesis of diaryl sulfones via S-arylation of sodium arenesulfinates, $ArSO_2Na$, by diaryliodonium salts has been reported [880].

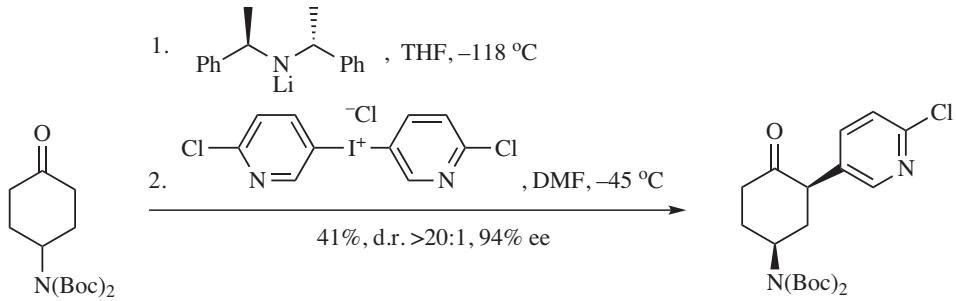
Arylations of carbon nucleophiles using diaryliodonium salts are particularly important. Compounds containing an active methylene group, such as malonates, or the respective carbanions formed *in situ,* react smoothly with diaryliodonium salts to yield α-arylated products [864, 881–883]. Iodonium salt **683** has been used in the asymmetric phenylation of 1-oxo-2-indancarboxylate (**682**) with low enantioselectivity (Scheme 3.274) [882].

Aggarwal and Olofsson have developed a direct asymmetric α-arylation of prochiral ketones using chiral lithium amide bases and diaryliodonium salts [881]. In a representative example, the deprotonation of cyclohexanone derivative **684** using chiral Simpkins' (*R,R*)-base followed by reaction with the pyridyl iodonium salt gave the arylated product **685** in 94% ee (Scheme 3.275). This reaction has been employed in a short total synthesis of the alkaloid (–)-epibatidine [881].

Quideau and coworkers have reported a regioselective dearomatizing phenylation of phenols and naphthols using diaryliodonium salts [884, 885]. For example, the treatment of naphthols **686** substituted at the *ortho*

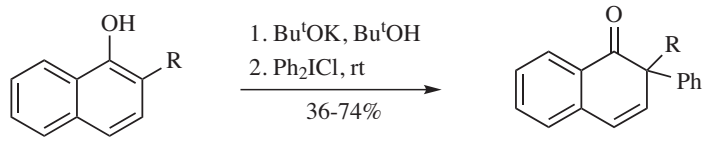


Scheme 3.274



684 **685**

Scheme 3.275

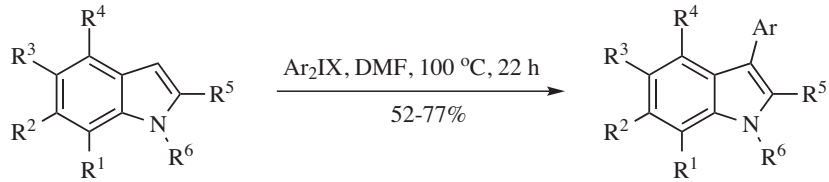


686 R = Me, OMe, NO **687**

Scheme 3.276

position by a small electron-donating group with diphenyliodonium chloride leads to regioselective *ortho*-phenylation to give products **687** (Scheme 3.276). The mechanism of this reaction involves a nonradical direct coupling of the ligands on the hypervalent iodine center [884]. The formation of phenol ethers due to the O-phenylation can also occur when the reaction of phenolate anion with diphenyliodonium chloride is carried out in a polar aprotic solvent such as dimethylformamide [884].

Indoles **688** and pyrroles can be efficiently arylated by aryliodonium salts at position 3 in the absence of metal catalysts to give products **689** (Scheme 3.277) [886]. The reaction of unsymmetrically substituted diaryliodonium salts results in the preferential transfer of the less sterically hindered aromatic ring.



688 **689**

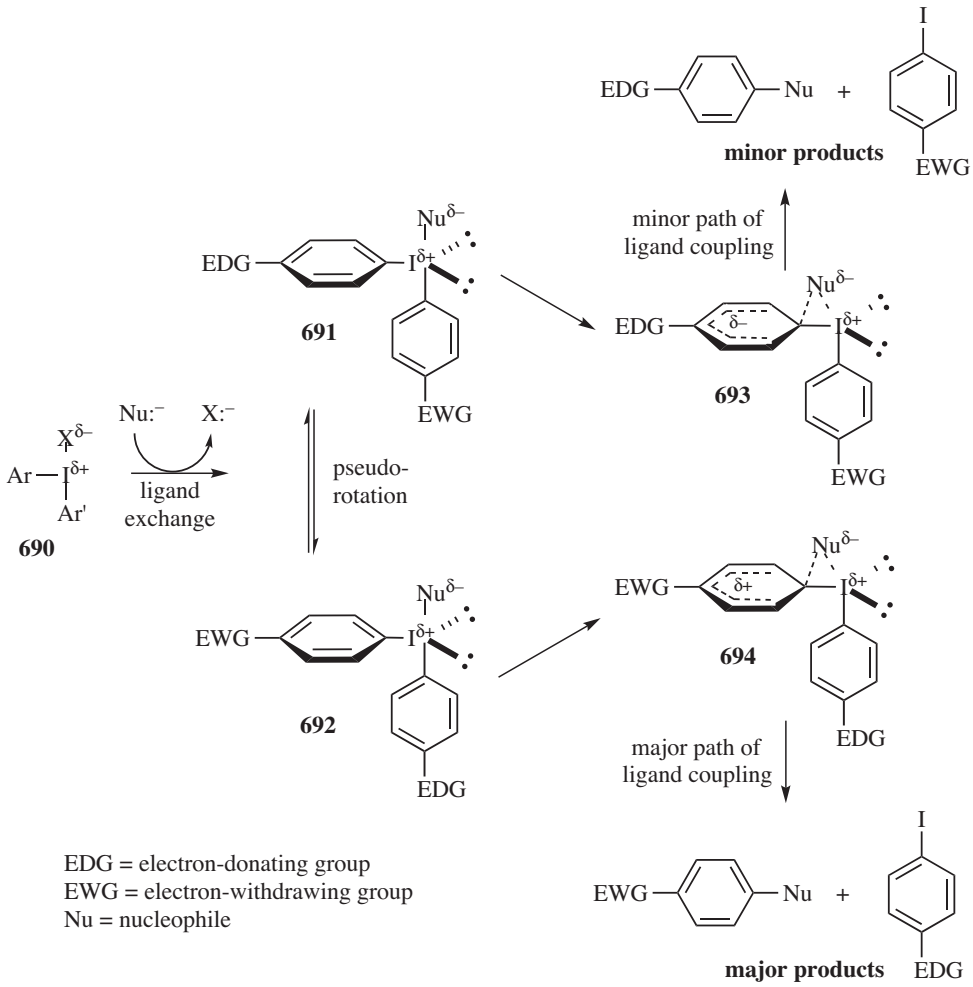
R^1 - R^4 = H, Me, Cl
R^5 = H or Me; R^6 = H, Me, Pr, Bu, Bn
Ar = Ph, 4-$MeOC_6H_4$, 4-$Bu^tOC_6H_4$, etc.

Scheme 3.277

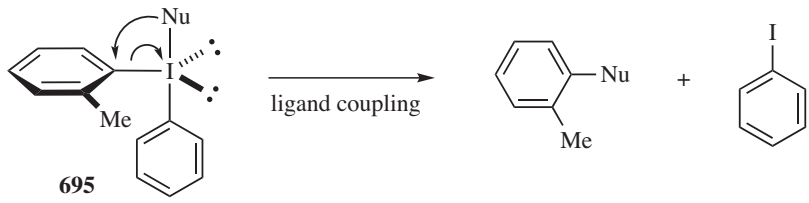
Aryliodonium salts can be used for the arylation of carbon surfaces [887, 888]. Various iodonium salts have been employed as functional groups carriers, which allow covering of a carbon surface by a wide range of electron-withdrawing or electron-donating functional groups.

Several mechanistic studies on the reactions of diaryliodonium salts with nucleophiles have been published. Ochiai and coworkers performed a mechanistic study on the phenylation of β-keto ester enolates with diaryliodonium salts. An aryl radical trap was added to the reaction without affecting the outcome, which indicates that radical pathways are unlikely and the reaction occurs by direct coupling of the ligands on the hypervalent iodine center [889].

In the reaction of unsymmetric diaryliodonium salts **690** with nucleophiles, it has been shown that the most electron-deficient aryl group is transferred to the nucleophile with varying selectivities in agreement with the mechanism outlined in Scheme 3.278. The initial ligand exchange leads to the hypervalent intermediates **691** and **692** with the electronegative ligand Nu occupying an axial position (Section 1.5.1). Rapid pseudorotation



Scheme 3.278



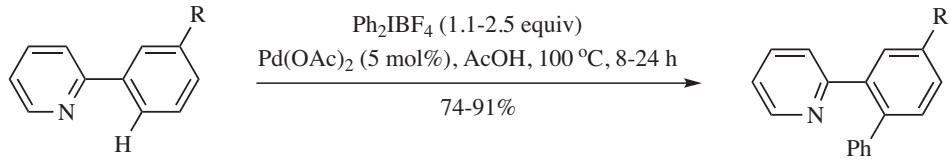
Scheme 3.279

occurs between intermediates **691** and **692,** which provides two different transition states, **693** and **694** [882, 890]. Of the two possible transition states for the subsequent ligand coupling, **694** is more favorable than **693,** because both the negative charge on the aromatic ring and the enhanced positive charge on the iodine(III) are stabilized by the substituents more effectively [889].

The so-called "ortho-effect" is observed in the reactions between a nucleophile and a diaryliodonium salt where one aryl ligand has an *ortho*-substituent, such as methyl. In these reactions the *ortho*-substituted aryl ligand is often coupled with the nucleophile, even if it is more electron rich [891, 892]. This has been explained by the predominant conformation **695** of the Ar(Ph)INu intermediate with the most bulky aryl ligand and the two lone pairs occupying the equatorial position for steric reasons (Scheme 3.279). Ligand coupling in the intermediate **695** leads to a reductive elimination of PhI and transfer of the nucleophile to the *ortho*-substituted aryl group situated in the equatorial position, even though it is the more electron-rich aromatic ring.

The mechanism of solvolysis of methoxy-substituted diaryliodonium tetrafluoroborates, $ArI^{+}Ph\ {}^{-}BF_4$, in methanol and 2,2,2-trifluoroethanol has been investigated [893]. The solvolysis products include alkoxide substitution products (ArOR and PhOR) as well as iodoarenes (PhI and ArI). The ratios of products, ArOR/PhOR, range from 8 : 2 to 4 : 6. The results of this study provide experimental evidence against the formation of aryl cation under these conditions and support the pathways via ligand coupling or S_NAr2 mechanisms involving a solvent molecule as a nucleophile in the transition state [893]. If the reaction is performed in inert (not nucleophilic) solvent, various nucleophiles may be involved in the reaction with iodonium salt.

Arylations with diaryliodonium salts can be effectively catalyzed by transition metals. Diaryliodonium salts can serve as efficient reagents in the copper-catalyzed arylation of lithium enolates [894], α-aryl carbonyl compounds [895], thiophenes [896], 5-aryl-2*H*-tetrazole [897], uracil nucleosides [898], aniline and phenol derivatives [899] and alkenes [900]. Palladium salts and complexes are efficient catalysts in the cross-coupling reactions of diaryliodonium salts with various substrates, such as organoboron compounds [901], organostannanes [902], silanes [903], organolead triacetates [904], organobismuth(V) derivatives [905], carbon monoxide [906], allylic alcohols [907], functionalized allenes [908, 909], Grignard reagents [910], alkenes [911, 912], terminal alkynes [913], simple arenes [914] and arenecarboxylic acids via decarboxylative cross-coupling reaction [915]. Particularly interesting is the palladium-catalyzed directed C—H activation/phenylation of substituted 2-phenylpyridines and indoles with aryliodonium salts reported by Sanford and coworkers [916,917]. In a representative example, 2-pyridyl substituted substrates **696** are selectively phenylated to the *ortho*-position, affording products **697** in good yields (Scheme 3.280). Preliminary mechanistic experiments have provided evidence in support of a rare Pd(II)/(IV) catalytic cycle for this transformation [917]. The preparation of stable triorganyl Pd(IV) complexes by the electrophilic arylation of palladium(II) bipyridine complexes using $Ph_2I^{+}TfO^{-}$ has been reported by Canty and coworkers [918]. It was also demonstrated that the carbamate (R_2NCO_2) function is an excellent directing group for palladium-catalyzed direct arylation reactions using diaryliodonium salts [919].



696 R = Me, Ac, etc. **697**

Scheme 3.280

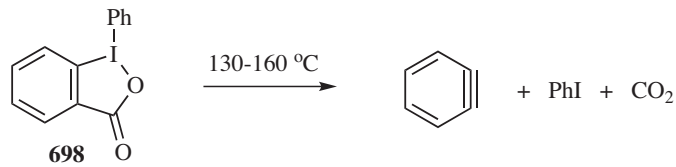
McMillan and Allen have accomplished the enantioselective α-arylation of aldehydes using diaryliodonium salts and a combination of copper and organic amine catalysts. This asymmetric protocol has been applied to the rapid synthesis of (*S*)-ketoprofen, a commercially successful oral and topical analgesic [920].

Phenyl benziodoxolone **698** (Section 2.1.8.1.9) is a classical reagent that is commonly used to generate benzyne under heating (Scheme 3.281) [921–923].

In a more recent work, Kitamura and coworkers have developed more efficient benzyne precursors based on diaryliodonium salts [924–928]. Of particular use is phenyl[2-(trimethylsilyl)phenyl]iodonium triflate **699,** which is readily prepared by the reaction of 1,2-bis(trimethylsilyl)benzene with the $PhI(OAc)_2$/TfOH reagent system [924]. Treatment of reagent **699** with tetrabutylammonium fluoride in dichloromethane at room temperature generates benzyne, which can be trapped with a diene to afford the respective benzyne adducts in high yields [924]. Examples of synthetic applications of reagent **699** as benzyne precursor include O-arylation of carboxylic acids leading to aryl esters **700** [929], preparation of 2-aryl-substituted nitriles **702** by arylation of nitriles **701** via a benzyne reaction [930] and cycloaddition/elimination reaction of thiophene *S*-oxide **703** with benzyne leading to product **704** (Scheme 3.282) [931]. Reagent **699** has also been used in the synthesis of spiro(imidazolidine-2,3′-benzo[*b*]thiophene) by a one-pot reaction of benzyne, aryl isothiocyanates and N-heterocyclic carbenes [932] and for the preparation of benzo[*b*]seleno[2,3-*b*]pyridines by the reaction of acetic acid 2-selenoxo-2*H*-pyridin-1-yl esters with benzyne [933].

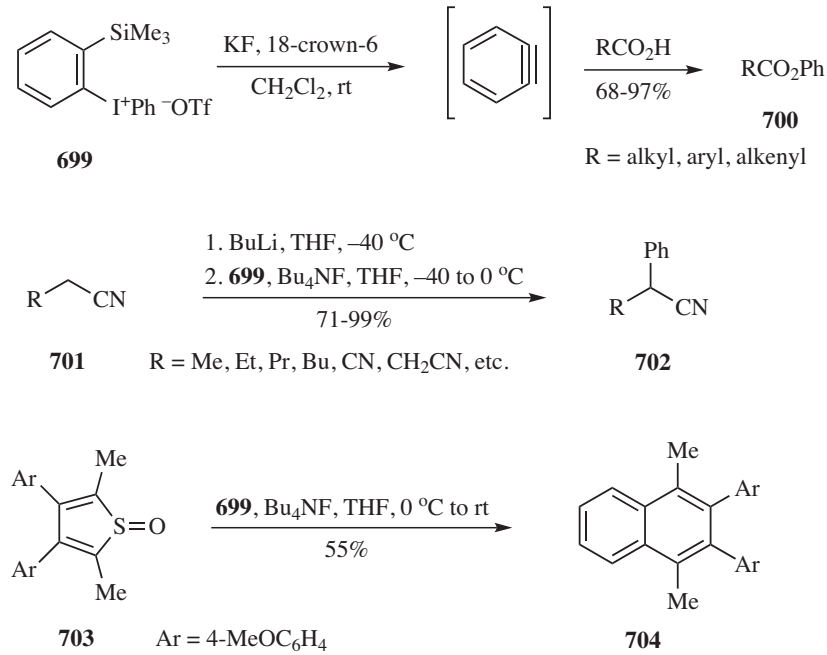
The efficient acylbenzyne precursors, [5-acyl-2-(trimethylsilyl)phenyl]iodonium triflates **705** have been prepared by reaction of the appropriate 1,2-bis(trimethylsilyl)benzenes with $PhI(OAc)_2$ in the presence of trifluoromethanesulfonic acid in dichloromethane at room temperature. Treatment of these reagents with Bu_4NF in dichloromethane generates acylbenzynes **706,** which can be trapped by furan to give adducts **707** in high yield (Scheme 3.283) [927].

The carborane analog of benzyne, 1,2-dehydrocarborane, can be generated similarly from phenyl[*o*-(trimethylsilyl)carboranyl]iodonium acetate by treatment with CsF in ether and trapped with dienes such as anthracene, naphthalene, norbornadiene and 2,5-dimethylfuran to give the respective 1,2-dehydrocarborane adducts in high yield [934].



698

Scheme 3.281

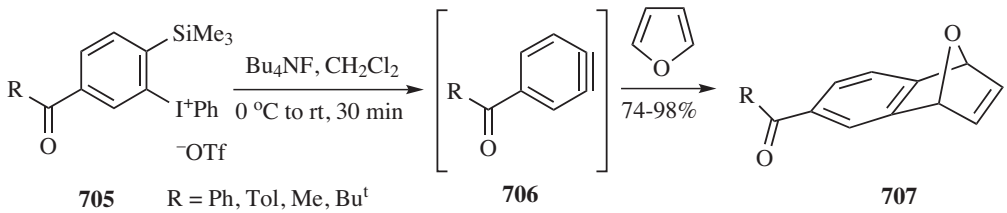


Scheme 3.282

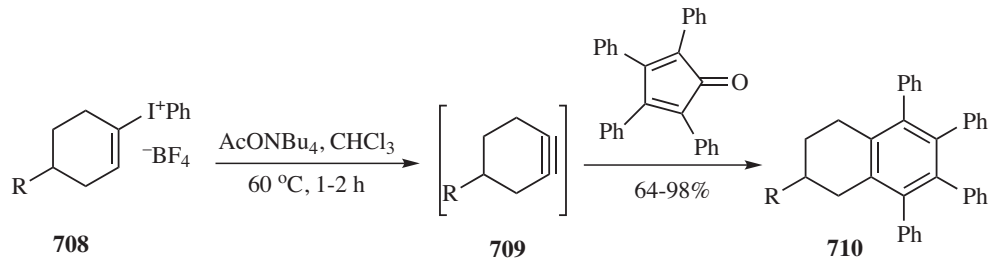
3.1.22.2 Reactions of Alkenyl(Aryl)Iodonium Salts

The chemistry of alkenyliodonium salts has been summarized in the reviews of Ochiai [935, 936], Okuyama [937–939] and Zefirov [940]. Alkenyl(phenyl)iodonium salts are very reactive compounds because of the exceptional leaving group ability of the phenyliodonium moiety (10^{12} times greater than for iodine itself) combined with its high electron-withdrawing properties (the Hammett substituent constant σ_m for the PhI^+ group is 1.35) [941]. Several research groups have been involved in mechanistic studies of the nucleophilic substitution in alkenyliodonium salts [942–949]. Several mechanisms, including S_N1, S_N2, ligand coupling and Michael addition–elimination, have been observed in these reactions. The mechanistic aspects of the reactions of vinylic iodonium salts with nucleophiles have been reviewed by Okuyama [937] and by Ochiai [935].

