Recent Developments in the Chemistry of Polyvalent Iodine Compounds

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I. Introduction

The organic chemistry of polyvalent iodine compounds has experienced an unprecedented, explosive development during the last decade of the 20th century. A quick SciFinder Scholar search of the *Chemical Abstracts* databases reveals thousands of papers and patents published in this area just in the last five years. This surging interest in iodine compounds is mainly due to the very useful oxidizing properties of polyvalent organic iodine reagents combined with their benign environmental character and commercial availability. Several areas of organic polyvalent iodine chemistry have recently attracted especially active interest and research activity. These areas include the synthetic applications of the Dess−Martin periodinane and similar oxidizing reagents based on iodine(V), the use of iodosylbenzene in the transition-metal-catalyzed biomimetic oxygenations, catalytic imidations with iodonium imides, azidations with azidoiodanes, the chemistry of benziodoxoles and benziodazoles, and synthetic and mechanistic studies of alkynyl and alkenyl iodonium salts.

The purpose of the present review is to summarize the data that appeared in the literature following publication of our original review in 1996.[1] The review is organized according to the classes of organic polyvalent iodine compounds with emphasis on their synthetic application. A number of other reviews, some comprehensive, most dealing with specific aspects of polyvalent organoiodine chemistry, have appeared in the last six years.[2−22] Most notable is the monograph by Varvoglis on the application of hypervalent iodine compounds in organic synthesis.[2] Several specialized reviews on [hydroxy(tosyloxy)iodo]-benzene,[13] the chemistry of iodonium salts,[14−18] electrophilic perfluoroalkylations,[19] and the chemistry of benziodoxoles[20] and phenyliodine(III) carboxylates[21,22] have been published recently.

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Viktor V. Zhdankin was born in 1956 in Sverdlovsk, Russia. His M.S. (1978), Ph.D. (1981), and Dr.Chem.Sci. (1986) degrees were earned at Moscow State University in the research laboratories of Professor N. S. Zefirov. In 1987 he was appointed as Senior Research Fellow—Head of Research Group at the Department of Chemistry, Moscow State University, Moscow. He moved to the University of Utah in 1990, where he worked as Instructor of organic chemistry and Research Associate. In 1993 he joined the faculty of the University of Minnesota, Duluth, where he is currently a Professor of Chemistry. He has published more than 150 research papers as well as 10 reviews and book chapters. His main research interests are in the fields of synthetic and mechanistic organic chemistry of hypervalent main-group elements (iodine, xenon, selenium, sulfur, and phosphorus) and organofluorine chemistry.

Peter J. Stang earned his B.S. degree in Chemistry in 1963 at DePaul University in Chicago and his Ph.D. degree in 1966 from the University of California—Berkeley. After postdoctoral work at Princeton University he joined the faculty at the University of Utah, where he is currently a Distinguished Professor of Chemistry. His research interests include, inter alia, supramolecular chemistry, self-assembly, polyvalent iodine chemistry, as well as reactive intermediates. He is a member of the US National Academy of Sciences, and after serving as Editor-in Chief of the *Journal of Organic Chemistry* for two years, since January 2002 he is the Editor of the *Journal of the American Chemical Society*.

The general aspects of structure and bonding in polyvalent iodine compounds have been previously discussed in our original review[1] and in the 1992 monograph by Varvoglis.[23] More recently, general aspects of structure and reactivity of hypervalent organic compounds have been summarized by Akiba.[24] In the present review, the results of recent structural studies on polyvalent iodine compounds will be briefly discussed in the sections on the appropriate classes of compounds. Literature coverage is through the end of 2001.

II. Iodine(III) Compounds

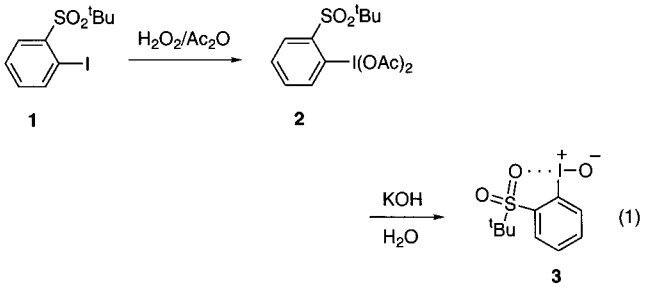
Iodine(III) compounds, or λ^3-iodanes according to the IUPAC nomenclature, are commonly classified according to the type of ligands attached to the iodine atom.[1,23] The following general classes of iodine(III) compounds have found broad application in organic synthesis: (i) iodosylarenes ArIO and their acyclic derivatives $ArIX_2$ bearing two non-carbon ligands X, (ii) five-membered iodine heterocycles, benziodoxoles and benziodazoles, (iii) iodonium salts $R_2I^+X^-$, (iv) iodonium ylides $ArI{=}CR_2$, and (v) iodonium imides ArI═NR. The chemical properties and synthetic applications of these classes are very different. Iodosylarenes and their derivatives in general are strong oxidizing agents and have found broad application in organic synthesis as reagents for oxygenation and oxidative functionalization of organic substrates. The most important feature of heterocyclic iodanes is a considerably higher stability than that of their acyclic analogues, which makes possible the isolation and practical use of several otherwise unstable iodine(III) derivatives. Iodonium salts in general do not possess any significant oxidizing properties but have a diverse reactivity pattern mainly due to the exceptional leaving group ability of the −IAr fragment. Iodonium ylides and imides are excellent carbene and nitrene precursors, respectively.

A. Iodosylarenes

1. Structural Aspects

Despite wide application of iodosylarenes as oxidizing reagents, their structural details are still limited. It has been demonstrated by various spectroscopic studies that iodosylbenzene has a zigzag polymeric structure in which monomeric units of $PhI^+{-}O^-$ are linked by intermolecular I···O secondary bonds. Most notable are the recent studies of $(PhIO)_n$ by EXAFS analysis and by solid-state NMR spectroscopy.[25,26] In particular, the EXAFS revealed the T-shaped geometry around the iodine centers with the primary I−O single bond of 2.04 Å, the secondary, intermolecular, I···O bond of 2.377(12) Å, and an I−O−I angle of 114°.[25] It has also been demonstrated by Koser and co-workers that polymeric chains of PhIO most likely are terminated by HO endcaps and thus the actual structure of iodosylbenzene can be shown as $HO(PhIO)_nH$.[27] A solid state ^{13}C NMR spectroscopy study of $(PhIO)_n$ and several *para*-substituted iodosylarenes (4-MeC_6H_4IO, 4-$MeOC_6H_4IO$, 4-PrC_6H_4IO, 4-*iso*-PrC_6H_4IO, 4-$NO_2C_6H_4IO$) confirmed the truly amorphous polymeric structure of iodosylbenzene but indicated some degree of crystallinity of the *para*-methoxy, propyl, and isopropyl derivatives.[26]

Due to the polymeric structure, iodosylbenzene is insoluble in all nonreactive solvents; however, soluble derivatives of iodosylbenzene can be realized by placing an appropriate substituent on the ortho position of the phenyl ring. Protasiewicz and coworkers recently reported the preparation and X-ray structure of the monomeric iodosylarene **3** (eq 1) in which the intramolecular secondary I···O bond replaces the intermolecular interactions that are typical of polymeric iodosylbenzene.[28,29]

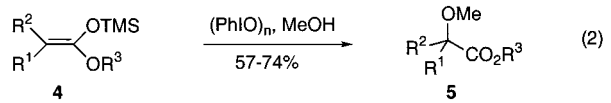


1 2 3 (1)

Iodosylarene **3** is readily soluble in organic solvents (up to 0.08 M in chloroform) and can be analyzed by NMR in solution.[28] Single-crystal X-ray analysis of **3** showed a structure resembling benziodoxoles with an intramolecular distance of 2.707(5) Å between one of the sulfone oxygen atoms and the hypervalent iodine center.[29] The I−O bond length in the iodosyl group of **3** is 1.848(6) Å, and the intramolecular O−I−O bond angle is 167.3(2)°. The iodine centers in **3** achieve a pseudo-square-planar geometry by the formation of a intermolecular I···O secondary bond (2.665(6) Å) to a neighboring iodosyl oxygen atom.[29] Because of the excellent solubility in common organic solvents, compound **3** has powerful oxidizing properties. In particular, it reacts readily with tertiary phosphines and organic sulfides with the formation of the respective phosphine oxides and sulfoxides in high yield.[28]

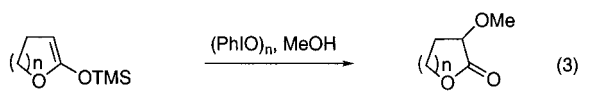
2. Oxidations with Iodosylbenzene

Reactions of iodosylbenzene are usually carried out in the presence of a catalyst (such as a Lewis acid, bromide anion, or a transition-metal complex) or a hydroxylic solvent, which is required to depolymerize $(PhIO)_n$ and generate the actual oxidizing monomeric species in solution. Only a few noncatalytic oxidations with iodosylarenes have been reported in the recent literature. Moriarty, Prakash, and co-workers reported a series of oxidations with iodosylbenzene in hydroxylic solvents.[30,31] In a typical example, iodosylbenzene oxidation of trimethylsilyl ketene acetals of esters (**4**) and lactones (**6**) in methanol affords the corresponding α-methoxylated carbonyl compounds **5** (eq 2) and **7** (eq 3) in good yields.[30] It is assumed that the actual oxidizing monomeric species in this reaction is $PhI(OMe)_2$.[30]



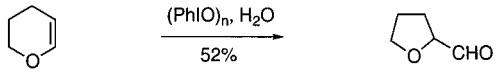
4 5 (2)