Cyclohexyne intermediates **709** have been observed as the result of β-elimination in the reactions of 1-cyclohexenyl(phenyl)iodonium salts **708** with mild bases, such as tetrabutylammonium acetate, fluoride ion,



Scheme 3.283



708 **709** **710**

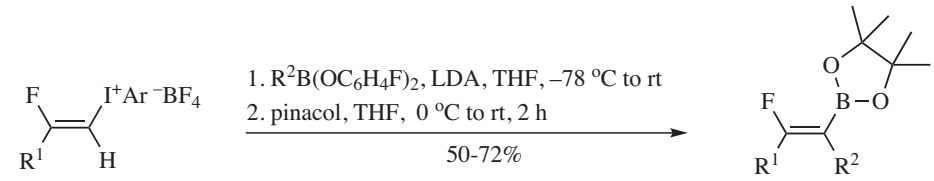
R = H, Me, Et, Bu^t, Ph, CN

Scheme 3.284

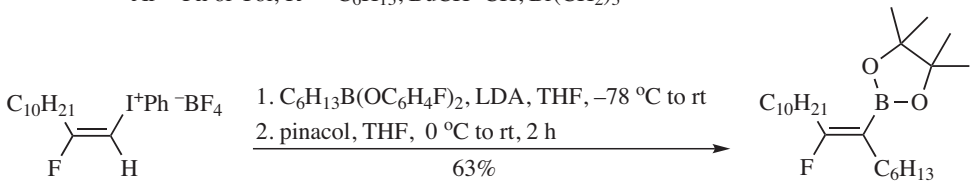
alkoxides and amines in aprotic solvents [941, 946, 948]. Cyclohexynes **709** have been effectively trapped with tetraphenylcyclopentadienone to give products of [4+2] cycloaddition **710** in high yields (Scheme 3.284). The analogous cycloheptyne intermediates can be generated under similar conditions from the appropriate 1-cycloheptenyl(phenyl)iodonium precursors [941, 946, 948].

Alkenyl(phenyl)iodonium salts have found synthetic application as alkenylating reagents in the reactions with various nucleophilic substrates. In most cases these reactions proceed with retention of configuration at the carbon atom double bond via the addition–elimination mechanism or ligand coupling on the iodine. Examples of alkenylations with alkenyliodonium salts under non-catalytic conditions include the reactions with the following nucleophiles: thioamides [950], sodium dithiocarbamates and potassium carbonotrithioates [951], sodium tellurolates and selenolates [952,953], potassium phosphorothioates, phosphorodithioates and phosphoroselenoates [954–956], group 15 element nucleophiles [957], formamides [958], tetrafluoroborate anion upon thermolysis leading to fluoroalkenes [959], potassium thiocyanate [960] and benzotriazole [961].

(*E*)- and (*Z*)-(Fluoroalkenyl)boronate derivatives **712** and **714** have been prepared stereospecifically by the reaction of (*E*)- or (*Z*)-(2-fluoroalkenyl)iodonium salts **711** and **713** with [bis(4-fluorophenoxy)]alkylboranes, followed by transesterification to pinacol esters (Scheme 3.285). The mechanism of this reaction involves

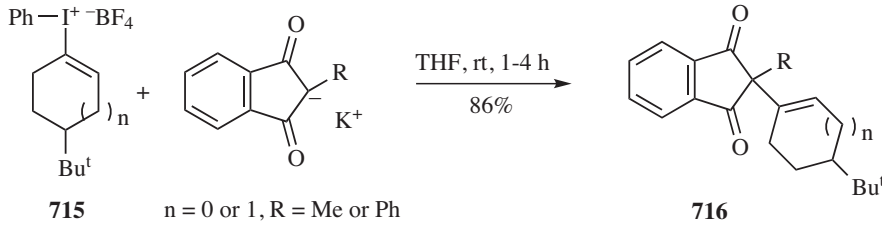


711 $R^1 = C_{10}H_{21}$, $AcO(CH_2)_9$, $BnO(CH_2)_3$, $BnO_2C(CH_2)_3$, etc.
Ar = Ph or Tol; $R^2 = C_6H_{13}$, BuCH=CH, $Br(CH_2)_3$ **712**



713 **714**

Scheme 3.285



Scheme 3.286

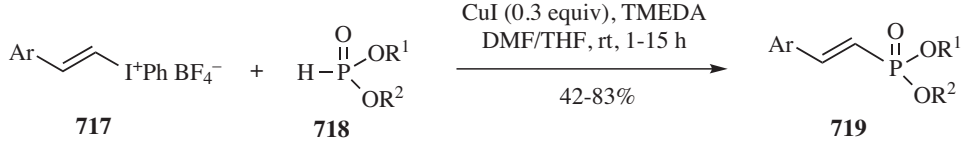
initial generation of 2-fluoroalkylideneiodonium ylide by the α-deprotonation of iodonium salts with lithium diisopropylamide (LDA) followed by its reaction with [bis(4-fluorophenoxy)]alkylboranes [962, 963].

Few examples of non-catalytic alkenylations of carbon nucleophiles have been published. For example, enolate anions derived from various 1,3-dicarbonyl compounds can be vinylated with cyclohexenyl or cyclopentenyl iodonium salts **715** to afford products **716** (Scheme 3.286) [964].

The selectivity of the alkenylation reactions and the yields of products can be significantly improved by carrying out the reaction of alkenyliodonium salts with carbon nucleophiles in the presence of transition metal compounds in stoichiometric or catalytic amounts. In the presence of a copper(I) catalyst iodonium salts selectively react with iodide anion [965, 966], organoborates [967], Grignard reagents [968] and terminal alkynes [969] to afford the respective products of cross-coupling in high yields with complete retention of geometry. An example of such a reaction is represented by the copper-mediated cross-coupling of *H*-phosphonates **718** with vinyliodonium salts **717** leading to 2-arylvinylphosphonates **719** under mild conditions (Scheme 3.287) [970].

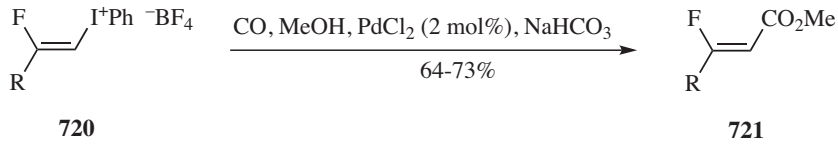
Alkenyliodonium salts have been used as highly reactive reagents for Heck-type olefination [39, 971], Sonogashira-type coupling with alkynes [965, 972] and similar other palladium-catalyzed cross-coupling reactions [966, 973, 974]. In a specific example, (*Z*)-β-fluoro-α,β-unsaturated esters **721** were stereoselectively synthesized from (*Z*)-2-fluoro-1-alkenyliodonium salts **720** by the Pd-catalyzed methoxycarbonylation reaction (Scheme 3.288) [974]. This reaction proceeds at room temperature and is compatible with various functional groups on the substrate.

Reactions of alkenyliodonium salts with strong bases may lead to the generation of alkylidenecarbenes via a base-induced α-elimination. Alkylidenecarbenes generated by this method can undergo cyclization by a 1,5-C—H bond insertion, providing a useful route for the construction of substituted cyclopentenes [975–977]. For example, a synthesis of fluorocyclopentenes **723** by the reaction of (*Z*)-(2-fluoroalkenyl)iodonium salts **722** with potassium *tert*-butoxide has been developed (Scheme 3.289). The mechanism of this reaction



Ar = Ph, 2-FC_6H_4, 2-MeC_6H_4, 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$NO_2C_6H_4$, etc.
R^1, R^2 = Me, Et, Bu, Bn, Ph, etc.

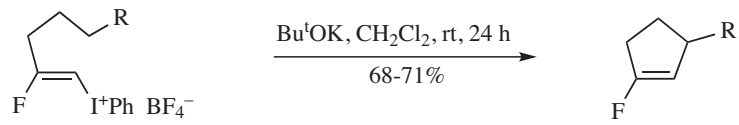
Scheme 3.287



720 **721**

R = $C_{10}H_{21}$, (*cyclo*-C_6H_{11})CH_2, Ph, $Cl(CH_2)_9$, $Pr^iO_2C(CH_2)_8$, $Bu^tCO(CH_2)_8$

Scheme 3.288



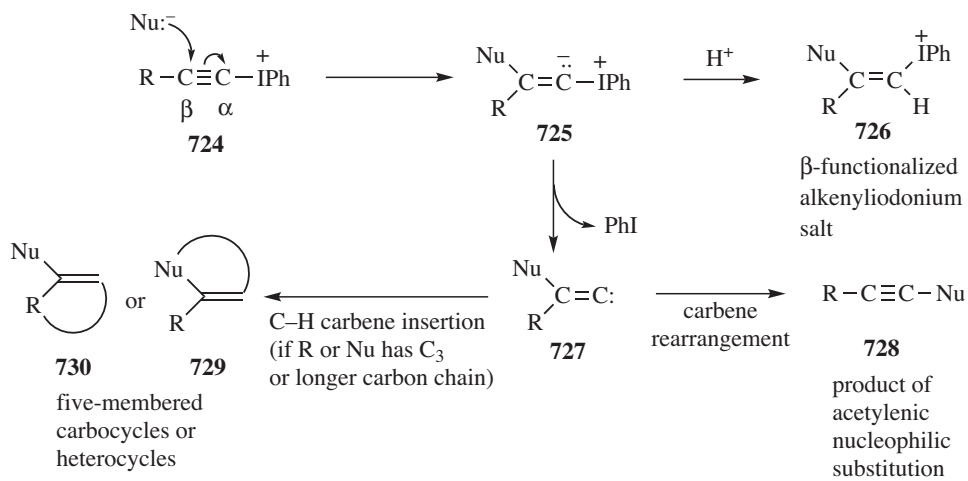
722 R = $AcO(CH_2)_6$, $Cl(CH_2)_6$, $Bu^tCO(CH_2)_5$, etc. **723**

Scheme 3.289

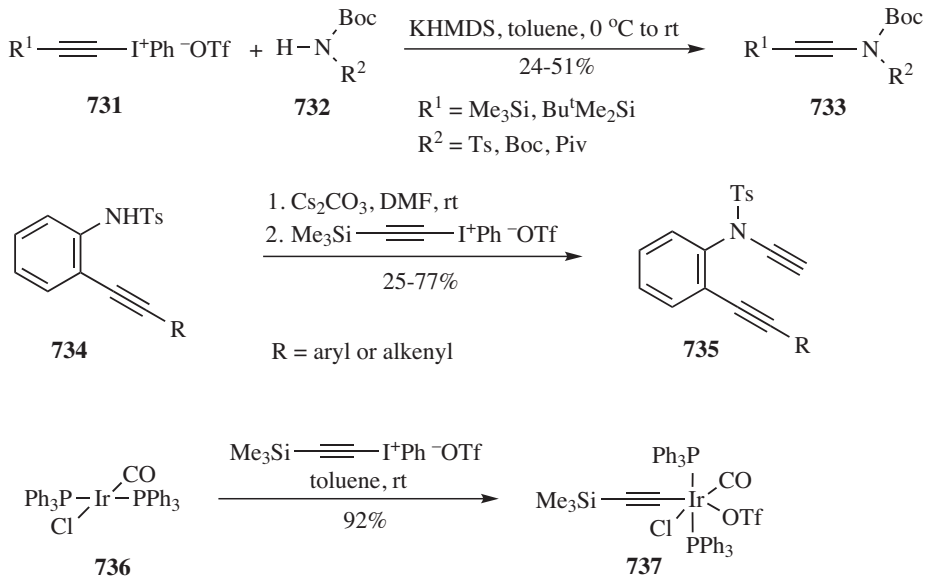
involves initial generation of (α-fluoroalkylidene)carbenes, which give fluorocyclopentenes via 1,5-C—H insertion [975].

3.1.22.3 Reactions of Alkynyl(aryl)iodonium Salts and Alkynylbenziodoxoles

The chemistry of alkynyliodonium salts has been summarized in several reviews [856, 978, 979]. Reactions of alkynyliodonium salts **724** with nucleophiles proceed via an addition–elimination mechanism involving alkylideneiodonium ylides **725** and alkylidene carbenes **727** as key intermediates (Scheme 3.290). Depending on the structure of the alkynyliodonium salt **724,** the specific reaction conditions and the nucleophile employed, this process can lead to the following products: β-functionalized alkenyliodonium salt **726** due to



Scheme 3.290



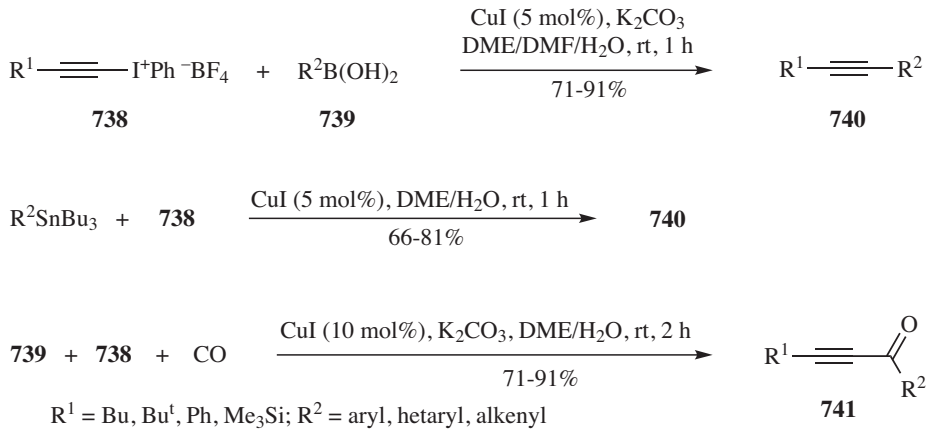
Scheme 3.291

the protonation of ylide **725,** a substituted alkyne **728** due to the carbene rearrangement, or cyclic products **729** or **730** via intramolecular 1,5-carbene insertion [856]. These reaction pathways have been widely utilized in organic synthesis.

Alkynyl(phenyl)iodonium salts have found synthetic application for the preparation of various substituted alkynes by the reaction with appropriate nucleophiles, such as enolate anions [980, 981], selenide and telluride anions [982–984], dialkylphosphonate anions [985], benzotriazolate anion [986], imidazolate anion [987], N-functionalized amide anions [988–990] and transition metal complexes [991–993]. Scheme 3.291 shows several representative reactions: the preparation of *N*-alkynyl carbamates **733** by alkynylation of carbamates **732** using alkynyliodonium triflates **731** [989], synthesis of ynamides **735** by the alkynylation/desilylation of tosylanilides **734** using trimethylsilylethynyl(phenyl)iodonium triflate [990] and the preparation of Ir(III) σ-acetylide complex **737** by the alkynylation of Vaska's complex **736** [991].

Alkynyl(phenyl)iodonium salts can be coupled with organocopper reagents [994], or with organoboronic acids or organostannanes in the presence of Cu(I) catalysts [995, 996]. For example, the copper iodide-catalyzed cross-coupling and carbonylative coupling reactions of alkynyliodonium salts **738** with organoboronic acids **739** or organostannanes (R^2SnBu_3) under mild conditions afford acetylenes **740** and alkynyl ketones **741,** respectively, in high yields (Scheme 3.292) [996]. Interestingly, alkynyl(phenyl)-iodonium tetrafluoroborates **738** are more efficient in these coupling reactions than the corresponding iodonium triflates and tosylates.

Various five-membered heterocycles can be prepared by inter- or intramolecular addition/cyclizations of appropriate nucleophiles with alkynyliodonium salts via alkylidene carbene intermediates [856, 978, 979]. The intermolecular variant of this cyclization has been employed in the synthesis of 3-substituted-5,6-dihydroimidazo[2,1-*b*]thiazoles [997], 2-substituted imidazo[1,2-*a*]pyrimidines [998] and 2-substituted-imidazo[1,2-*a*]pyridines [999]. In a representative example, 2-substituted imidazo[1,2-*a*]pyridines **744** were synthesized in good yield by cyclocondensation of 2-aminopyridine (**742**) with alkynyl(phenyl)iodonium tosylates **743** under mild conditions (Scheme 3.293) [999]. The mechanism of this cyclization involves

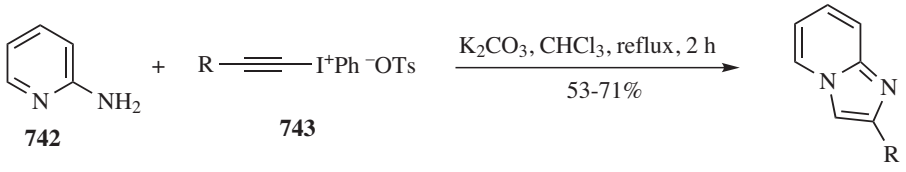


Scheme 3.292

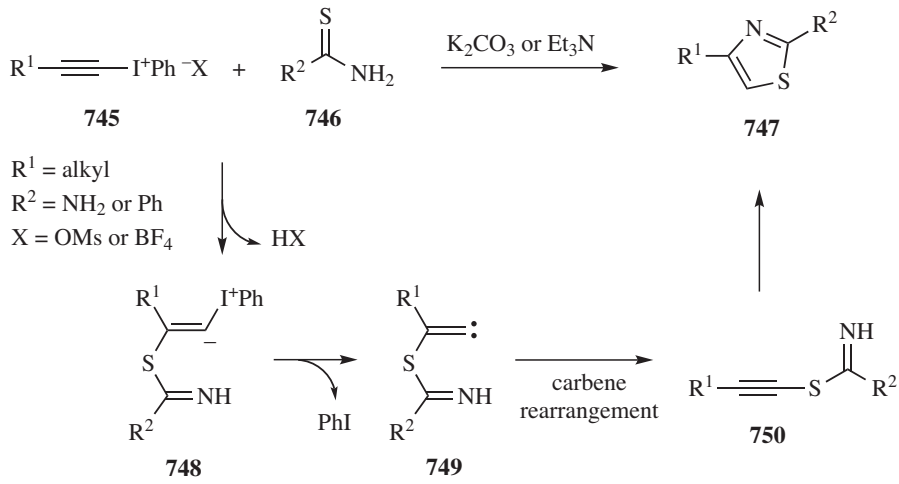
initial nucleophilic addition of the amino group of 2-aminopyridine to the triple bond of the alkynyliodonium salt followed by generation and subsequent cyclization of the intermediate alkylidene carbene (Scheme 3.290).

Ochiai and coworkers have investigated the mechanism for the one-pot synthesis of 2,4-disubstituted thiazoles **747** by cyclocondensation of alkynyliodonium salts **745** with thioureas or thioamides **746** (Scheme 3.294) [1000]. This reaction was originally reported by Wipf and Venkatraman in 1996 [1001]. Ochiai and coworkers have isolated and identified by X-ray analysis intermediate products **750** (as mesylate or tetrafluoroborate salts), which suggests a mechanism involving Michael addition of sulfur nucleophile **746** to alkynyliodonium salt **745** giving intermediate alkylideneiodonium ylide **748** followed by the 1,2-rearrangement of sulfenyl groups in the resulting alkylidene carbene **749** (Scheme 3.294) [1000].

The intramolecular variant of the alkylidene carbene cyclization is achieved by treating functionalized alkynyliodonium salts with a suitable nucleophile. These cyclizations are exemplified by the following works: the preparation of various functionalized 2,5-dihydrofurans by treatment of 3-alkoxy-1-alkynyl-(phenyl)iodonium triflates with sodium benzenesulfinate [1002], employment of the alkylidene carbene cyclization in the total syntheses of natural products agelastatin A and agelastatin B [1003] and preparation of the tricyclic core of (±)-halichlorine through the use of an alkynyliodonium salt/alkylidenecarbene/1,5 C—H insertion sequence [1004]. In particular, Wardrop and Fritz have employed the sodium benzenesulfinate-induced cyclization of alkynyliodonium triflate **751** for the preparation of dihydrofuran **752** (Scheme 3.295), which is a key intermediate product in the total synthesis of (±)-magnofargesin [1002].