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



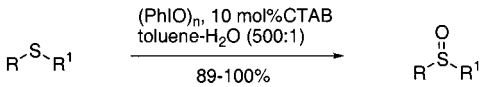
6 n = 1 or 2 7 (3)

The oxidation of dihydropyran, cyclohexene, and styrene with iodosylbenzene under similar conditions leads predominantly to rearranged products.[31] Thus, the oxidation of dihydropyran with iodosylbenzene in water gave tetrahydro-2-furaldehyde **9** via carbocationic ring contraction (eq 4).[31]



8 9 (4)

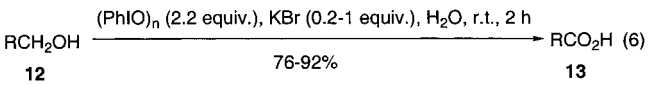
Kita, Tohma, and co-workers found that iodosylbenzene can be activated in a variety of solvents by addition of bromide salts to the reaction mixture.[32,33] The oxidation of various sulfides **10** with iodosylbenzene in the presence of catalytic amounts of quaternary ammonium bromides affords the appropriate sulfoxides **11** in high yields (eq 5).[32]



10 11 (5)

R, R^1 = Ph, 2-MeC_6H_4, 2-$MeOC_6H_4$, $C_6H_4CH_2$, Me, Et

The best catalytic effect in this reaction (eq 5) 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). In the first publication, the authors explained the catalytic effect of CTAB exclusively by the formation of a micellar or a reversed micellar system, which enhanced the solubility and thereby the reactivity of iodosylbenzene.[32] However, in their subsequent publication, Kita and co-workers demonstrated that the bromide anion is essential for the depolymerization of $(PhIO)_n$.[33] Specifically, it was found that the addition of catalytic amounts of KBr resulted in a remarkable activation of iodosylbenzene in water. The PhIO/KBr system is applicable to the oxidation of a variety of primary and secondary alcohols, even in the presence of sensitive functional groups such as ether, ester, sulfonamide, and azido groups. Primary alcohols **12** under these conditions afford carboxylic acids **13** (eq 6), while the oxidation of various secondary alcohols under similar conditions results in the formation of the appropriate ketones in almost quantitative yield.[33]



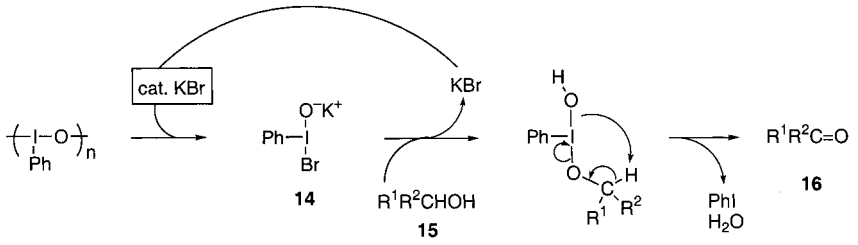
12 13 (6)

R = $Ph(CH_2)_2$, $BnO(CH_2)_3$, $EtO_2C(CH_2)_4$, $N_3(CH_2)_4$

This catalytic activation is explained by the initial depolymerization of $(PhIO)_n$ with the formation of a highly reactive intermediate **14**, which reacts with alcohols **15** to yield the corresponding carbonyl compound **16** with regeneration of KBr (Scheme 1).[33]

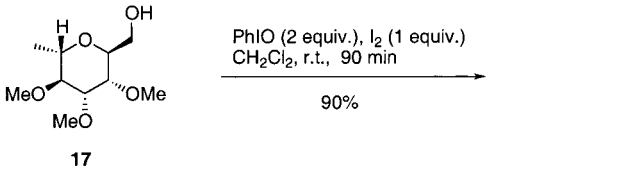
Iodosylbenzene can be activated in the solid state by pulverization with natural clays or silica gels.[34,35] The oxidation of various alkyl aryl sulfides with $(PhIO)_n$ supported on natural (montmorillonite, KSF, and bentonite clay) as well as cation-exchanged K10-montmorillonite clays affords sulfoxides in excellent yields. A mechanism involving depolymerization of $(PhIO)_n$ by the acidic SiOH sites on the clay is proposed for this reaction.[34] In another procedure,

Scheme 1



iodosylbenzene is activated by crushing and grinding with an HCl-treated silica gel by a pestle in a mortar.[35] Reactions with unsaturated solid substrates under these conditions are complete in a few minutes at room temperature, affording products of halogenation or oxygenation in good yield. Under similar conditions, various organic sulfides are smoothly converted to sulfonyl chlorides in excellent yields. A plausible mechanism for this reaction includes the initial depolymerization of $(PhIO)_n$ by HCl on the surface of silica gel.[35]

Iodosylbenzene and some other hypervalent iodine reagents react with alcohols in the presence of iodine with the formation of the respective alkoxy radicals, presumably through an alkyl hypoiodite intermediate.[36] Suàrez and co-workers developed a valuable synthetic methodology based on a sequential fragmentation of alkoxy radicals generated from alcohols, iodosylbenzene, and iodine. Recently, this methodology was applied in the synthesis of carbohydrate derivatives **18** (eq 7) and imino sugars **20** (eq 8).[37,38] (Diacetoxyiodo)benzene can also be used in this reaction instead of iodosylbenzene (see section II.C.7).



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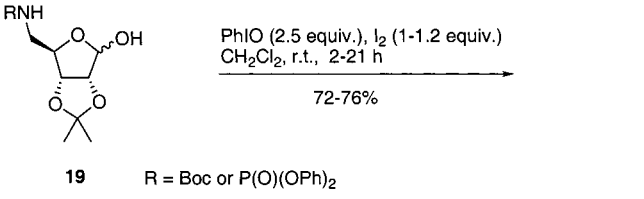
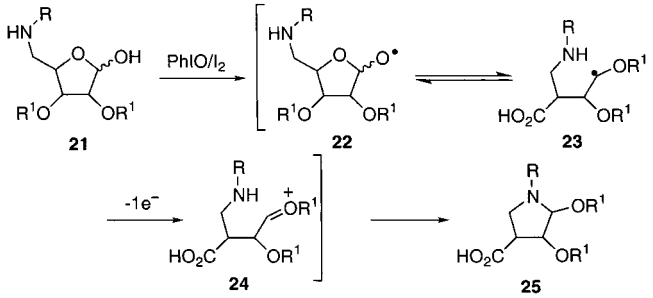


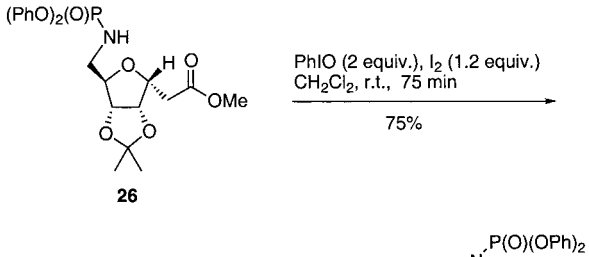
(8)

The proposed mechanism for this reaction involves a β-fragmentation of the initially formed alkoxy radical **22** leading to a carbon-centered radical **23**, which is further oxidized by an excess of the reagent to the oxycarbenium ion **24** (Scheme 2). The intramolecular nucleophilic cyclization of **24** affords the final sugar derivative **25**.[38]

Scheme 2



Recently, Suàrez and co-workers developed a similar methodology based on the generation of *N*-centered radicals from the reaction of amides with iodosylbenzene and iodine. This methodology was applied in the synthesis of homochiral 7-oxa-2-azabicyclo[2.2.1]heptane derivatives **27** and **29** from the respective phosphoramidate derivatives of carbohydrates **26** and **28** (eqs 9 and 10).[39]



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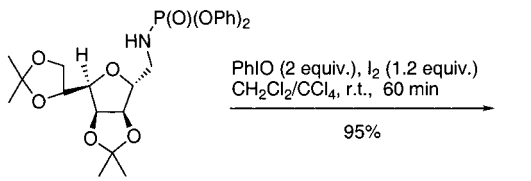
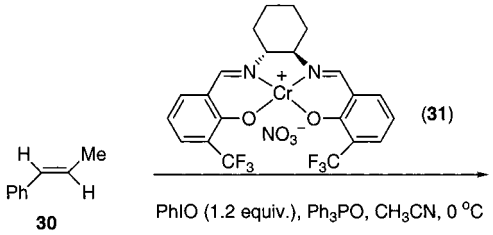


(10)

3. Transition-Metal-Catalyzed Oxygenations

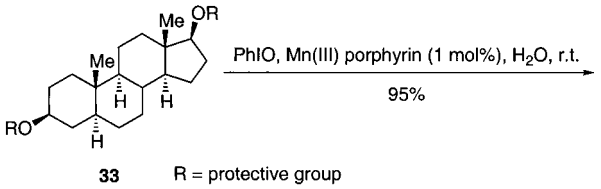
A significant current interest in iodosylbenzene as an oxidant in the transition-metal-catalyzed oxygenations originated from the mechanistic studies of cytochrome P-450, a heme-containing monooxygenase enzyme, and its metalloporphyrin models.[40] It was found early on that iodosylbenzene in the presence of cytochrome P-450 or iron porphyrins converts alkanes to alcohols and alkenes to epoxides, often with high regioselectivity and stereoselectivity.[1] In the last 5−6 years the research activity in this area has surged and shifted from mechanistic studies to the development of new synthetic methodologies. It has been demonstrated that not only metalloporphyrins, but also numerous other transition-metal complexes can catalyze oxygenations with iodosylbenzene. One of the most impressive recent findings was the development of asymmetric epoxidations of alkenes with iodosylbenzene in the presence of chiral complexes of transition metals.[41−62] In a representative recent example, Gilheany and co-workers reported a highly enantioselective alkene epoxidation catalyzed by chiral nonracemic chromium salen complexes.[44−46] Iodosylbenzene was found to be the only applicable oxidant in these reactions, and the highest 92% ee was achieved in the epoxidation of (*E*)-*β*-methylstyrene **30** mediated by the chromium salen complex **31** in stoichiometric mode and in the presence of Ph_3PO as a donor ligand (eq 11).[46] Carrying out this reaction in catalytic mode (5−10 mol % of chromium complex) or use of other substituted salen ligands results in a slightly lower enantioselectivity.[44−46]