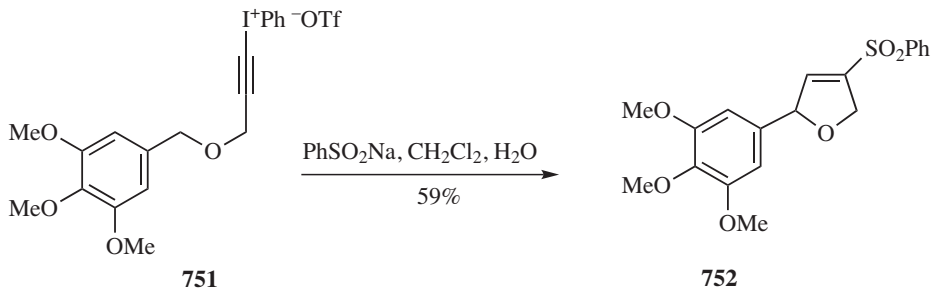
Scheme 3.293



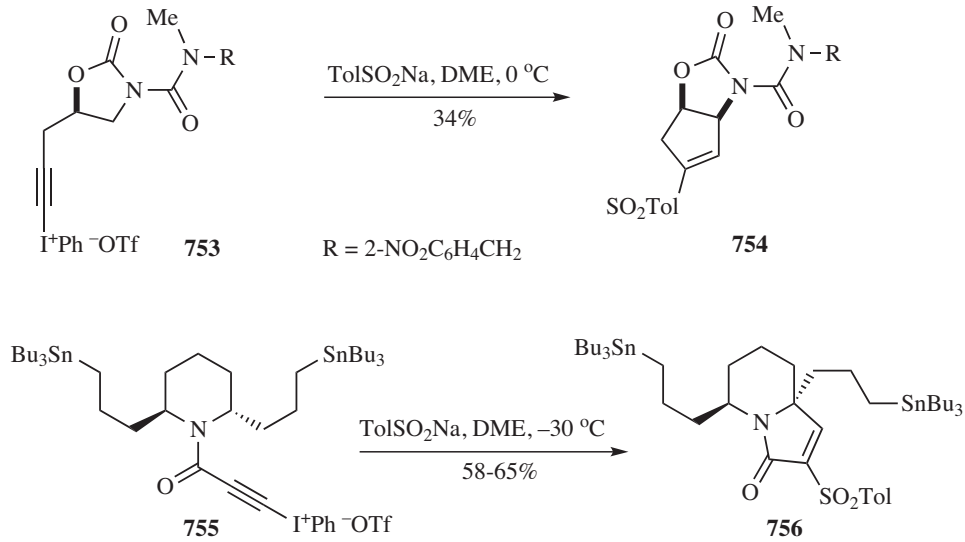
Scheme 3.294

Feldman and coworkers have employed the sodium *p*-toluenesulfinate-induced cyclizations of alkynyliodonium salts **753** and **755** in the preparation of compounds **754** and **756** (Scheme 3.296), which are key intermediates in the total syntheses of agelastatins [1003] and (±)-halichlorine, respectively [1004].

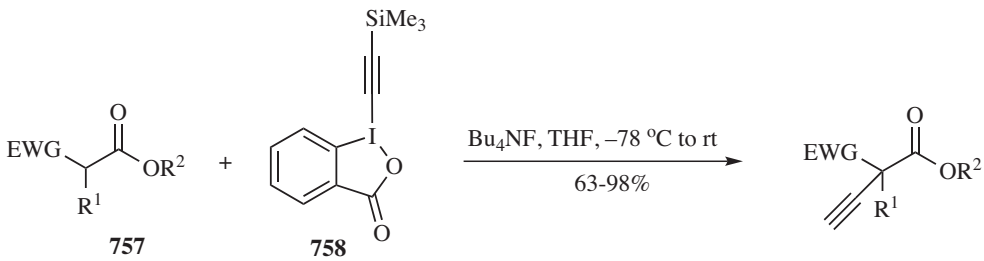
Waser and coworkers have demonstrated that triisopropylsilyl and trimethylsilyl substituted ethynylbenziodoxolones (Section 2.1.8.1.8) are excellent acetylene transfer reagents, both in metal-free and metal-catalyzed reactions [858, 1005–1012]. In particular, reagent **758** efficiently alkynylates β-dicarbonyl compounds and other C—H acidic substrates **757** in the presence of fluoride source in THF under mild conditions (Scheme 3.297) [1012]. Indoles (e.g., **759,** Scheme 3.297), pyrroles and thiophenes are directly alkynylated by reagent **760** in the presence of AuCl as catalyst [1005, 1006, 1008, 1010]. Additional examples include palladium-catalyzed intramolecular oxyalkynylation of non-activated olefins using triisopropylsilylethynylbenziodoxolone [1011], palladium-catalyzed alkynylations of *o*-allylphenols and carboxylic acids [858] and *para*-selective gold-catalyzed direct alkynylation of anilines [1009]. Aubineau and Cossy have found that trimethylsilyl substituted ethynylbenziodoxolone is a useful reagent for direct chemoselective alkynylation of *N*-sulfonylamides [1013].



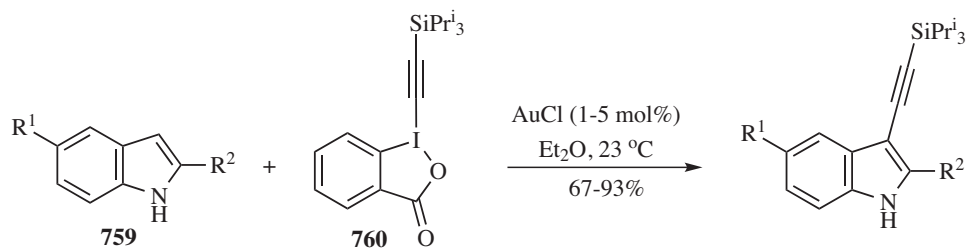
Scheme 3.295



Scheme 3.296

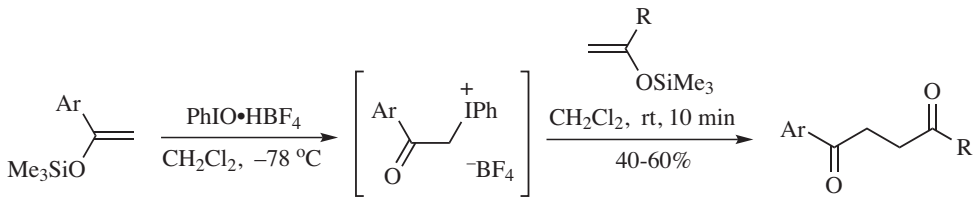


EWG = C(O)R, CN, NO_2; R^1 = Me, Et, $PhCH_2$, 4-$BrC_6H_4CH_2$, Ph, allyl; R^2 = Me, Et, Bu^t



R^1 = H, OH, CO_2H, Br, NO_2; R^2 = H, Ph, $HOCH_2$

Scheme 3.297



761 **762**

Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$
R = alkyl or aryl

Scheme 3.298

3.1.22.4 Alkylations and Fluoroalkylations

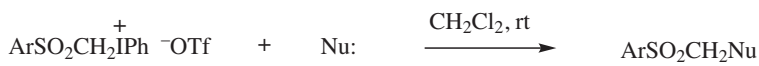
The unstable β-oxoalkyl(phenyl)iodonium salts **762,** generated *in situ* by a low-temperature reaction of silyl enol ethers **761** with a complex of iodosylbenzene and tetrafluoroboric acid (Section 2.1.9.5), have been utilized in synthetically useful carbon–carbon bond forming reactions with various silyl enol ethers (Scheme 3.298) and other C–nucleophiles to afford the respective products of C—C bond formation [209, 1014, 1015].

The relatively stable (arylsulfonylmethyl)iodonium salts **763** (Section 2.1.9.5) are efficient electrophilic alkylating reagents towards various organic nucleophiles (thiophenolate anion, amines, pyridine, triphenyl phosphine and silyl enol ethers). All these reactions proceed under mild conditions and selectively afforded the appropriate product of alkylation along with iodobenzene as the by-product (Scheme 3.299) [1016].

Fluoroalkyl(aryl)iodonium salts are the most stable and practically important class of alkyl(aryl)iodonium derivatives. The application of such salts as electrophilic fluoroalkylating reagents was reviewed in 1996 by Umemoto [1017]. Perfluoroalkyl(phenyl)iodonium triflates (FITS reagents) **764** are efficient perfluoroalkylating reagents toward various nucleophilic substrates, such as arenes, carbanions, alkynes, alkenes, carbonyl compounds, amines, phosphines and sulfides [1017]. Scheme 3.300 shows several representative examples of electrophilic perfluoroalkylations using FITS reagents.

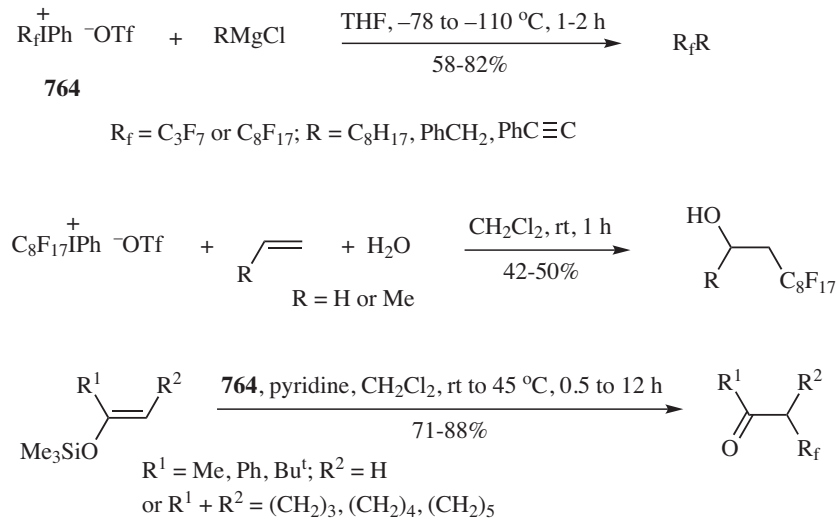
(Dihydroperfluoroalkyl)phenyliodonium triflates, $R_fCH_2I(Ph)OTf$, are electrophilic fluoroalkylating reagents with a reactivity pattern similar to FITS reagents **764** [1017]. The fluoroalkylation of amines is a particularly important reaction. For example, trifluoroethyl(phenyl)iodonium triflate **765** has been used for the N-trifluoroethylation of aminoalcohols (Scheme 3.301) [1018].

Likewise, fluoroalkyliodonium salt **766** (Section 2.1.9.5) is a useful reagent for fluoroalkylation of amino acids and peptides [1019–1024]. In particular, the reaction of iodonium salt **766** with the *tert*-butyl carboxyl ester of tyrosine (**767**) in the presence of collidine results in quantitative formation of the monoalkylation product **768** (Scheme 3.302) [1021, 1024]. Owing to this reactivity, iodonium salt **766** and other

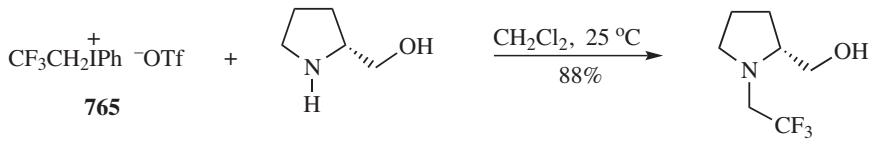


763 Ar = Ph or 4-MeC_6H_4
Nu: = PhS^-, PhO^-, R_3N, Ph_3P, silyl enol ethers, etc.

Scheme 3.299



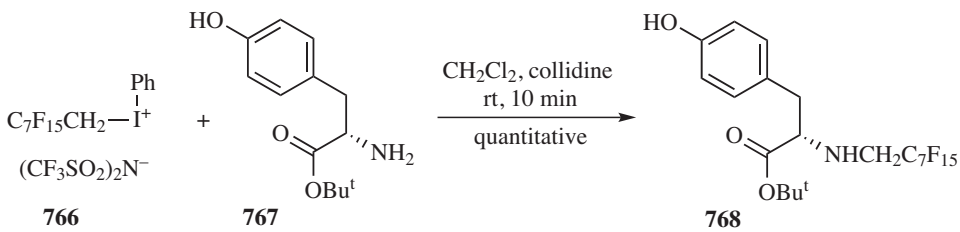
Scheme 3.300



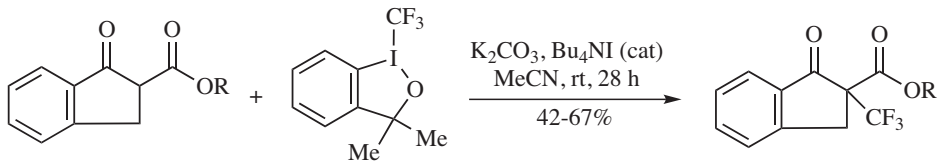
Scheme 3.301

(dihydroperfluoroalkyl)phenyliodonium triflimides can be used as fluorous capping reagents for facile purification of peptides synthesized on a solid phase [1021, 1024]. It has also been demonstrated that (dihydroperfluoroalkyl)phenyliodonium triflimide salts are useful for the regioselective N- or C-fluoroalkylation of imidazoles [1025].

Togni and coworkers have found that 1-trifluoromethylbenziodoxole **770** is a useful reagent for electrophilic trifluoromethylation of nucleophilic substrates. This reagent, in particular, reacts with β-ketoesters **769** under mild conditions in the presence of potassium carbonate to give α-trifluoromethylated product **771** in good yield (Scheme 3.303) [1026, 1027]. Likewise, this mild electrophilic trifluoromethylating



Scheme 3.302



769 R = Me, Et, Bu^t **770** **771**

Scheme 3.303

reagent can be used to transfer a CF_3 group to other C-centered nucleophiles, such as α-nitro esters [1027], as well as to S-centered nucleophiles (thiols and S-hydrogen phosphorothioates) [1027–1029], O-centered nucleophiles (alcohols, phenols and triflate anions) [1030–1033], N-centered nucleophiles (azoles and nitriles) [1034, 1035] and P-centered nucleophiles (secondary or primary aryl- and alkylphosphines) [1036–1038].

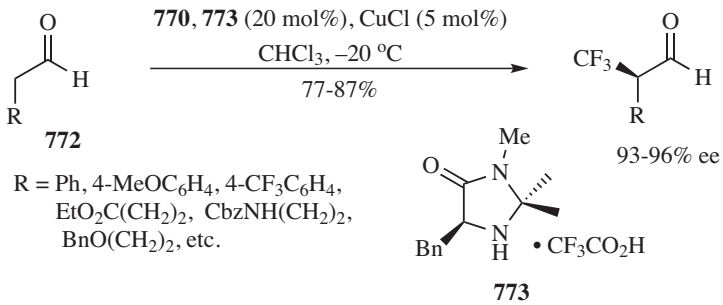
MacMillan and coworkers have reported the combination of organo- and Lewis acid-catalysis for the asymmetric α-trifluoromethylation of aldehydes **772** using hypervalent iodine reagent **770** and imidazolidinone catalyst **773** (Scheme 3.304) [1039]. The use of Lewis acid is crucial to obtain the product in high yield. A range of Lewis acids have been tried in this reaction and CuCl gave the best yield and enantioselectivity. The proposed mechanism starts from the initial Lewis acid-mediated opening of the benziodoxole reagent **770** followed by a sequence of steps including the formation of chiral enamine intermediate from the aldehyde and imidazolidinone catalyst and trifluoromethylation of this intermediate by the activated iodine(III) reagent [1039].

The analog of **770** bearing a $PhSO_2CF_2$ substituent on iodine (Section 2.1.8.1.11) has been found to act as an electrophilic (phenylsulfonyl)difluoromethylating reagent for various S-nucleophiles under mild reaction conditions [1040].

3.1.22.5 Cyanation

The stable cyanobenziodoxole **775** can be used as an efficient cyanating reagent toward *N,N*-dialkylarylamines. In a typical example, reagent **775** reacts with *N,N*-dimethylanilines **774** in 1,2-dichloroethane at reflux to afford the respective *N*-cyanomethyl-*N*-methylanilines **776** in good yield (Scheme 3.305) [1041].

This procedure has been applied to the synthesis of *N*-cyanomethyl-*N*-cyclopropylamine, which is a possible metabolite of cyclopropylamine-derived drugs [1042].

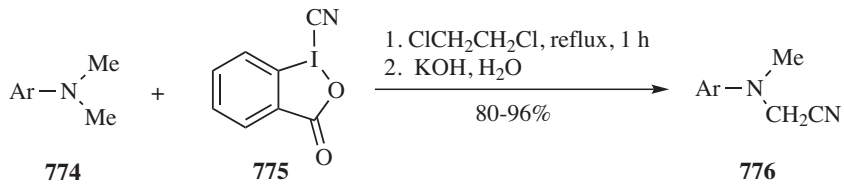


772

R = Ph, 4-MeOC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$, EtO$_2$C(CH$_2$)$_2$, CbzNH(CH$_2$)$_2$, BnO(CH$_2$)$_2$, etc.

773

Scheme 3.304



Ar = Ph, 4-BrC_6H_4, 4-MeC_6H_4, 1-naphthyl

Scheme 3.305

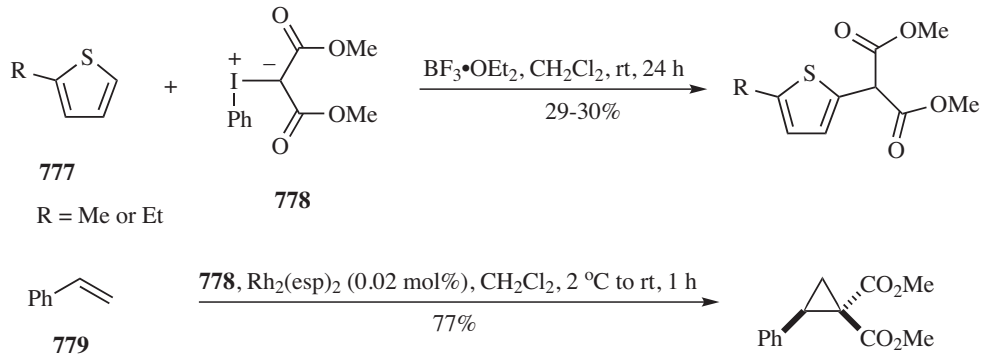
3.1.23 Reactions of Iodonium Ylides

Iodonium ylides can serve as convenient precursors to the respective carbene intermediates under thermal, photochemical, or catalytic conditions. A detailed discussion of the reaction mechanisms and synthetic applications of iodonium ylides as carbene precursors can be found in the 2004 review of Muller [1043].

Bis(methoxycarbonyl)(phenyliodinio)methanide (**778**), the most common iodonium ylide derived from malonate methyl ester, has found synthetic applications in the C—H insertion reactions [1044–1048] and the cyclopropanation of alkenes [1049–1055], including enantioselective cyclopropanations in the presence of chiral rhodium complexes [1056–1058]. Representative examples of these reactions are shown in Scheme 3.306 and include the BF_3-catalyzed bis(carbonyl)alkylation of 2-alkylthiophenes **777** [1045] and the optimized procedure for rhodium-catalyzed cyclopropanation of styrene **779** [1052].

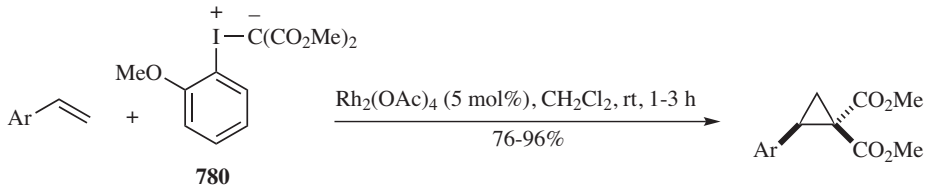
A particularly useful reagent in these carbenoid reactions is the highly soluble and reactive iodonium ylide **780** derived from malonate methyl ester and bearing an *ortho* methoxy substituent on the phenyl ring [1059]. This reagent shows higher reactivity than common phenyliodonium ylides in the Rh-catalyzed cyclopropanation, C–H insertion and transylidation reactions under homogeneous conditions. Scheme 3.307 shows representative examples of the carbenoid reactions of ylide **780** [1059].

Another synthetically useful reagent of this type is 5,5-dimethyl-1,3-cyclohexanedione phenyliodonium ylide (**781**) (Scheme 3.308), a relatively stable iodonium ylide synthesized by condensation of $PhI(OAc)_2$ with dimedone under basic condition [1060, 1061]. Under catalytic, thermal, or photochemical conditions, ylide **781** serves as an excellent carbenoid precursor; the transfer of such a carbenoid moiety to a suitable



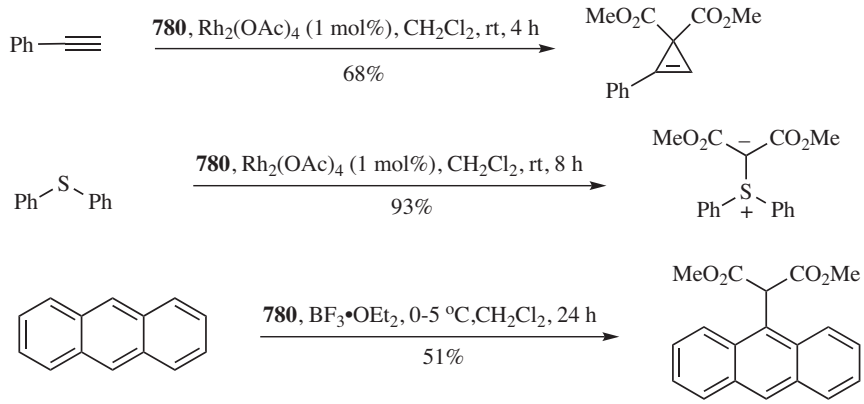
$Rh_2(esp)_2$ = bis[rhodium(α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid)]

Scheme 3.306

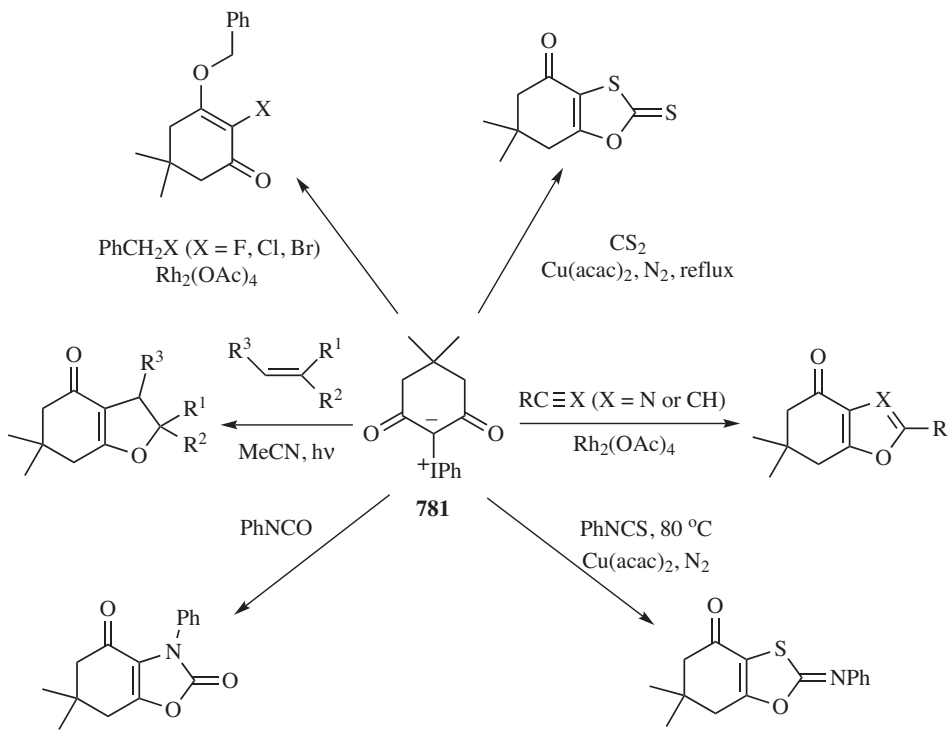


780

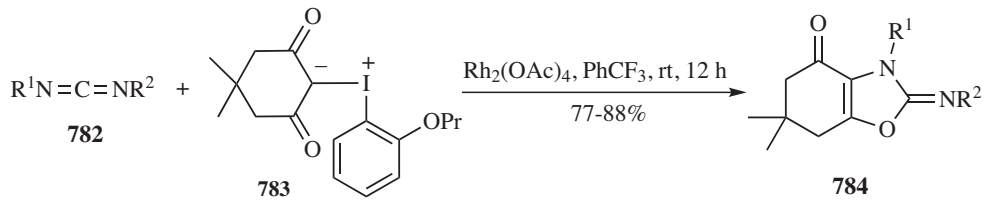
Ar = Ph, 4-MeC_6H_4, 4-$CF_3C_6H_4$, 4-BrC_6H_4, 4-ClC_6H_4, 3-MeC_6H_4, 4-$MeOC_6H_4$, etc.



Scheme 3.307



Scheme 3.308



$R^1 = R^2 = Pr^i$, *cyclo*-C_6H_{11}, 4-MeC_6H_4, 2,6-$Pr^i{}_2C_6H_3$, Me_3Si
or $R^1 = Et$, $R^2 = Me_2N(CH_2)_3$

Scheme 3.309

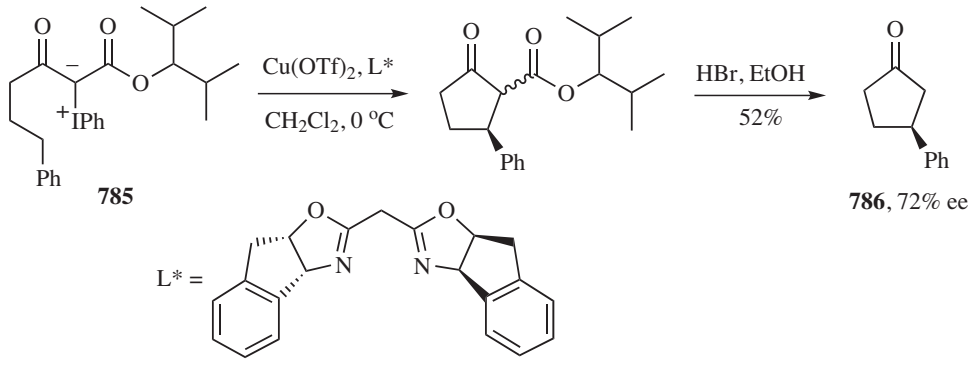
acceptor has found application in the synthesis of carbocycles or five-membered heterocycles as outlined in Scheme 3.308. Cycloadditions are typically observed in the reactions of ylide **781** with acetylenes [1062], ketenes [1060], nitriles [1062, 1063], isocyanates [1060, 1064], isothiocyanates [1065, 1066] and dienes [1067, 1068].

A modified, *o*-alkoxy-substituted ylide **783** has an improved solubility in nonpolar solvents, such as aromatic hydrocarbons and has a generally higher reactivity than ylide **781** [1069]. In particular, ylide **783** is a useful reagent for the preparation of oxazole derivatives **784** in the reaction with carbodiimides **782** under homogeneous conditions in the presence of Rh(II) or Cu(II) catalysts (Scheme 3.309) [1069].

The carbenoid reactions of iodonium ylides are effectively catalyzed by rhodium(II) or copper complexes [1043, 1058, 1070]. The product composition in the rhodium(II)-catalyzed reactions of iodonium ylides was found to be identical to that of the corresponding diazo compounds, which indicates that the mechanisms of both processes are similar and involve metallocarbenes as key intermediates as it has been unequivocally established for the diazo decomposition [1071]. Additional examples of the transition-metal-catalyzed carbenoid reactions of iodonium ylides are represented by the following publications: Rh(II)- or Cu(I)-catalyzed cyclopropanation reactions using the unstable ylides $PhIC(H)NO_2$ [1072] and $PhIC(CO_2Me)NO_2$ [1073, 1074] generated *in situ* from nitromethane and methyl nitroacetate; Rh(II)-catalyzed three-component coupling of an ether with a nitromethane-derived carbenoid generated from $PhIC(H)NO_2$; [1075] Rh(II)- or Cu(II)-catalyzed insertion of carbene into alkenyl C—H bond in flavones [1076] and highly phenylated ethylenes; [1077] Rh(II)-catalyzed reaction of iodonium ylides with conjugated compounds leading to efficient synthesis of dihydrofurans, oxazoles and dihydrooxepines [1068]; synthesis of various heterocycles by Rh(II)-catalyzed reactions of iodonium ylides with vinyl ethers, carbon disulfide, alkynes and nitriles [1055]; Rh(II)-catalyzed reaction of iodonium ylides with electron-deficient and conjugated alkynes leading to substituted furans [1078]; efficient synthesis of β-substituted α-haloenones by Rh(II)-catalyzed reactions of iodonium ylides with benzyl halides and acid halides [1079]; Rh(II)- or Cu(II)-catalyzed generation/rearrangement of onium ylides of allyl and benzyl ethers via iodonium ylides [1080]; and Rh(II)- or Cu(II)-catalyzed stereoselective cycloaddition of disulfonyl iodonium ylides with alkenes leading to 1,2,3-trisubstituted benzocyclopentenes [1081] or functionalized indanes [1082–1084].

The metal-catalyzed carbenoid decomposition of iodonium ylides has been applied in asymmetric reactions [1047, 1053, 1074, 1085]. For example, the copper(II)-catalyzed intramolecular C—H insertion of phenyliodonium ylide **785** in the presence of chiral ligands followed by hydrolysis and decarboxylation affords product **786** in moderate yield with up to 72% ee (Scheme 3.310) [1047].

Ochiai and coworkers have reported several useful reactions of the unstable monocarbonyl iodonium ylides **788**, which can be quantitatively generated from (*Z*)-(2-acetoxyvinyl)iodonium salts **787** via an ester exchange reaction with lithium ethoxide in THF at low temperature (Scheme 3.311) [1086–1088]. Ylide **788,** generated



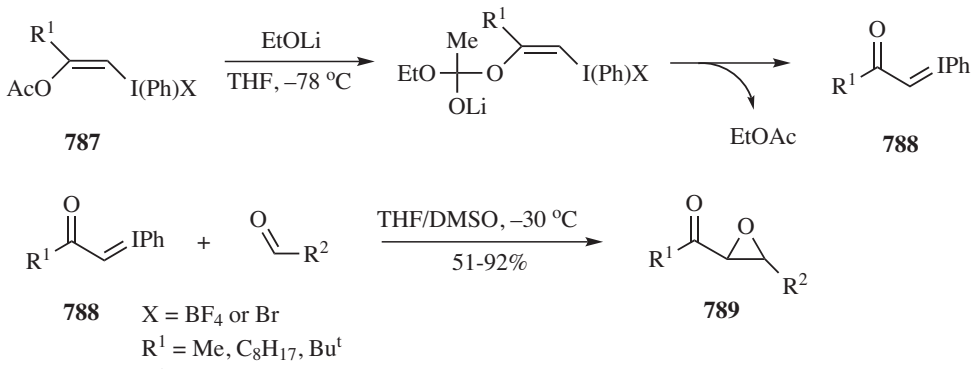
Scheme 3.310

in situ from iodonium salts **787,** reacts with aldehydes in THF/DMSO at low temperature to afford α,β-epoxy ketones **789** with predominant formation of the *trans* isomers. A Hammett reaction constant ($\rho = 2.95$) for this reaction indicates that monocarbonyl iodonium ylides **788** are moderately nucleophilic [1086].

Monocarbonyl iodonium ylides, generated *in situ* from iodonium salts **787,** undergo alkylidene transfer reactions to activated imines **790,** yielding 2-acylaziridines **791** in good yields (Scheme 3.312). The stereochemical outcome of this aziridination is dependent on both the activating groups of the imines and the reaction solvents; for example, aziridination of *N*-(2,4,6-trimethylbenzenesulfonyl)imines in THF affords *cis*-aziridines as a major product, while that of *N*-benzoylimines in THF/DMSO or THF gives the *trans* isomer stereoselectively [1087, 1088].

Treatment of iodonium tetrafluoroborates **792** with triethylamine in methanol in the presence of triphenylphosphine and aldehydes results in Wittig olefination to give products **793** (Scheme 3.313), which involves the intermediacy of monocarbonyl iodonium ylides **788** and their subsequent conversion into the respective phosphonium ylides upon the *in situ* reaction with Ph_3P [1089].

The interaction of monocarbonyl iodonium ylides, generated by the ester exchange of (*Z*)-(2-acetoxyvinyl)iodonium salts **792** with EtOLi, with organoboranes affords ketones **795,** probably via intermediate formation of the hitherto unknown α-boryl ketones **794** (Scheme 3.314) [1090].

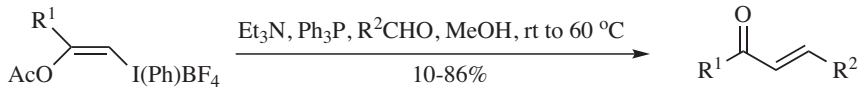


Scheme 3.311

787 **790** **791**

X = BF_4 or Br
R^1 = Me, C_8H_{17}, Bu^t
R^2 = Ph, R^3 = SO_2Ph; R^2 = Ph, R^3 = COPh; R^2 = Ph, R^3 = SO_2Me; etc.

Scheme 3.312



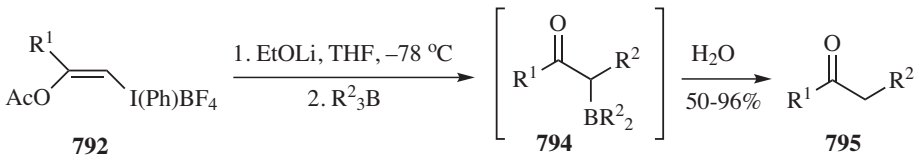
792 R^1 = Me, C_8H_{17}, $Ph(CH_2)_3$, Bu^t **793**
R^2 = Ph, C_9H_{19}, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-ClC_6H_4, etc.

Scheme 3.313

The mixed phosphonium–iodonium ylides (Section 2.1.10.1), such as the tosylate **796,** represent a useful class of reagents that combine in one molecule the synthetic advantages of a phosphonium ylide and an iodonium salt [1091–1100]. Specifically, phosphorane-derived phenyliodonium tosylate **796** reacts with soft nucleophiles, such as iodide, bromide, benzenesulfinate and thiophenolate anions, to form selectively the respective α-functionalized phosphonium ylides **797** (Scheme 3.315), which can be further converted into alkenes (e.g., **798**) by the Wittig reaction with aldehydes [1092]. The analogous arsonium–iodonium ylides have a similar reactivity toward nucleophiles [1091, 1094, 1101].

3.2 Synthetic Applications of Iodine(V) Compounds

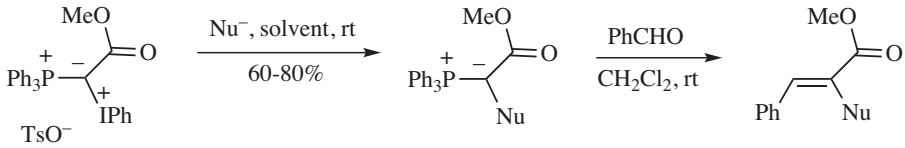
The chemistry of λ^5-iodanes in general has been less developed than with the λ^3-iodanes [1102]. Significant interest in these compounds originated in 1983, when Dess and Martin reported a simple two-step preparation of the triacetate **800** via the bromate oxidation of 2-iodobenzoic acid to 2-iodoxybenzoic acid (IBX, **799**) followed by heating with acetic anhydride (Scheme 3.316) [1103]. The authors have also found that the



792 **794** **795**

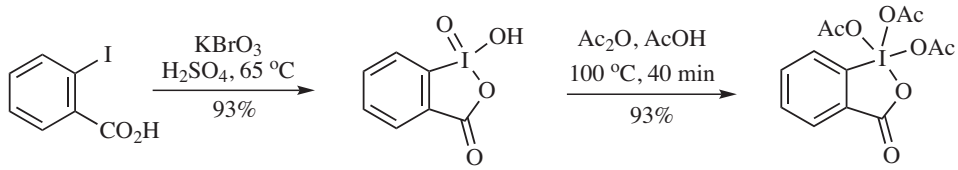
R^1 = C_8H_{17}, $Ph(CH_2)_3$, Bu^t
R^2 = Et, Bu, Bu^s, $Ph(CH_2)_3$, cyclohexyl, cyclopentyl, Ph, 4-MeC_6H_4

Scheme 3.314



Nu = I, Br, PhS, $PhSO_2$, etc.
solvent = MeOH, CH_2Cl_2, or CH_2Cl_2/DMSO

Scheme 3.315



Scheme 3.316

triacetate **800,** which they referred to as periodinane, is a useful reagent for the facile and efficient oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. Within a few years of publication of this paper, compound **800** found widespread application in organic synthesis under the name of the Dess–Martin periodinane (DMP).

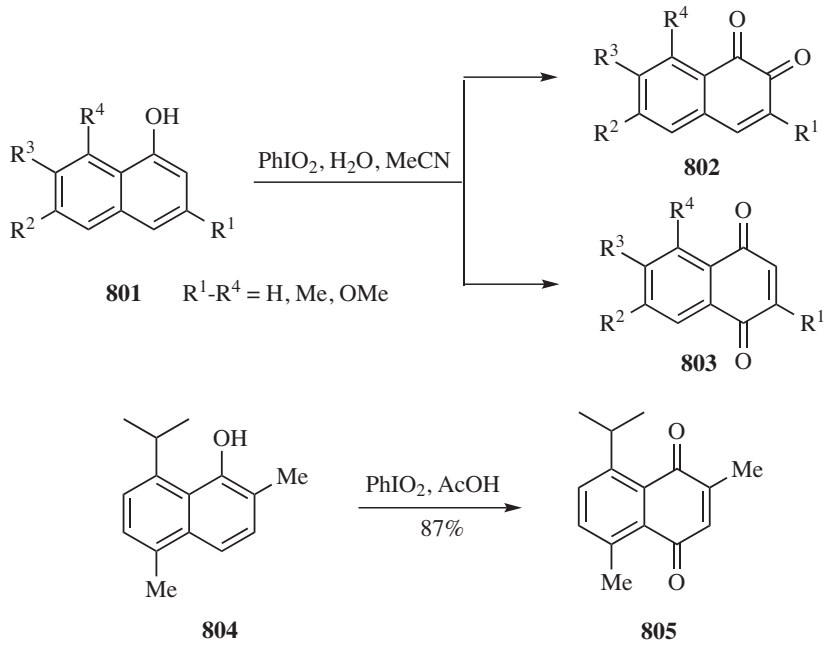
Both IBX (**799**) and DMP (**800**) are now extensively employed in organic synthesis as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds, as well as for various other synthetically useful oxidative transformations [1102, 1104–1106]. For optimized experimental procedures for the preparation of IBX (Section 2.2.3.1) and DMP (Section 2.2.3.2), see Chapter 2.

Despite their importance, IBX and DMP are not perfect reagents and have some serious drawbacks. IBX is potentially explosive and it is insoluble in common organic solvents due to strong intermolecular secondary bonding, which creates a three-dimentional polymeric structure, while DMP is highly sensitive to moisture. In addition, IBX and DMP are not perfect with respect to the principles of green chemistry since they are normally used as non-recyclable, stoichiometric reagents in non-recyclable organic solvents, which have potentially damaging environmental effects. Several polymer-supported, recyclable IBX derivatives and analogs with improved properties have been introduced in the twenty-first century and utilized in organic synthesis (Chapter 5).