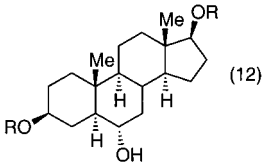
30 **32**, 92% ee (11)

Asymmetric 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).[47−54] 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 yields with 91−96% ee.[48] Additional recent examples include epoxidation of alkenes with iodosylbenzene catalyzed by various metalloporphyrins,[55−59] corrole metal complexes,[60] ruthenium−pyridinedicarboxylate complexes of terpyridine, and chiral bis(oxazolinyl)pyridine.[61]

Iodosylbenzene can be used as an effective oxidant in hydrocarbon hydroxylation catalyzed by metalloporphyrins.[62−67] Various iron(III) and manganese(III) porphyrines can be used as catalysts in the hydroxylations of cyclohexane, cyclohexene, adamantane, and aromatic hydrocarbons.[62−64] Breslow and co-workers recently reported regioselective hydroxylations of several steroidal derivatives catalyzed by metalloporphyrins.[65−67] Specifically, an androstanediol derivative **33** was hydroxylated at the 6α carbon with complete positional selectivity in the presence of a manganese(III) porphyrin catalyst (eq 12).[65] Presumably, this selective hydroxylation (eq 12) is directed by the geometry of the catalyst−substrate complex, as in the enzyme.

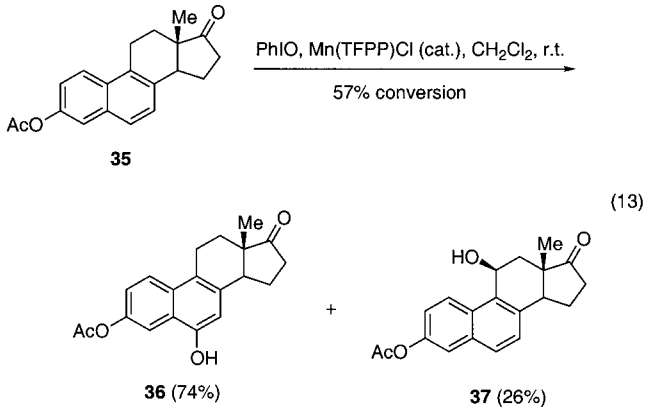


33 R = protective group



34 (12)

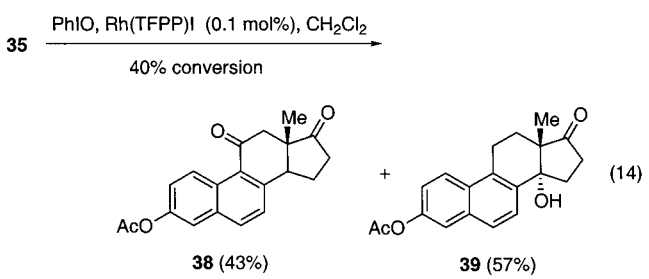
The aromatic steroid equilenin acetate (**35**) undergoes regioselective and stereoselective hydroxylation catalyzed by a manganese porphyrin using iodosylbenzene as the oxidant (eq 13).[66]



35 **36** (74%) + **37** (26%) (13)

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

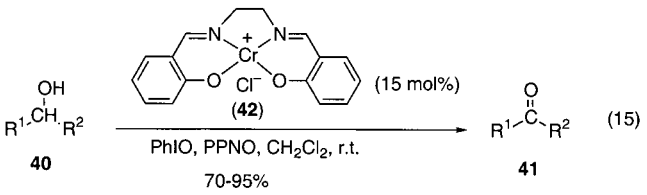
A different selectivity was observed in a similar reaction in the presence of rhodium(III) porphyrin as a catalyst (eq 14).[67]



35 **38** (43%) + **39** (57%) (14)

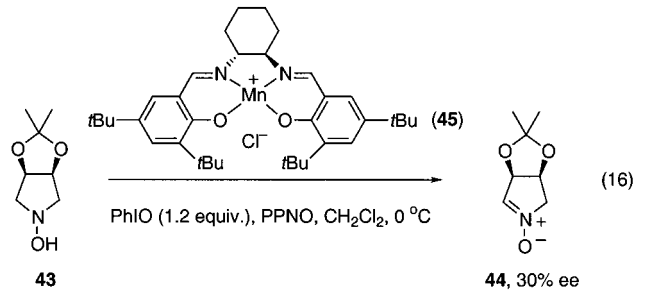
Various primary and secondary alcohols **40** can be chemoselectively oxidized to the corresponding car-

bonyl compounds **41** by iodosylbenzene or (diacetoxyiodo)benzene in the presence of a (salen)Cr(III) complex **42** as the catalyst (eq 15).[68,69]