3.2.1 Noncyclic and Pseudocyclic Iodylarenes

Noncyclic iodylarenes have received only limited practical application because of their explosive properties and insolubility in organic solvents. In particular, iodylbenzene, $PhIO_2$, can oxidize alcohols to ketones [1107], or it can be used to generate alkoxy radicals from alcohols under photochemical conditions [1108]. Owing to its polymeric structure and insolubility in organic solvents, iodylbenzene has a relatively low reactivity as an oxidizing reagent and its reactions are usually conducted at high temperature or in the presence of a catalyst.

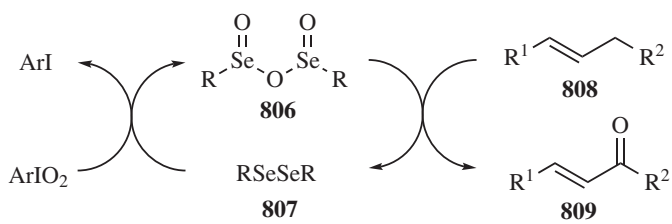
Several examples of synthetic application of iodylbenzene are illustrated below in Schemes 3.317–3.327. Specifically, iodylbenzene in an aqueous acetonitrile or acetic acid media oxidizes activated aromatic rings,



Scheme 3.317

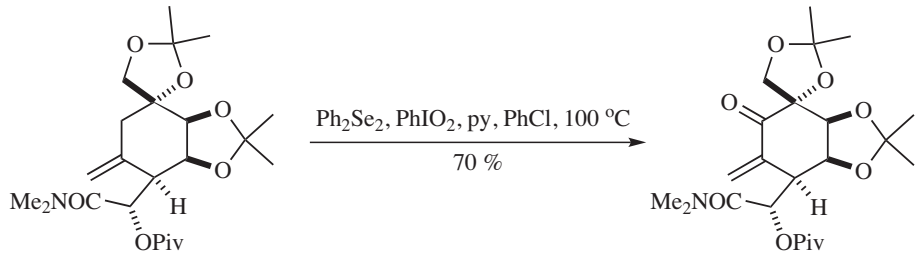
yielding quinones or quinone imines [1109]. For example, substituted 1-naphthols **801** can be converted into corresponding 1,2- and 1,4-naphthoquinones **802** and **803** (Scheme 3.317) [1109]. This protocol was utilized in the synthesis of cadalenquinone (**805**), a naturally occurring sesquiterpene, starting from naphthol **804** [1110].

Several catalytic oxidative systems using iodylbenzene as a stoichiometric co-oxidant have been developed. Barton and coworkers have developed an efficient allylic oxidation protocol with 2-pyridineseleninic anhydride **806** (R = 2-Py) as the principal oxidant, generated *in situ* by oxidation of the corresponding diselenide **807** with iodylbenzene or 3-iodylbenzoic acid (Scheme 3.318) [1111]. This reaction proceeds in chlorobenzene at 100 °C within 2.5–3 h. Most likely, the initial oxidation of alkenes **808** leads to the formation of allylic alcohols, which undergo further oxidation into α,β-unsaturated ketones **809.** In contrast with the



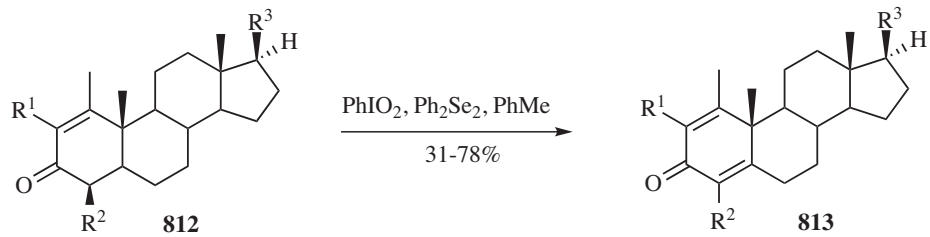
Ar = Ph or 3-C_6H_4; R = Ph or 2-Py; R^1 and R^2 = alkyl

Scheme 3.318



810 **811**

Scheme 3.319



812 **813**

R^1 = H, R^2 = Me, R^3 = OTBDMS; R^1 = Me, R^2 = H, Me, R^3 = OAc

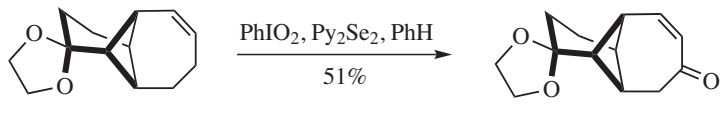
Scheme 3.320

classic allylic oxidation technique employing selenium dioxide, only a catalytic amount of the corresponding diselenide is required.

This convenient oxidation protocol has been used in several syntheses of complex organic molecules. In the stereoselective synthesis of (–)-tetrodotoxin by Du Bois and coworkers, the protected pentaol **810** was oxidized with $PhIO_2/Py_2Se_2$ to afford the unsaturated carbonyl compound **811** in a good yield (Scheme 3.319) [1112].

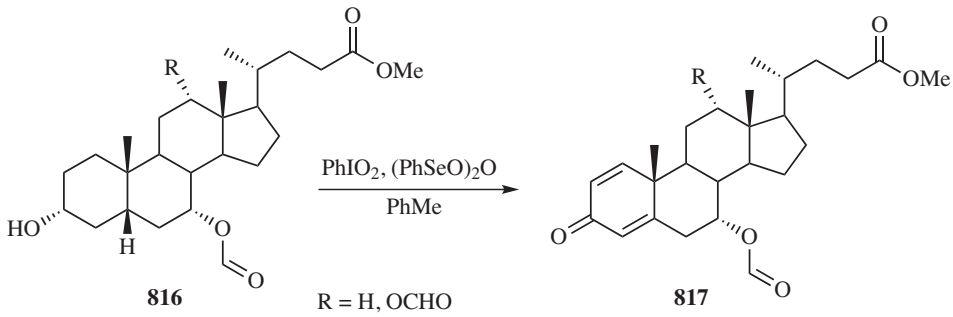
Based on this oxidizing system, a dehydrogenation protocol in the regioselective synthesis of ring A of polymethylated steroids has been developed. Intermediates **812** were converted into the corresponding 1,4-dienes **813,** which were key precursors to the target steroids (Scheme 3.320) [1113].

The procedure, employing 2-pyridyldiselenide, was used in the synthesis of tricyclo[5.4.0.$0^{2,8}$]undeca-3,5,9-triene, an interesting spiro compound with two mutually perpendicular π-systems [1114]. During this synthesis, the protected ketone **814** was oxidized to give the unsaturated ketone **815** in 51% yield (Scheme 3.321).



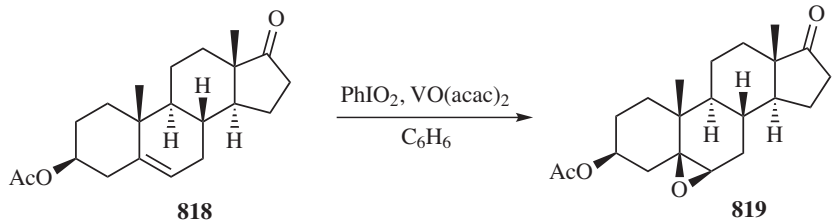
814 **815**

Scheme 3.321



816 **817**

Scheme 3.322



818 **819**

Scheme 3.323

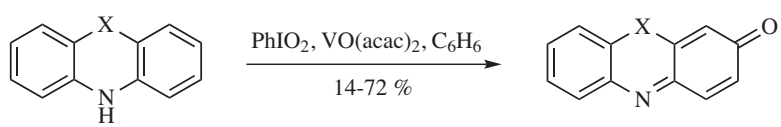
A method for the preparation of allochenodeoxycholic and allocholic acids from the corresponding cholic acids has been reported. The key step in the synthesis is the oxidation–dehydrogenation of 3α-hydroxy-5β-bile acid formyl esters **816** to give oxodienes **817** (Scheme 3.322) [1115].

A series of oxidative transformations with iodylbenzene as the co-oxidant of vanadyl bis(acetylacetonate) have been reported [1116–1118]. In the presence of $VO(acac)_2$, iodylbenzene oxidizes Δ^5-steroids into epoxides; a radical mechanism was suggested for this reaction. Epoxidation of cholest-5-ene-3-one occurred with high α-selectivity, while the remaining substrates gave mainly β-epoxides. Oxidation of *trans*-dehydroepiandrosterone acetate (**818**) afforded epoxide **819** (Scheme 3.323) [1116].

A new route to quinone imines has been introduced based on this oxidizing system. The oxidation of the tricyclic scaffold **820** gives quinone imines **821** in moderate yields (Scheme 3.324) [1117].

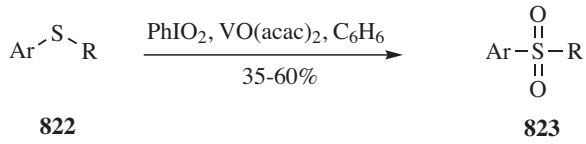
Aryl sulfides **822** could be also converted by this reagent system into sulfoxides, sulfones and S-dealkylated products. Repeated treatment affords sulfones **823** in moderate yields (Scheme 3.325) [1118].

Kita and coworkers developed a catalytic asymmetric oxidation using iodoxybenzene in a cationic reversed micellar system in the presence of chiral tartaric acid derivatives. Under these conditions, sulfides **824**



820 X = S, O, CH_2CH_2 **821**

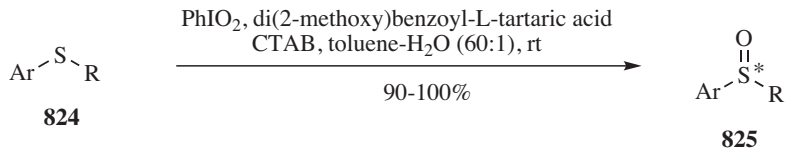
Scheme 3.324



822 **823**

Ar = Ph, 4-FC_6H_4
R = Me, $MeO(CO)CH_2$, $Ph(CO)CH_2$, CH_2CN, $PhCH_2$

Scheme 3.325



824 **825**

R = Me or Et
Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 4-CNC_6H_4, 4-BrC_6H_4, 3-$NO_2C_6H_4$, 2-naphthyl, etc.

up to 72% ee

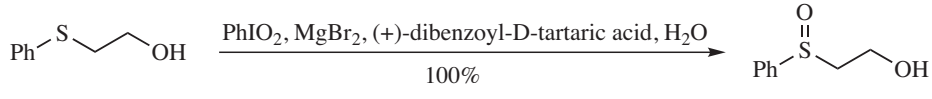
Scheme 3.326

are oxidized to sulfoxides **825** in high chemical yield with moderate to good enantioselectivity (Scheme 3.326) [1119].

A purely water-based oxidation procedure has been developed by Kita using magnesium bromide as a catalyst instead of cetyltrimethylammonium bromide (CTAB). An asymmetric oxidizing reagent is formed by mixing (+)-dibenzoyl-D-tartaric acid, $MgBr_2$ and $PhIO_2$ in water for 5 min at room temperature. Treatment of 4-MeC_6H_4SMe with this oxidizing reagent at 0 °C for 24 h affords (*R*)-4-$MeC_6H_4S(O)Me$ in quantitative yield and 59% enantiomeric excess. Oxidation of 2-(phenylthio)ethanol (**826**) under these conditions gives sulfoxide **827,** leaving the primary hydroxyl group unaffected (Scheme 3.327) [1120].

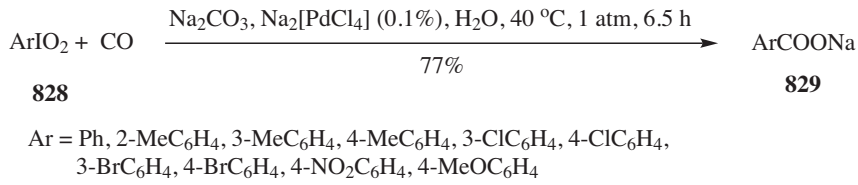
Iodylarenes **828** react with CO in water in the presence of sodium tetrachloropalladate(II) and sodium carbonate at ambient temperature to furnish the corresponding carboxylic acid salts **829** (Scheme 3.328) [1121].

Iodylaryl derivatives bearing an appropriate substituent in the *ortho*-position to the iodine are characterized by the presence of a pseudocyclic structural moiety due to a strong intramolecular secondary bonding between the hypervalent iodine center and the oxygen atom in the *ortho*-substituent. Compared to the noncyclic aryliodyl derivatives, pseudocyclic iodine(V) compounds have much better solubility, which is explained by a partial disruption of their polymeric nature due to the redirection of secondary bonding [1122–1126]. Particularly useful reagents of this type are IBX esters (Section 2.2.2). IBX esters can oxidize alcohols to the respective aldehydes or ketones in the presence of trifluoroacetic acid or boron trifluoride etherate



826 **827**

Scheme 3.327



Scheme 3.328

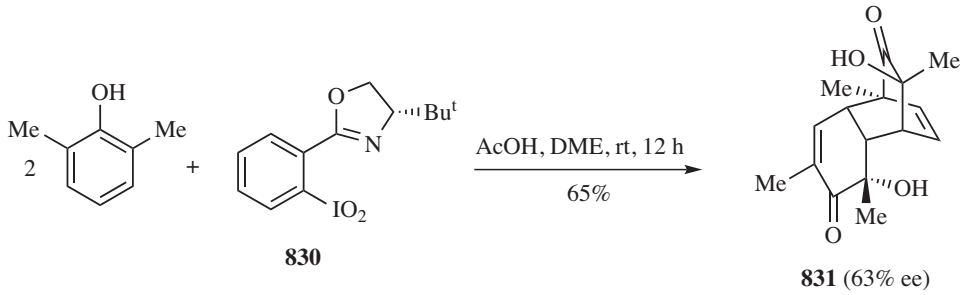
[1123]. Isopropyl 2-iodoxybenzoate is a useful reagent for the clean, selective oxidation of organic sulfides to sulfoxides [1127]. This reaction proceeds without overoxidation to sulfones and is compatible with the presence of the hydroxy group, double bond, phenol ether, benzylic carbon and various substituted phenyl rings in the molecule of organic sulfide. Duschek and Kirsch have reported that isopropyl 2-iodoxybenzoate in the presence of trifluoroacetic anhydride can be used for the α-hydroxylation of β-keto esters at room temperature in THF [1128].

IBX esters can serve as stable and efficient sources of oxygen in the metalloporphyrin-catalyzed oxidations of hydrocarbons and the reactivity of isopropyl 2-iodoxybenzoate as an oxygenating reagent is similar to that of commonly used iodosylbenzene, which is a thermally unstable and potentially explosive compound [713, 1129, 1130].

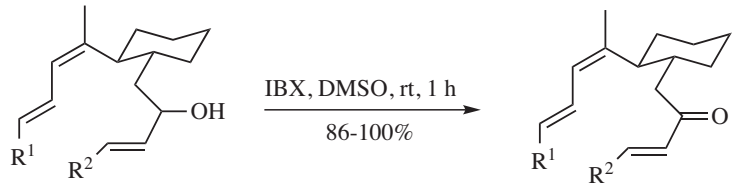
The chiral, pseudocyclic 2-(*o*-iodoxyphenyl)-oxazolines **830** have been found to transform *ortho*-alkylphenols into *ortho*-quinol Diels–Alder dimers (e.g., **831**) with significant levels of asymmetric induction (Scheme 3.329) [1131].

3.2.2 2-Iodoxybenzoic Acid (IBX)

Applications of IBX in organic synthesis have been summarized in several comprehensive reviews [1105, 1106]. IBX is a particularly useful oxidant for the selective oxidation of alcohols to carbonyl compounds, even in complex molecules in the presence of other functional groups. Primary alcohols are oxidized by IBX in DMSO to the corresponding aldehydes at room temperature without overoxidation to the acids. The chiral primary alcohols are oxidized without epimerization and various functional groups like thioethers, amines, carboxylic acids, esters, carboxamides and both conjugated and isolated double bonds are compatible with IBX [1132, 1133]. Several representative examples of alcohol oxidations using IBX in DMSO are shown below in Schemes 3.330–3.335.

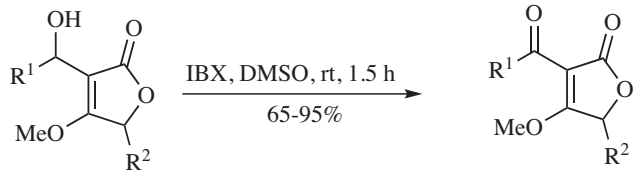


Scheme 3.329



832 R^1 = H, SPh;
R^2 = H, SO_2Ph, CO_2Me, Ts

833



834 **835**

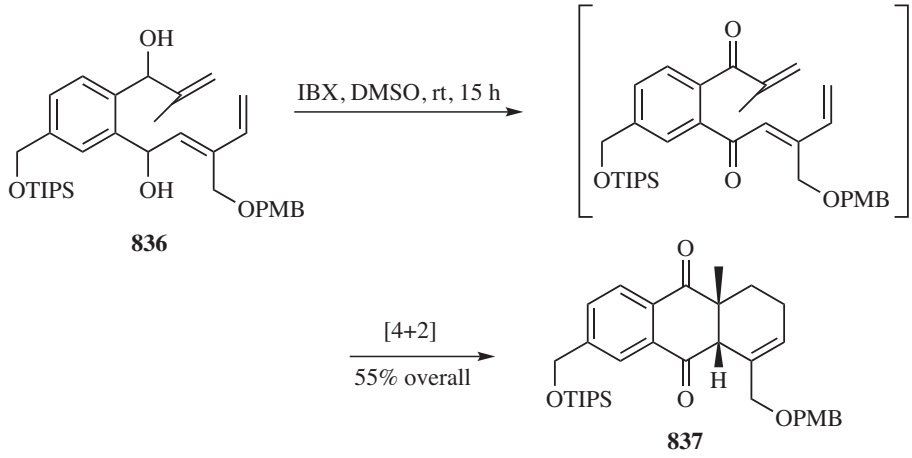
R^1 = Bu^i, Bu^t, Pr, Ph, $(CH_2)_2CH_2OTBDMS$; R^1 = H, Me

Scheme 3.330

Specifically, the allylic alcohols **832** are selectively oxidized by IBX to ketones **833** in high yield (Scheme 3.330) [1134]. The oxidation of alcohols **834** with IBX selectively affords 5-monosubstituted 3-acyl-4-*O*-methyl tetronates **835,** which are structurally similar to the tetrodecamycin antibiotics [1135].

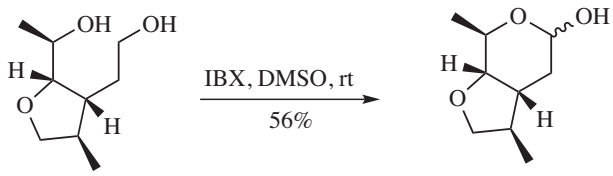
The IBX oxidation of diol **836** has been utilized in the synthesis of the functionalized hexahydroanthracene dione **837** (Scheme 3.331), a model for the D ring of taxoids [1136].

Likewise, the total synthesis of the antifungal agent GM222712 was accomplished by a selective oxidation of diol **838** to hemiacetal **839** (Scheme 3.332) [1137].