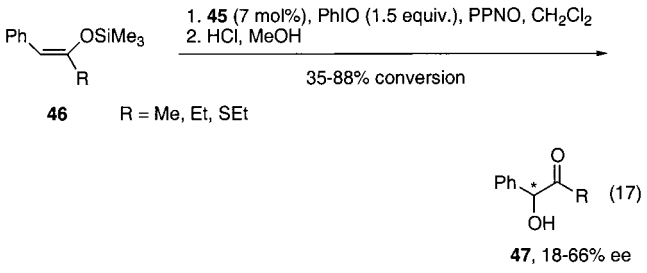


R^1, R^2 = H, alkyl, alkenyl, aryl; PPNO = 4-phenylpyridine *N*-oxide

N,*N*-Disubstituted hydroxylamines can be oxidized to nitrones by iodosylbenzene in the presence of catalytic amounts (3−5%) of the chiral (salen)Mn(III) complex **45** (Jacobsen catalyst).[70] *Meso-cis*-3,4-isopropylidenedioxy-1-hydroxypyrrolidine **43** under these conditions affords the corresponding *N*-oxide **44** with moderate enantioselectivity (eq 16).[70]



The enantioselective oxidation of silyl enol ethers **46** or ketene acetals by iodosylbenzene in the presence of the chiral (salen)Mn(III) complex **45** affords optically active α-hydroxy carbonyl compounds **47** in generally good yields (eq 17).[71,72]



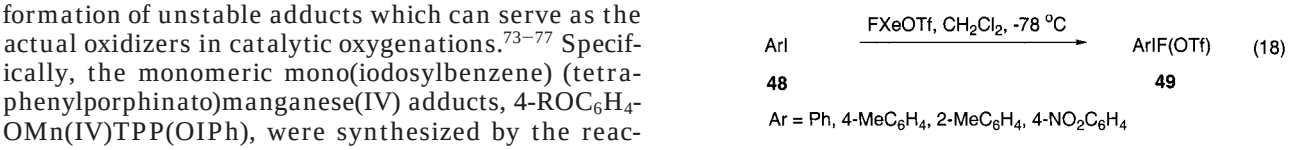
It is generally agreed that the intermediate high-valent oxo complexes are responsible for the oxygen transfer from iodosylbenzene to the organic substrate. However, the details of the initial interaction of iodosylbenzene with metal complex are still under consideration. Interestingly, it was shown in recent papers that iodosylbenzene reacts with metalloporphyrins and some other metal complexes with the formation of unstable adducts which can serve as the actual oxidizers in catalytic oxygenations.[73−77] Specifically, the monomeric mono(iodosylbenzene) (tetraphenylporphinato)manganese(IV) adducts, 4-ROC_6H_4-OMn(IV)TPP(OIPh), were synthesized by the reaction of the corresponding (tetraphenylporphinato)-manganese(III) derivatives with iodosylbenzene. These complexes were characterized by elemental analyses and visible, IR, and ESR spectroscopy. The monomeric mono(iodosylbenzene) (tetraphenylporphinato)-manganese(IV) adducts were found to oxidize cyclohexane and styrene at room temperature with the formation of the respective oxidation products in high yields.[73] It was also demonstrated that the cytochrome P 450 model system forms different active oxidizing species from different iodosylarenes, which can be explained by the involvement of the respective catalyst−iodosylarene complexes.[74] The unstable and highly reactive PhIO−(salen)Mn(III) complexes were identified by electrospray ionization in combination with tandem mass spectrometric techniques.[75] The intermediate formation of such highly reactive adducts may explain the unique reactivity of iodosylbenzene as the source of oxygen in the catalytic oxygenation reactions.

B. Halides

1. Fluorides

(Difluoroiodo)arenes are potentially useful fluorinating reagents, but they have found only limited practical application due to the low stability and lack of convenient methods of preparation.[1] They are commonly prepared by the reaction of (dichloroiodo)-arenes with aqueous hydrofluoric acid and mercuric oxide[78] or by the electrochemical oxidation of *para*-substituted iodobenzenes in the presence of $Et_3N\cdot 3HF$.[79−83] Polyfluoro-substituted (difluoroiodo)benzenes can also be prepared by fluorination of the respective iodoarenes with fluorine, xenon difluoride, or other powerful fluorinating reagents.[84−86] Frohn and co-workers investigated the preparation of $C_6F_5IF_2$ and related iododifluorides by oxidative fluorination of the appropriate iodides using F_2, ClF, CF_3OCl, BrF_5, $C_6F_5BrF_2$, $C_6F_5BrF_4$, and XeF_2.[84,85] The highest purity and yield of $C_6F_5IF_2$ was achieved by a low-temperature fluorination with F_2.[84a] Prepared in this work, $C_6F_5IF_2$ was fully characterized by multinuclear NMR, IR, Raman spectroscopy and X-ray structural analysis.[84a] Another preparation of $C_6F_5IF_2$ in high yield (97%) involved the reaction of IF_3 with $Cd(C_6F_5)_2$ in dichloromethane at −78 °C.[85b] Naumann and co-workers prepared 2,6-$F_2C_6H_3IF_2$ in quantitative yield by oxidative fluorination of the corresponding aryliodide with XeF_2 in acetonitrile or with F_2/N_2 mixtures in CCl_3F.[86]