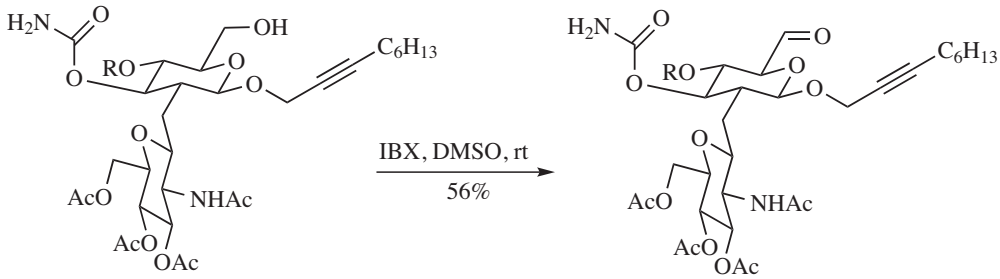
836 **837**

Scheme 3.331



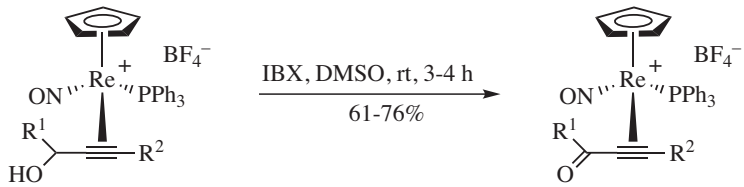
838 **839**

Scheme 3.332



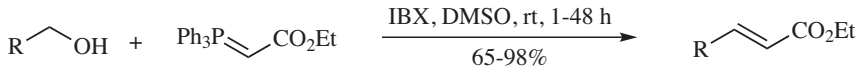
840 R = TBDMS

Scheme 3.333



841 R^1, R^2 = H or Me **842**

Scheme 3.334



843 **844**

R = Ph, PhCH=CH, Me_2C=$CHCH_2CH_2$(Me)C=CH, HC≡C, C_5H_{11}C≡C, etc.

Scheme 3.335

The IBX oxidation of carbohydrate **840** has been employed in synthetic studies of moenomycin A disaccharide analogs (Scheme 3.333) [1138].

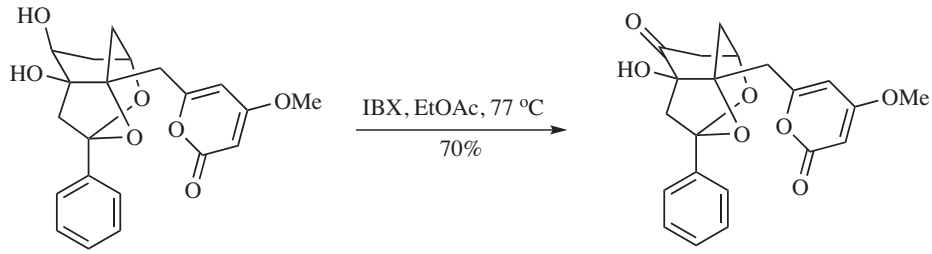
The chiral rhenium complexes of allylic and propargylic alcohols **841** are selectively oxidized by IBX to the unsaturated carbonyl compounds **842** in good yields (Scheme 3.334) [1139].

A one-pot oxidation of benzylic, allylic and propargylic alcohols, as well as diols, with IBX in the presence of the stabilized Wittig ylide **843** affords α,β-unsaturated esters **844** in generally good yields (Scheme 3.335) [1140]. This is a useful one-pot procedure because the intermediate aldehydes are often unstable and difficult to isolate.

Selective oxidation of alcohols using IBX has been utilized in numerous syntheses, such as the total synthesis of (–)-decarbamoyloxysaxitoxin [1141], total synthesis of abyssomicin C and atrop-abyssomicin C [1142], stereoselective synthesis of pachastrissamine (jaspine B) [1143], syntheses of (±)-pterocarpans and isoflavones [1144], total synthesis of (±)-nitidanin [1145], total synthesis of lagunamycin [1146], synthesis of (–)-agelastatin [1147], syntheses of heliannuols B and D [1148], total syntheses of (–)-subincanadines A and B [1149], synthesis of marine sponge metabolite spiculoic acid A [1150] and in the total synthesis of a cyclic depsipeptide somamide A [1151]. Likewise, the oxidation of alcohols with IBX in DMSO has also been used in the development of a new silyl ether linker for solid-phase organic synthesis [1152], in the synthesis of optically pure highly functionalized tetrahydroisoquinolines [1153], in the kinetic study of organic reactions on polystyrene grafted microtubes [1154] and in the preparation of Fmoc-protected amino aldehydes from the corresponding alcohols [1155].

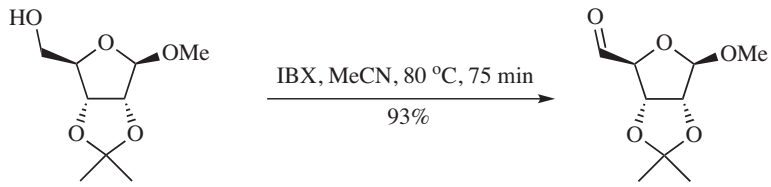
IBX is especially useful for the oxidation of 1,2-diols. Frigerio and Santagostino reported in 1994 that IBX, in contrast to DMP and iodylarenes, smoothly oxidizes 1,2-diols to α-ketols or α-diketones without cleaving the glycol C—C bond [1132]. More recently, Moorthy and coworkers have investigated the reactions of IBX with various vicinal diols and found that the oxidative cleavage of the C—C bond, as well as the oxidation to α-ketols or α-diketones, can occur in these reactions [1156]. In DMSO solutions, IBX oxidatively cleaves strained and sterically hindered *syn* 1,2-diols, while the non-hindered secondary glycols are oxidized to α-ketols or α-diketones. The use of trifluoroacetic acid as a solvent leads to efficient oxidative fragmentation of 1,2-diols of all types [1156]. The oxidation of 1,2-diols using IBX in DMSO has been utilized for the synthesis of α-ketols [1157–1159] or α-diketones [1160]. For example, in a key step of the total synthesis of the streptomyces maritimus metabolite wailupemycin B, IBX oxidation of the diol precursor **845** led to desired hydroxyketone **845** without any cleavage of the glycol C—C bond (Scheme 3.336) [1157].

The synthetic usefulness of IBX in general is significantly restricted by its low solubility in most organic solvents with the exception of DMSO. However, in several publications it has been shown that IBX can be used as effective oxidant in solvents other than DMSO [1161–1163]. More and Finney have found that primary and secondary alcohols can be oxidized into the corresponding aldehydes or ketones in excellent



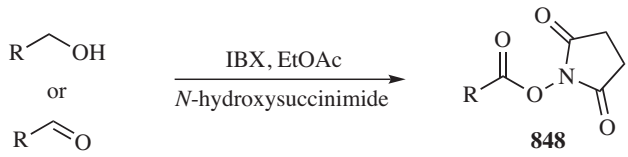
845 **846**

Scheme 3.336



847

Scheme 3.337



848

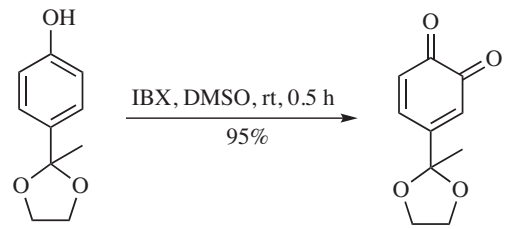
Scheme 3.338

yields (90–100%) by heating a mixture of alcohol and IBX in common organic solvents [1161]. All reaction by-products can be completely removed by filtration. This method has been used for the efficient preparation of the ribosyl aldehyde **847** (Scheme 3.337), the key intermediate in the stereoselective synthesis of the core structure of the polyoxin and nikkomycin antibiotics [1162].

An IBX-mediated conversion of primary alcohols (or aldehydes) into *N*-hydroxysuccinimide esters **848** has been developed by Giannis and coworkers [1164]. The generality of this procedure was demonstrated on various aliphatic, allylic and benzylic alcohols (Scheme 3.338).

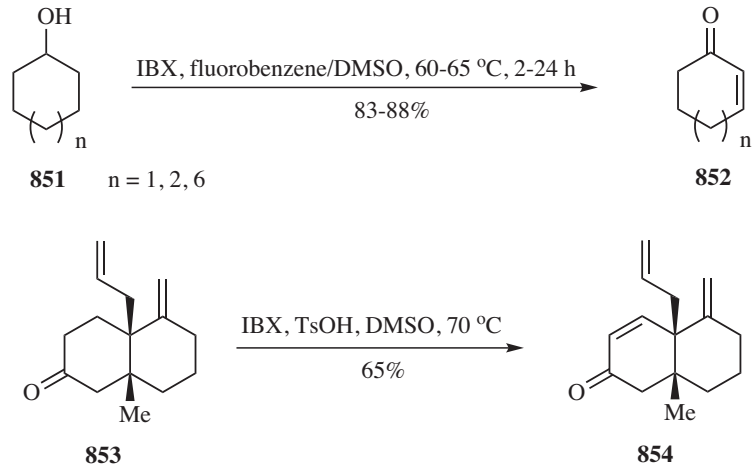
IBX in DMF or DMSO has been shown to be an excellent reagent for the oxidation of various phenols to *o*-quinones [1165]. This procedure was used for the oxidation of phenol **849** to quinone **850** (Scheme 3.339), the key intermediate in total synthesis of a novel cyclooxygenase inhibitor (±)-aiphanol [1166]. The same protocol was utilized in the synthesis of (±)-brazilin, a tinctorial compound found in the alcoholic extracts of trees collectively referred to as Brazil wood [1167].

The IBX-mediated oxygenative dearomatization of phenols leading to cyclohexa-2,4- or -2,5-dienone systems is a particularly useful synthetic transformation [292]. Representative examples include the use of IBX in key oxidation steps in the total synthesis of the resveratrol-derived polyphenol natural products



849 **850**

Scheme 3.339

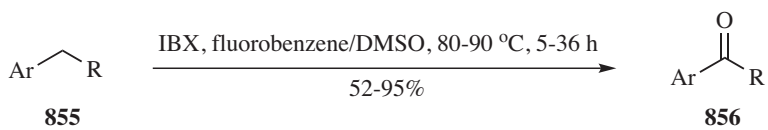


Scheme 3.340

(–)-hopeanol and (–)-hopeahainol A [1168], the synthesis of carnosic acid and carnosol [1169] and the total synthesis of the bis-sesquiterpene (+)-aquaticol [1170].

The practical value of IBX as a reagent has been extended to various other synthetically useful oxidative transformations. In a series of papers, Nicolaou and coworkers have demonstrated the utility of IBX for the one-step synthesis of α,β-unsaturated carbonyl systems from saturated alcohols and carbonyl compounds [1171–1173], for the selective oxidation of the benzylic carbon [1174, 1175], for the oxidative cyclization of anilides and related compounds [1176–1179] and for the synthesis of amino sugars and libraries thereof [1179]. Specifically, alcohols, ketones and aldehydes are oxidized to the corresponding α,β-unsaturated species in one pot using IBX under mild conditions [1172]. For example, cycloalkanols **851** react with two equivalents of IBX in a 2 : 1 mixture of either fluorobenzene or toluene and DMSO under gentle heating to afford the corresponding α,β-unsaturated ketones **852** in good yields (Scheme 3.340) [1172]. A similar oxidative dehydrogenation of a cyclohexanone derivative **853** to the respective enone **854** has been employed in the total synthesis of (–)-anominine [1180].

IBX is an efficient and selective reagent for the oxidation of alkylarenes **855** at the benzylic positions to give ketones **856** (Scheme 3.341) [1174]. This reaction is quite general and can tolerate various substituents within the aromatic ring. Overoxidation to the corresponding carboxylic acids is not observed even in the presence of electron-rich substituents.

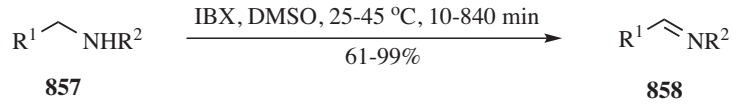


855 **856**

Ar = Ph, 4-Bu^{t}C$_6$H$_4$, 2-MeC$_6$H$_4$, 3-IC$_6$H$_4$, 4-BrC$_6$H$_4$, 3,4-(MeO)$_2$C$_6$H$_3$, 2-PhC$_6$H$_4$, 4-(4-pyridyl)C$_6$H$_4$, etc.

R = H, C$_3$H$_7$, etc.

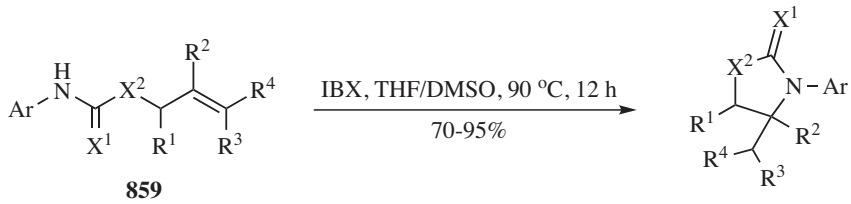
Scheme 3.341



857 **858**

R^1 = Ph, 4-BrC_6H_4, 4-$MeOC_6H_4$, etc.
R^2 = 4-BrC_6H_4, 4-$MeOC_6H_4$, Me, OH, OBn, etc.

Scheme 3.342



859 **860**

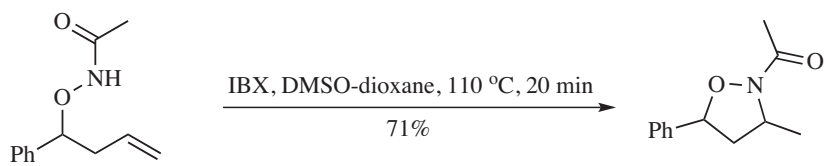
X^1 = O, S; X^2 = CH_2, O, N
Ar = Ph, 3-EtC_6H_4, 3-BrC_6H_4, 3-FC_6H_4, 4-EtC_6H_4, etc.
R^1 - R^4 = H, alkyl, cycloalkyl, etc.

Scheme 3.343

Similar to the oxidation of alcohols, secondary amines **857** can be oxidized with IBX in DMSO to yield the corresponding imines **858** in good to excellent yields (Scheme 3.342) [1175].

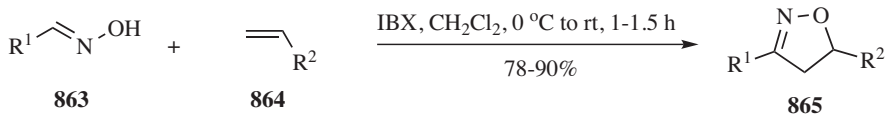
Various heterocycles **860** can be synthesized by the treatment of unsaturated aryl amides, carbamates, thiocarbamates and ureas **859** with IBX (Scheme 3.343) [1176, 1177]. The mechanism of this reaction has been investigated in detail [1178]. On the basis of solvent effects and D-labeling studies, it was proposed that the IBX-mediated cyclization of anilides in THF involves an initial single-electron transfer (SET) to a THF–IBX complex followed by deprotonation, radical cyclization and concluding termination by hydrogen abstraction from THF [1178]. A similar IBX-mediated cyclization has been applied in the synthetic protocol for the stereoselective preparation of amino sugars [1179].

Studer and Janza have developed a method for the generation of alkoxyamidyl radicals starting from the corresponding acylated alkoxyamines using IBX as a SET oxidant [1181]. For example, the stereoselective 5-*exo* cyclization of the respective N-centered radical generated from alkoxyamide **861** affords isoxazolidine **862** (Scheme 3.344) [1181].



861 **862**

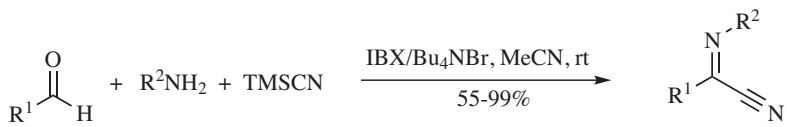
Scheme 3.344



863 **864** **865**

R^1 = aryl, heteroaryl; R^2 = CO_2Me, CN, OAc

Scheme 3.345



866

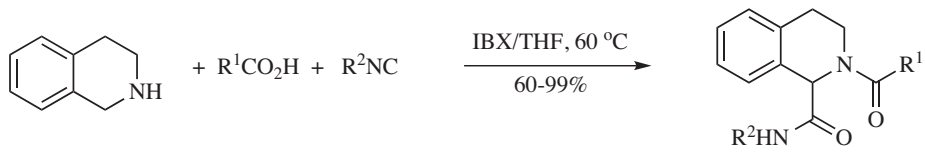
R^1 = Ph, 4-$MeOC_6H_4$, 2,6-$Cl_2C_6H_3$, PhC=CH, $Ph(CH_2)_2$, Pr^i, etc.
R^2 = $Ph(CH_2)_2$, Bu^t, 4-$MeOC_6H_4$, Ph, etc.

Scheme 3.346

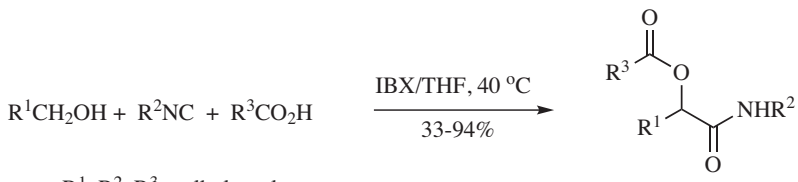
IBX has also been used for the preparation of the 3,5-disubstituted isoxazolines **865.** The oxidation of aldoximes **863** with IBX produces the respective nitrile oxides, which then undergo 1,3-dipolar addition with an alkene component **864** to give final products **865** (Scheme 3.345) [1182].

A one-pot three-component synthesis of α-iminonitriles **866** via an IBX/tetrabutylammonium bromide-mediated oxidative Strecker reaction has been developed (Scheme 3.346) [1183]. This methodology was employed in a two-step synthesis of indolizidines via a microwave-assisted intramolecular cycloaddition of α-iminonitriles.

The IBX-mediated oxidative Ugi-type multicomponent reaction of tetrahydroisoquinoline with isocyanides and carboxylic acids affords the nitrogen- and carbon-functionalized tetrahydroisoquinolines **867** in good to excellent yields [1184]. Likewise, the three-component Passerini reaction of an alcohol, carboxylic acid and an isonitrile in the presence of IBX affords the corresponding α-acyloxy carboxamides **868** in generally high yields (Scheme 3.347) [1185].



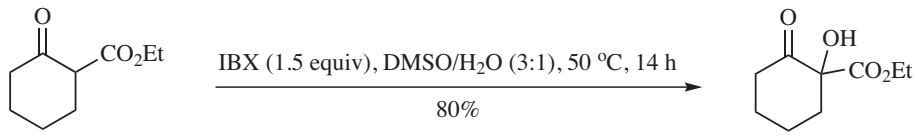
867



R^1, R^2, R^3 = alkyl, aryl, etc.

868

Scheme 3.347



869

Scheme 3.348

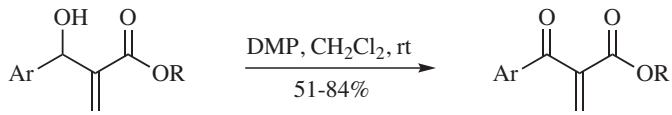
Kirsch and coworkers have further investigated the reactions of IBX with carbonyl compounds and found that, depending on a functional group at the α-position of a carbonyl compound, the reaction may lead either to oxidative dehydrogenation or to α-oxygenation [1128, 1186, 1187]. In particular, β-keto esters and some other suitably substituted carbonyl compounds can be selectively α-hydroxylated by treatment with IBX in aqueous DMSO at 50 °C; a representative example of the α-hydroxylation reaction of β-keto ester (**869**) is shown in Scheme 3.348 [1128].

Additional representative examples of synthetic applications of IBX include the following oxidative transformations: the aromatization of tetrahydro-β-carbolines under mild conditions applied in a total synthesis of the marine indole alkaloid eudistomin U [1188], oxidation of glycosides to the respective 6-carbaldehydes used as precursors in the synthesis of amino-bridged oligosaccharides [1189], oxidation of amidoximes to carboxamides or nitriles with IBX or IBX/tetraethylammonium bromide [1190], aromatic hydroxylations of flavonoids [1191], hydroxylation of resveratrol diacyl derivatives [1192], synthesis of DOPA and DOPA peptides by oxidation of tyrosine residue [1193], oxidative preparation of γ-hydroxy-α-nitroolefins from α,β-epoxyketoximes [1194], aromatization of 1,4-dihydropyridines using IBX in water/acetone in the presence of β-cyclodextrin [1195], iodohydroxylation of alkenes and iodination of aromatics using IBX/I_2 in aqueous acetone [1196], conversion of alkenes and alkynes into α-iodo ketones using IBX/I_2 in water [1197], oxidation of primary amines to nitriles [1198,1199], oxidative cleavage of acetals using IBX/tetraethylammonium bromide in water [1200], one-pot synthesis of trifluoromethyl-containing pyrazoles via sequential Yb$(PFO)_3$-catalyzed three-component reaction and IBX-mediated oxidation [1201], oxidative thiocyanation of indoles, pyrrole and arylamines [1202], oxidative functionalization of Baylis–Hillman adducts [1203–1205], construction of multisubstituted 2-acyl furans by the IBX-mediated cascade oxidation/cyclization of *cis*-2-en-4-yn-1-ols [1206], one-pot synthesis of substituted salicylnitriles via oxidation of the corresponding imines with IBX [1207], conversion of indoles into isatins using indium(III) chloride/IBX [1208], synthesis of iminoquinones from anilines [1209] and the oxidative transformation of primary carboxamides into one-carbon dehomologated nitriles [1210].

3.2.3 Dess–Martin Periodinane (DMP)

In modern organic synthesis Dess–Martin periodinane (DMP, structure **800** in Scheme 3.316) has emerged as the reagent of choice for the oxidation of primary and secondary alcohols to the respective carbonyl compounds. DMP is commercially available or can be conveniently prepared by the reaction of IBX with acetic anhydride (Section 2.2.3.2) [1211]. The synthetic applications of DMP have been summarized in several overviews [1102, 1104, 1212, 1213].

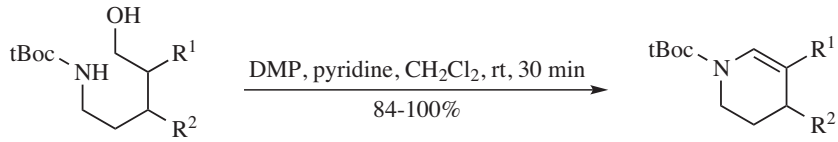
The DMP-promoted oxidations of alcohols proceed with high chemoselectivity under mild reaction conditions (room temperature, absence of acidic or basic additives). DMP is especially useful for the oxidation of alcohols containing sensitive functional groups and in the case of epimerization sensitive substrates DMP allows clean oxidation with no loss of enantiomeric excess. Oxidations with DMP are accelerated by the addition of water to the reaction mixture immediately before or during the reaction [1214].



870 **871**

Ar = Ph, 2-ClC_6H_4, 4-MeC_6H_4, 3,4-$F_2C_6H_3$, 4-FC_6H_4, 4-$CF_3C_6H_4$
R = Me, Et

Scheme 3.349



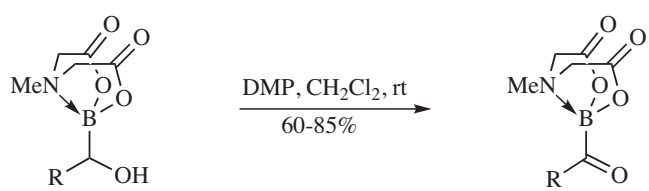
872 R^1 = H, Me, $CH_2OSi(Ph)_2Bu^t$ **873**
R^2 = H, OCH_2OMe, $OCH_2OCH_2CH_2SiMe_3$

Scheme 3.350

In numerous synthetic studies it has been demonstrated that DMP can be used for a selective oxidation of alcohols containing sensitive functional groups, such as unsaturated alcohols [297, 1215–1218], carbohydrates and polyhydroxy derivatives [1216, 1219–1221], silyl ethers [1222, 1223], amines and amides [1224–1227], various nucleoside derivatives [1228–1231], selenides [1232], tellurides [1233], phosphine oxides [1234], homoallylic and homopropargylic alcohols [1235], fluoroalcohols [1236–1239] and boronate esters [1240]. Several representative examples of these oxidations are shown below in Schemes 3.349–3.354. Specifically, the functionalized allylic alcohols **870,** the Baylis–Hillman adducts of aryl aldehydes and alkyl acrylates, are efficiently oxidized with DMP to the corresponding α-methylene-β-keto esters **871** (Scheme 3.349) [1217]. The attempted Swern oxidation of the same adducts **870** resulted in substitution of the allylic hydroxyl group by chloride.

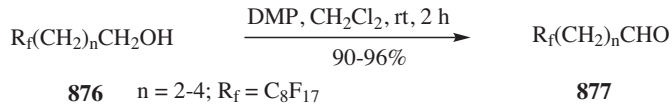
Cyclic enecarbamates **873** have been prepared in excellent yields by the oxidation of ω-hydroxycarbamates **872** with DMP followed by cyclocondensation–dehydration of the intermediate aminoaldehydes (Scheme 3.350) [1227].

α-Hydroxyboronates **874** have been selectively oxidized to acylboronates **875** through the Dess–Martin oxidation (Scheme 3.351) [1240].

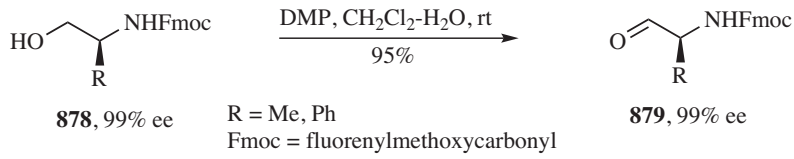


874 R = alkyl, aryl **875**

Scheme 3.351



Scheme 3.352



Scheme 3.353

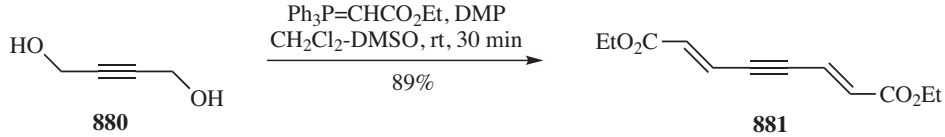
Polyfluorinated alcohols **876** can be selectively oxidized by DMP to the respective aldehydes **877** (Scheme 3.352) without the formation of dehydrofluorinated by-products [1238, 1239].

DMP is especially useful for the oxidation of the optically active, epimerization-sensitive substrates without loss of enantiomeric purity [1224, 1241, 1242]. In a typical example, DMP was found to be a superior oxidant for the efficient, epimerization-free synthesis of optically active N-protected α-amino aldehydes **879** from the corresponding N-protected β-amino alcohols **878** (Scheme 3.353) [1224]. In contrast, the Swern oxidation of amino alcohols **878** afforded products **879** of only 50–68% ee.

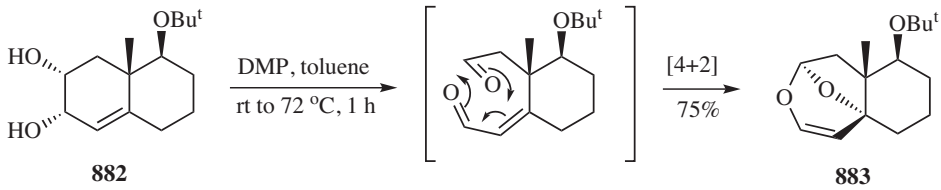
Primary alcohols can be oxidized with DMP in the presence of stabilized phosphonium ylides to afford the respective α,β-unsaturated esters in one pot [1232, 1243, 1244]. This is a useful procedure, especially when the intermediate aldehydes are unstable and difficult to isolate. In a representative example, a highly unstable dialdehyde, 2-butynedial, was generated by the oxidation of propargylic diol **880** with DMP and trapped by phosphonium ylide *in situ* to afford the adduct **881** as a 4 : 1 mixture of *trans-trans* and *trans-cis* isomers (Scheme 3.354) [674].

The DMP oxidation of 1,2-diols generally cleaves the glycol C—C bond, as illustrated by the synthesis of tricyclic enol ether **883** from diol **882** via tandem 1,2-diol cleavage–intramolecular cycloaddition (Scheme 3.355) [1220].

Because of the unique oxidizing properties and convenience of use, DMP has been widely employed in the synthesis of biologically important natural products. Representative examples include the use of DMP in key oxidation steps of the following total syntheses: (±)-deoxypreussomerin A [1245], racemic brevioxime [1246], erythromycin B [1247], (+)-cephalostatin 7 [1248], (+)-cephalostatin 12 [1248], (+)-ritterazine K [1248], fredericamycin A [1249], angucytcline antibiotics [1250], tricyclic β-lactam antibiotics [1251], ent-hyperforin [1252], (–)-spirotryprostatin B [1253], (+)-peloruside A [1254], (+)-ambruticin S [1255], (±)-platensimycin [1256], (–)-pseudolaric acid B [1257], azadirachtin [1258], salvinorin A [1259], amphidinol 3 [1260], FD-891 16-membered macrolide [1261], (+)-bretonin B [1262], (±)-maoecrystal V [1263], resolvin



Scheme 3.354



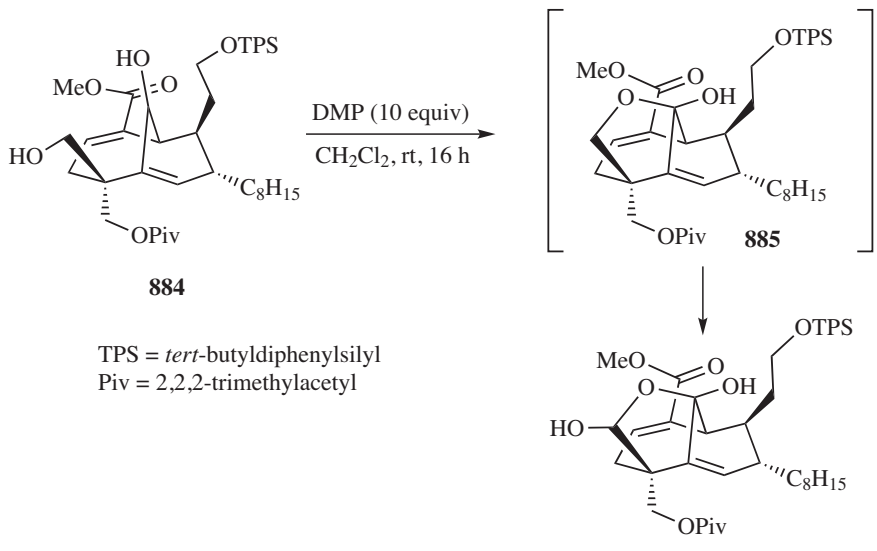
882 **883**

Scheme 3.355

D1 [1264], (–)-tirandamycin C [1265], gambieric acid A [1266], (+)-sieboldine A [1267], ripostatin B [1268], 15-deoxyripostatin A [1269], spirastrellolide A methyl ester [1270], (–)-fusarisetin A [1271], halichondrin C [1272], 16-membered macrolide FD-891 [1261] and numerous other synthetic works.

The unique oxidizing properties of DMP are best illustrated by its numerous applications in the total synthesis of the CP-molecules, lead structures for cardiovascular and anticancer drugs, published by Nicolaou and coworkers in 2002 [1273–1275]. For example, in the course of this synthetic study, a hindered secondary alcohol **884** was oxidized with DMP to give stable diol **886** via intermediate formation of hemiketal **885** (Scheme 3.356) [1274].

The practical value of DMP as a reagent has been extended to various other synthetically useful oxidative transformations, such as the dehydration of primary alcohols under extraordinarily mild conditions [1276], synthesis of various polycyclic heterocycles via the oxidative cascade cyclization of anilides with pendant double bonds [1277], one-pot oxidative allylation of Morita–Baylis–Hillman adducts with allyltrimethylsilane promoted by DMP/$BF_3{\cdot}OEt_2$ [1278], synthesis of 2-amino-1,4-benzoquinone-4-phenylimides from anilines via DMP oxidation [1279], α-tosyloxylation of ketones using DMP and *p*-toluenesulfonic acid [1280] and the DMP-mediated oxidative aromatization of 1,3,5-trisubstituted pyrazolines [1281].



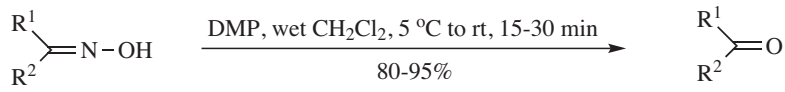
884

TPS = *tert*-butyldiphenylsilyl
Piv = 2,2,2-trimethylacetyl

885

886 (82%)

Scheme 3.356

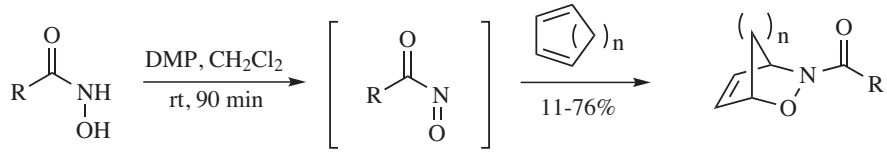


887 **888**

R^1 = Ph, 4-ClC_6H_4, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 2-furyl, PhCH=CH, 4-$Me_2NC_6H_4$, C_5H_{11}, C_7H_{15}, C_9H_{19}, PhC(O), Ph_2CHCH_2

R^2 = H, PhHC=CH, CO_2Me, Me, $(CH_2)_2CO_2H$, NH_2

Scheme 3.357



889 **890** **891**

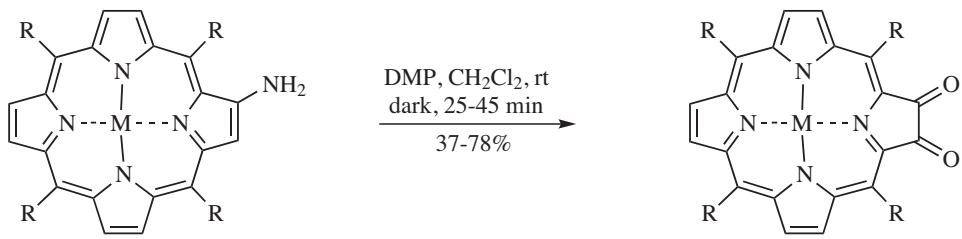
R = Ph, Me, OBu^t, OBn, NH_2; n = 1 or 2

Scheme 3.358

DMP can be used as an efficient and selective reagent for the oxidative cleavage of oximes [1282–1284] and tosylhydrazones [1284] to yield the corresponding carbonyl compounds under mild conditions in high yields. In a specific example, DMP oxidatively deoximates aldoximes or ketoximes **887** to give the respective carbonyl compounds **888** in excellent yields, smoothly in a short time and under mild conditions (Scheme 3.357) [1283]. Deoximation occurs selectively in the presence of primary, secondary and benzylic alcohols, *O*-methyl oximes and acid–sensitive groups.

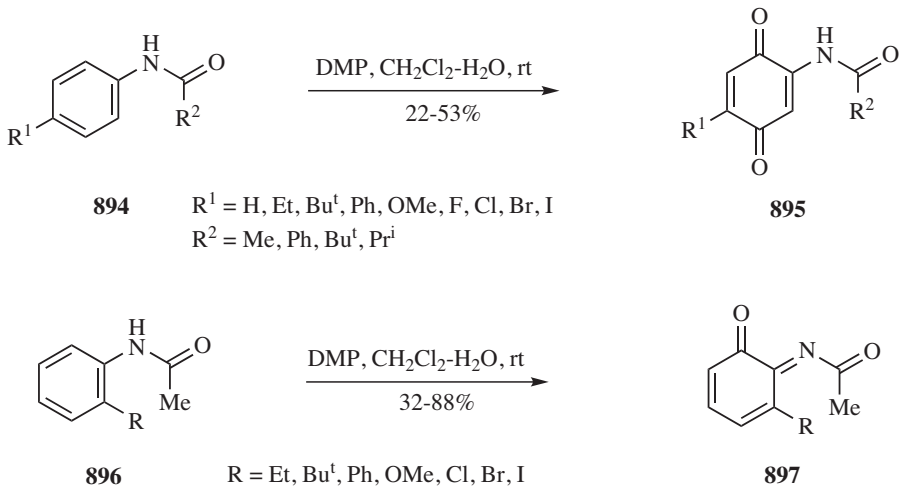
The oxidation of *N*-acyl hydroxylamines **889** with DMP generates the highly reactive acyl nitroso compounds **890,** which can be trapped by conjugated dienes to produce the corresponding cycloadducts **891** (Scheme 3.358) [1285].

2-Hydroxyporphyrins and 2-aminoporphyrins **892,** as well as 2,3-diaminoporphyrins, are oxidized by DMP to porphyrin-α-diones **893** (Scheme 3.359) [1286–1288]. This reaction has been applied to the preparation of *meso*-functionalized porphyrin-α-diones, which are the basic building blocks for bis-porphyrin arrays [1287].



892 R = 3,5-$Bu^t_2C_6H_3$; M = 2H, Cu, Zn **893**

Scheme 3.359



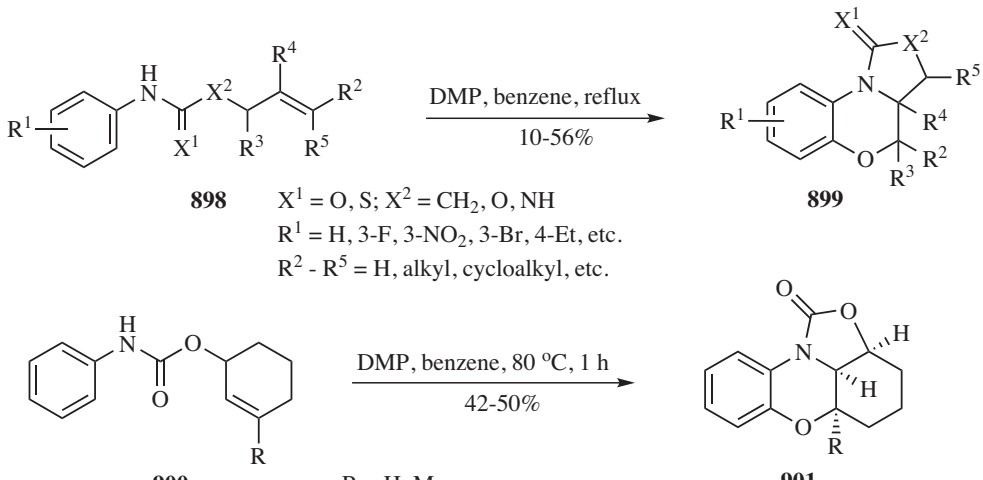
894 R^1 = H, Et, Bu^t, Ph, OMe, F, Cl, Br, I; R^2 = Me, Ph, Bu^t, Pr^i — **895**

896 R = Et, Bu^t, Ph, OMe, Cl, Br, I — **897**

Scheme 3.360

In a series of publications, Nicolaou and coworkers have demonstrated the utility of DMP for the selective oxidation of 4-substituted anilides **894** to *p*-quinones **895** and 2-substituted anilides **896** to *o*-azaquinones **897** (Scheme 3.360) [1289–1291]. The first process was applied to the short, efficient total synthesis of epoxyquinomycin B [1290], while the second type of oxidation allowed rapid access to complex analogs of pseudopterosin and elisabethin natural products [1291].