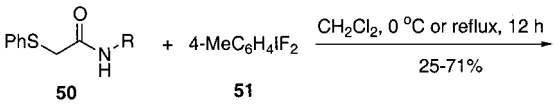
Zefirov, Brel, and co-workers developed a procedure for the preparation of [fluoro(trifluoromethylsulfonyloxy)iodo]arenes **49** by oxidative fluorination of iodoarenes **48** with FXeOTf, which can be generated in situ from XeF_2 and triflic acid (eq 18).[87−90] Reagents **49** can be further reacted with organic substrates in situ.

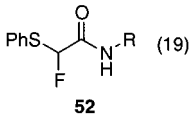


Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-$NO_2C_6H_4$

The analogous mesylate, PhIF(OMs), can be prepared from iodobenzene, XeF_2, and methanesulfonic acid by a similar procedure.[91,92]

(Difluoro)iodoarenes are powerful and selective fluorinating reagents. Motherwell and co-workers recently reported several synthetically useful fluorinations of various arylthio derivatives with 4-(difluoroiodo)toluene.[93−95] Specifically, α-(phenylthio)acetamides **50** are fluorinated in the α-position when treated with reagent **51** under mild conditions (eq 19).[93]





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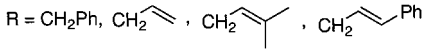
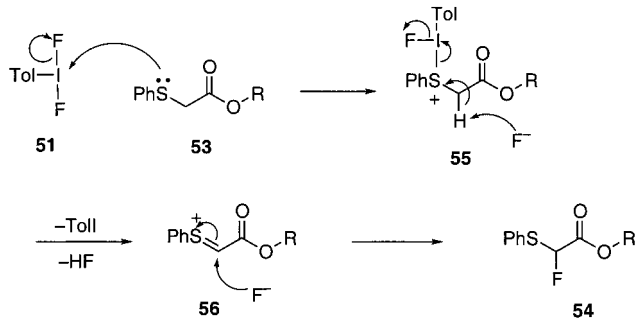
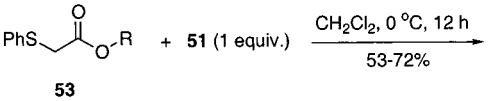


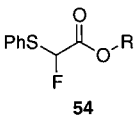
Under similar conditions α-phenylthio esters **53** afford fluorides **54** (eq 20). The mechanism of this Pummerer-type reaction involves the initial nucleophilic attack by the sulfur atom at the electrophilic iodine center to form the iodosulfonium salt **55** (Scheme 3). The liberated fluoride anion acts as a

Scheme 3



base with resultant formation of the classical Pummerer intermediate **56**. Subsequent trapping of cation **56** with fluoride anion yields the final product **54**.[94]





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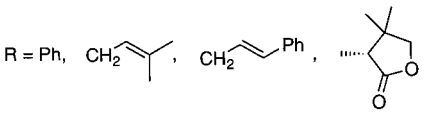
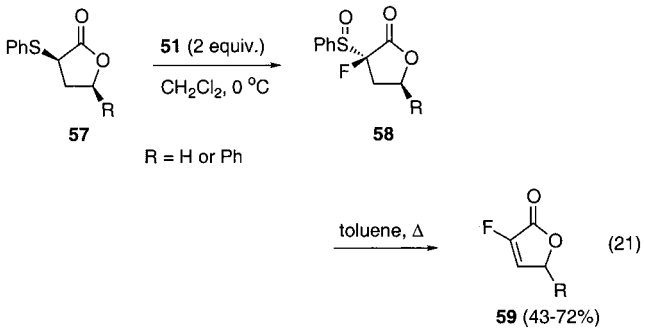


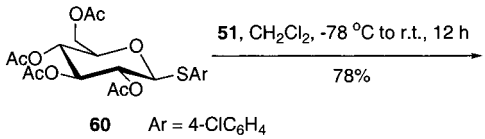
The use of excess reagent **51** in the reaction with lactones **57** can lead to further oxidation to α-fluoro sulfoxides **58**, which can then undergo thermal syn elimination to produce vinyl fluorides **59** (eq 21).[94]

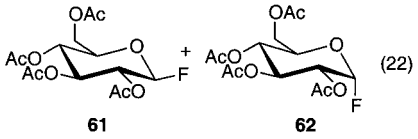
A treatment of the readily available thio- and selenoglycosides with reagent **51** leads to the formation of the corresponding fluoroglycosides in moderate