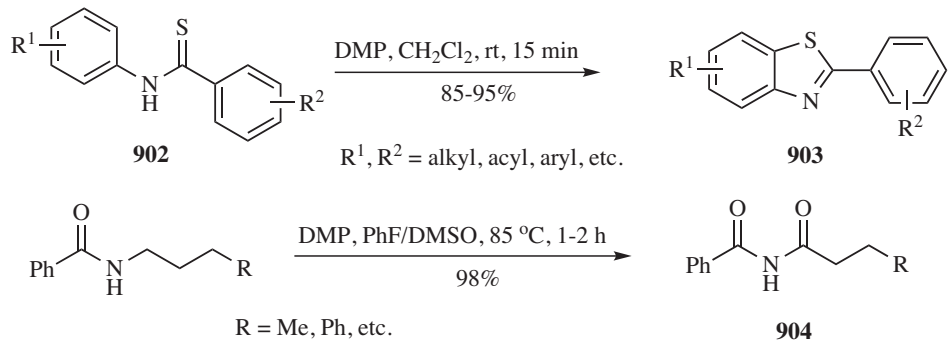
Anilides with pendant double bonds **898** undergo DMP-induced stereoselective oxidative cyclization to give complex and diverse natural product-like polycycles **899** (Scheme 3.361) [1176, 1277]. This oxidative cyclization is proposed to occur by the initial *ortho* directed oxidation of anilide **898** to give an *ortho*-hydroxylated benzene ring that is further oxidized to the quinone imine; intramolecular Diels–Alder cyclization of the



898 X^1 = O, S; X^2 = CH_2, O, NH; R^1 = H, 3-F, 3-NO_2, 3-Br, 4-Et, etc.; R^2 - R^5 = H, alkyl, cycloalkyl, etc. — **899**

900 R = H, Me — **901**

Scheme 3.361



Scheme 3.362

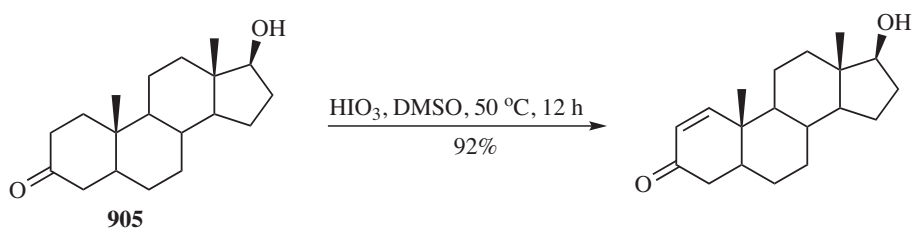
quinone imine with the pendant alkene gives the final product **899** [1176]. A specific example of the oxidation of carbamates **900** leading to the benzomorpholine derivatives **901** is shown in Scheme 3.361.

Additional examples of the DMP-mediated oxidations of nitrogen substrates include the synthesis of 2-substituted benzothiazoles **903** via oxidative cyclization of thioanilides **902** [445] and the synthesis of imides (e.g., **904**), N-acyl vinylogous carbamates and ureas and nitriles by the oxidation of amides and amines with DMP (Scheme 3.362) [1292].

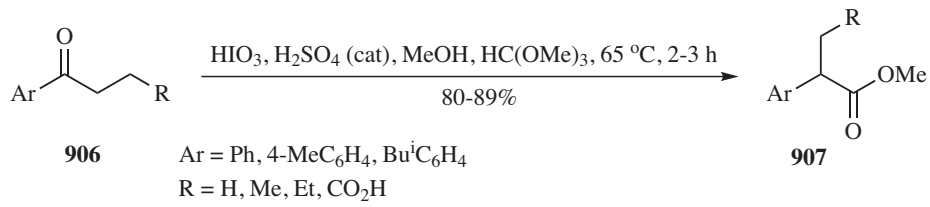
3.2.4 Inorganic Iodine(V) Reagents

Iodic acid (HIO_3), iodine pentoxide (I_2O_5) and inorganic iodate salts are commercially available, general-purpose oxidants, which are commonly used in organic synthesis. Applications of iodic acid in organic chemistry were summarized by Choghamarani in 2006 [1293]. Iodic acid has been used as a reagent in numerous organic reactions, such as oxidative iodination of aromatic compounds [1294–1296], oxidation of sulfides [1297, 1298], oxidation of aromatic amines to quinones [1299], deprotection of ketoximes and aromatic aldoximes [1300], deprotection of thioacetals and thioketals [1301], oxidative deprotection of trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers [1302], oxidative coupling of *N*,*N*-dimethylanilines [1303], oxidative rearrangements [1304, 1305] and dehydrogenation of aldehydes and ketones [1306]. The advantages of iodic acid as a reagent include cost-effectiveness, non-toxicity and easy workup of reaction mixtures.

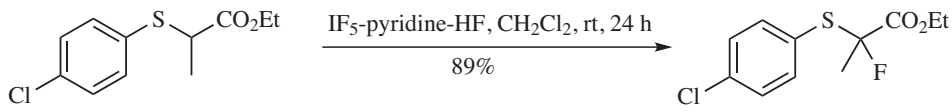
Schemes 3.363 and 3.364 show representative examples of the reactions of iodic acid. Nicolaou and coworkers have demonstrated that aldehydes and ketones can be selectively dehydrogenated to the corresponding 1,3-unsaturated carbonyl compounds with HIO_3 or I_2O_5 in DMSO at moderate heating, as illustrated by the reaction of steroidal substrate **905** (Scheme 3.363) [1306].



Scheme 3.363



Scheme 3.364



Scheme 3.365

Methyl esters of α-arylalkanoic acids **907** can be prepared by oxidative rearrangement of ketones **906** via a 1,2-aryl shift using iodic acid in methanol in the presence of trimethyl orthoformate and sulfuric acid (Scheme 3.364) [1304].

Iodine pentoxide can be used as a mild oxidant with generally similar reactivity to HIO_3. Representative examples of synthetic applications of I_2O_5 include α-thiocyanation of ketones using ammonium thiocyanate and iodine pentoxide [1307], thiocyanation of aromatic and heteroaromatic compounds using ammonium thiocyanate and iodine pentoxide [1308], oxidation of electron-rich alcohols in water using I_2O_5 or HIO_3 in the presence of KBr [1309] and oxidative decarboxylation of propiolic acids using the combination of iodine and I_2O_5 in methanol [1310].

Iodine pentafluoride, IF_5, has found some synthetic application as a powerful fluorinating reagent [1311, 1312]. For example, IF_5, in combination with pyridine and HF, can be used as a fluorination reagent for the introduction of fluorine atoms to the α-position in sulfides (Scheme 3.365) [1313]. A similar fluorination of sulfides using IF_5 without pyridine and HF affords a mixture of polyfluorinated products [1314].

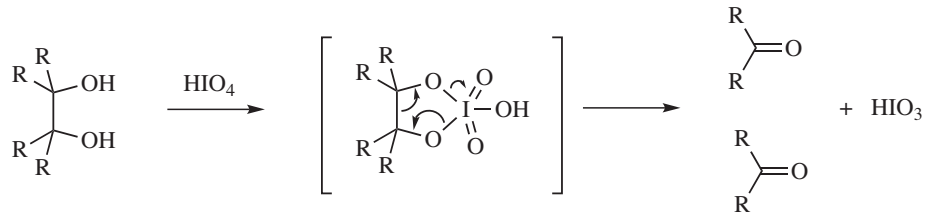
3.3 Synthetic Applications of Iodine(VII) Compounds

Periodic acid, $HIO_4{\cdot}2H_2O$ or H_5IO_6 and periodate salts (e.g., sodium metaperiodate, $NaIO_4$) are common, commercially available, powerful oxidants, which are widely used in oxidation or oxidative cleavage reactions for many types of organic substrates [1315]. Periodic acid is soluble in ethereal organic solvents as well as in water, allowing a wider scope of use compared to sodium periodate.

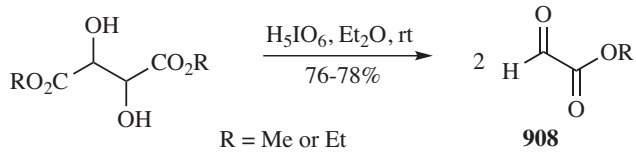
The glycol-cleavage oxidation reaction (Scheme 3.366) is the major area of application of periodic acid, which is particularly important in carbohydrate chemistry [1316, 1317].

This reaction can be performed in non-aqueous solvents, such as diethyl ether or THF and the workup generally requires a simple filtration of iodic acid followed by evaporation of the solvent. Application of this methodology is exemplified by a convenient preparation of alkyl glyoxylates **908** in high yield (Scheme 3.367) [1318].

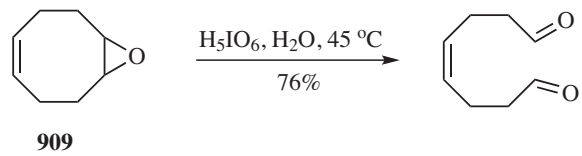
Periodic acid can also oxidatively cleave epoxides via a mechanism analogous to the glycol-cleavage shown in Scheme 3.366. The cleavage of terminal epoxides affords a single aldehyde, while cyclic substrates produce dialdehydes, as illustrated by the reaction of substrate **909** (Scheme 3.368) [1319]. The



Scheme 3.366



Scheme 3.367

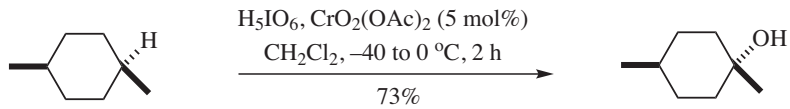


Scheme 3.368

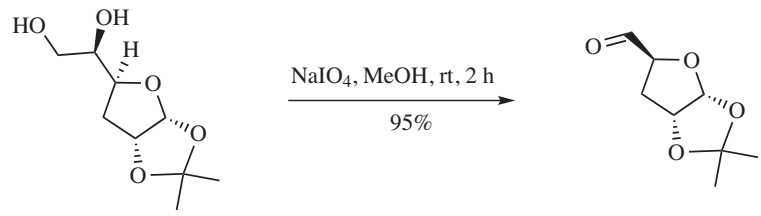
reaction can be performed in water or aqueous organic solvents and it is compatible with various functional groups [1315].

Periodic acid can be applied as the stoichiometric oxidant in several transition metal catalyzed oxidations. Particularly useful are the chromium-catalyzed oxidations. In the presence of catalytic chromoyl diacetate, tertiary C—H bonds are oxidized to produce tertiary alcohols in moderate yields with retention of the original C—H stereochemistry, as exemplified in Scheme 3.369 [1320].

Secondary alcohols are oxidized by H_5IO_6 in the presence of various chromium catalysts to ketones [1321–1325], while primary alcohols can be oxidized to aldehydes or to carboxylic acids depending on the catalyst. Primary alcohols in the presence of pyridinium chlorochromate (PCC)[1322] or chromium (III) acetylacetonate, $Cr(acac)_3$ [1321] are oxidized to aldehydes or ketones in excellent yields, while the use of CrO_3 [1326, 1327] or pyridinium fluorochromate [1323] as catalysts results in the oxidation to carboxylic acids. The periodic acid promoted oxidation of primary and secondary alcohols to carbonyl compounds can also be catalyzed by Cu(II) derivatives [1328, 1329], by bromide anion [1330] and by TEMPO [1331].



Scheme 3.369



Scheme 3.370

Chromium(VI) oxide is also an efficient catalyst for oxidation at the benzylic position with periodic acid as the terminal oxidant in acetonitrile. Substituted toluenes with an electron-withdrawing group at the 4- or 3-position and diarylmethanes such as Ph_2CH_2 and fluorene are oxidized to the respective substituted benzoic acids and ketones in excellent yields [1332]. Periodic acid in the presence of catalytic CrO_3 can be used for the oxidation of arenes, such as naphthalenes and anthracene, to the corresponding quinones; for example, 2-methylnaphthalene is oxidized to 2-methyl-1,4-naphthoquinone (vitamin K_3) by this catalytic system in high yield and regioselectivity [1333]. Sulfides can be oxidized by periodic acid to sulfoxides in the presence of catalytic $FeCl_3$ [1334], or to sulfones in the presence of CrO_3 [1335].

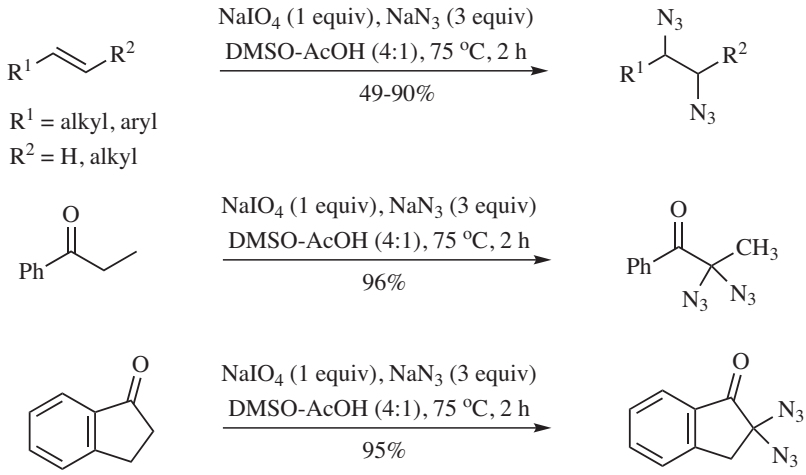
Additional examples of synthetic application of periodic acid as an oxidant include the oxidative iodination of aromatic compounds [1336–1341], iodohydrin formation by treatment of alkenes with periodic acid and sodium bisulfate [1342], oxidative cleavage of protecting groups (e.g., cyclic acetals, oxathioacetals and dithioacetals) [1315, 1343], conversion of ketone and aldehyde oximes into the corresponding carbonyl compounds [1344], oxidative cleavage of tetrahydrofuran-substituted alcohols to γ-lactones in the presence of catalytic PCC [1345] and direct synthesis of nitriles from alcohols or aldehydes using H_5IO_6/KI in aqueous ammonia [1346].

Sodium metaperiodate, $NaIO_4$, is a common, commercially available oxidant widely used in organic synthesis. As with periodic acid, sodium metaperiodate can be used for the glycol-cleavage oxidation reaction, which is particularly important in carbohydrate chemistry. Scheme 3.370 shows a representative example of a glycol-cleavage oxidation with $NaIO_4$; this reaction has been used in the synthesis of (2*S*,4*S*)-4-hydroxyproline from D-glucose [1347].

The glycol-cleavage oxidation has been utilized in numerous synthetic works, for example, the total syntheses of dipiperidine alkaloids virgidivarine and virgiboidine [1348], total synthesis of resolvin E2 [1349], synthesis of α-substituted oxazolochlorin aminals or acetals from *meso*-tetraaryldihydroxychlorins [1350], asymmetric synthesis of 1-(2- and 3-haloalkyl)azetidin-2-ones [1351], synthesis of 2-hydroxy-1,4-oxazin-3-ones through ring transformation of 3-hydroxy-4-(1,2-dihydroxyethyl)-β-lactams [1352], preparation of 1-O-protected (*R*)- and (*S*)-glycerols from L- and D-arabinose [1353], synthesis of unnatural glucose from cycloheptatriene [1354] and the synthesis of enantiomeric 2,3-disubstituted 5-norbornenes from D-mannitol [1355].

The combination of hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$ and sodium metaperiodate in dichloromethane at room temperature can be used as a mild oxidizing agent for selective oxidation of alcohols to carbonyl compounds [1356]. Various aliphatic, benzylic and heteroaryl substituted alcohols are oxidized to produce the corresponding carbonyl compounds in high yields; primary alcohols give the corresponding aldehydes without any noticeable further oxidation to acids. It is assumed that I_2 and NO, produced by the initial oxidation of $NH_2OH{\cdot}HCl$ with $NaIO_4$, act as the actual oxidants of alcohols under these conditions [1356].

A combination of $NaIO_4$ and KI in aqueous NH_3 converts alcohols into nitriles in moderate to good yield [1357]. This transformation, proceeds via an *in situ* oxidation–imination–aldimine oxidation sequence.



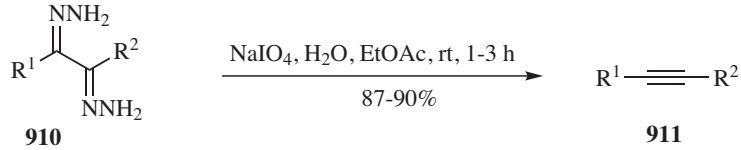
Scheme 3.371

The combination of $NaIO_4$, KI and NaN_3 is an efficient, simple and inexpensive reagent system for the β-azidoiodination of alkenes [1358]. This reaction proceeds in an anti-Markovnikov fashion to give β-iodo azides in excellent yields. Likewise, the $NaIO_4$–NaN_3 combination has been found to be an excellent reagent system suitable for the direct diazidation of styrenes, alkenes, benzylic alcohols and aryl ketones to produce the corresponding vicinal and geminal diazides, respectively, in high yields under mild reaction conditions (Scheme 3.371) [1359].

Sodium metaperiodate can be used for the oxidation of dihydrazones of α-diketones **910** to acetylenes **911** in high yields under mild condition (Scheme 3.372) [1360]. This procedure is also suitable for the deprotection of monohydrazones of aldehydes and ketones. This mild and efficient procedure is applicable to substrates with either electron-withdrawing or electron-donating substituents [1360].

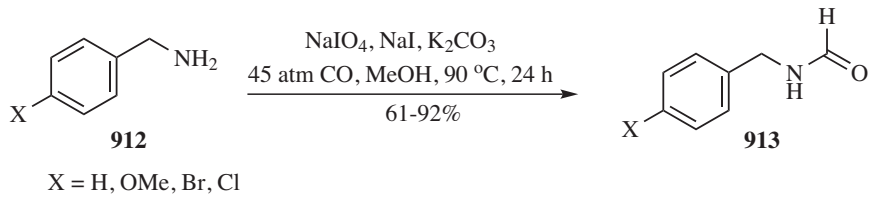
McElwee-White and Gerack have developed a metal-free procedure for carbonylation of benzylamines **912** in methanol in the presence of $NaIO_4$, producing formamide derivatives **913** in good to excellent yields (Scheme 3.373) [1361]. Secondary amines can also be formylated under these conditions to give respective formamides in 51–58% yields. Labeling experiments have established that CO is the source of the formyl carbonyl, while its hydrogen is derived from the protic solvent.

Sodium metaperiodate has been applied as the stoichiometric oxidant in numerous transition metal catalyzed oxidations. Of particular use is a one-pot oxidative cleavage of olefins to aldehydes by the OsO_4–$NaIO_4$ catalytic system, as exemplified in Scheme 3.374 [1362]. This oxidative cleavage, with some modifications,

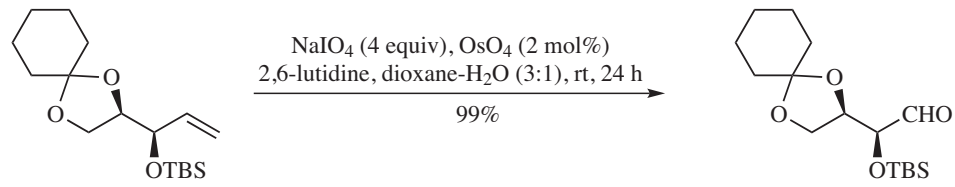


R1 and R2 = aryl or hetaryl

Scheme 3.372



Scheme 3.373



Scheme 3.374

has been utilized in numerous synthetic works [1363–1369]. A similar oxidative cleavage of olefins can be achieved by using catalytic RuO_4 (generated *in situ* from RuO_2 or $RuCl_3$) and $NaIO_4$ as the stoichiometric oxidant [1370].

Additional examples of the synthetic application of sodium metaperiodate as an oxidant in transition metal catalyzed oxidations include the hydroxylation of alkanes with $NaIO_4$ catalyzed by tetrakis(*p*-inophenyl)porphyrinatomanganese(III) chloride [1371], the use of $NaIO_4$ as a mild and efficient terminal oxidant for C—H oxidations with Cp^*Ir ($Cp^* = C_5Me_5$) precatalysts [1372], oxidation reactions of olefins with $NaIO_4$ using iron(III) *meso*-tetraarylporphyrins as the catalysts [1373], asymmetric epoxidation of unfunctionalized olefins with $NaIO_4$ using axially coordinated chiral salen Mn(III) complexes as the catalysts [1374], epoxidation of alkenes with $NaIO_4$ using multiwall carbon nanotube supported manganese(III) tetraphenylporphyrin [1375], oxidation of 2-imidazolines to 2-imidazoles with $NaIO_4$ catalyzed by manganese(III) tetraphenylporphyrin [1376], oxidation of 2-imidazolines to 2-imidazoles with $NaIO_4$ catalyzed by polystyrene-bound manganese(III) porphyrin [1377], oxidation of 2-imidazolines to 2-imidazoles with $NaIO_4$ catalyzed by Mn(salophen)Cl [1378] and numerous other works.

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