(21)

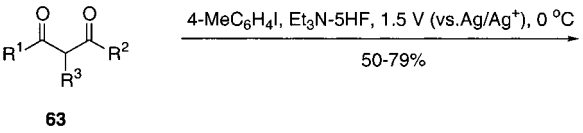
to good yield.[95] In a typical representative example, the treatment of the glucose derivative **60** with 4-(difluoroiodo)toluene **51** under mild conditions affords fluoroglycosides **61** and **62** in a 3:2 ratio (eq 22).[95]

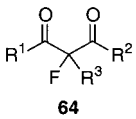




(22)

β-Ketoesters and *β*-dicarbonyl compounds are selectively fluorinated at the α-position by 4-(difluoroiodo)toluene and a HF−pyridine complex.[81,82] This fluorination can be performed electrochemically using 4-(difluoroiodo)toluene as the mediator generated in situ from iodotoluene. Thus, the electrolysis of a 1:1 mixture of iodotoluene and various *β*-dicarbonyl compounds **63** in Et_3N-5HF in an undivided cell under constant potential affords the respective α-fluoro-*β*-dicarbonyl compounds **64** in good yield (eq 23).[82]

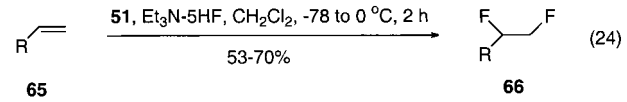




(23)

R^1 = Me, Et, Pr, *cyclo*-C_6H_{11}, Ph
R^2 = OEt, OBu, Pr, *i*-Pr, Ph; R^3 = H, Me

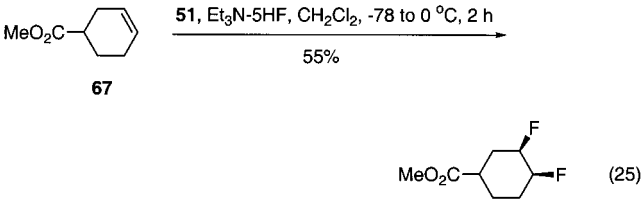
It has been known for many years that iodoarene difluorides react with aryl-substituted alkenes to afford the rearranged, geminal difluorides, due to the migration of the aryl group.[1,78] Recently, Hara, Yoneda, and co-workers investigated the reaction of the electrochemically generated 4-(difluoroiodo)toluene **51** with other common alkenes.[96,97] They found that terminal alkenes **65** react with reagent **51** in Et_3N-5HF to give *vic*-difluoro products **66** selectively (eq 24).[96]



65 **66**

R = $C_{10}H_{21}$, HOC_9H_{18}, $AcOC_9H_{18}$, $AcOC_4H_8$, $MeO_2CC_8H_{16}$, ClC_9H_{18}, etc.

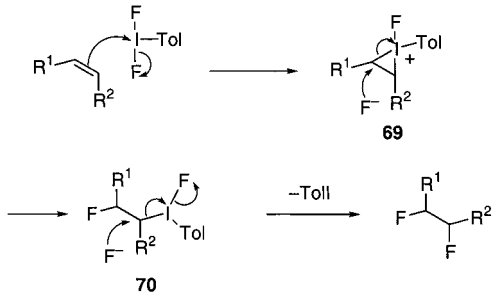
Under similar conditions, the cyclohexene derivative **67** reacts with reagent **51** with the stereoselective formation of *cis*-adduct **68** (eq 25).



67 **68**

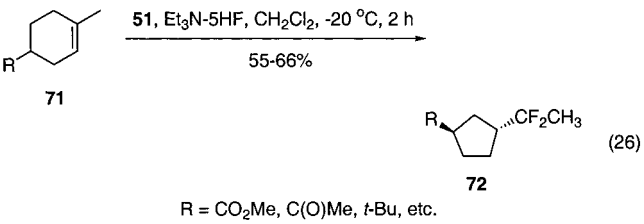
The observed *syn*-stereoselectivity of this difluorination is explained by a two-step mechanism involving the *anti*-addition of the reagent to the double bond through cyclic iodonium intermediate **69** at the first step and then nucleophilic substitution of iodotoluene with fluoride anion in **70** at the second step (Scheme 4).[96]

Scheme 4



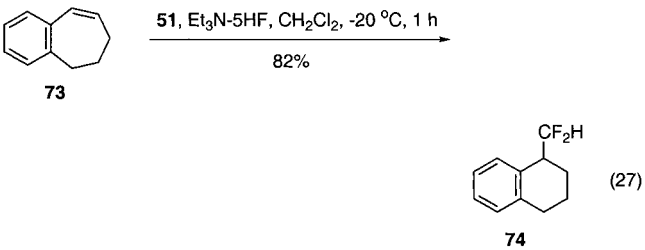
69 **70**

The reaction of substituted cyclic alkenes with reagent **51** 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 **71** affords (1,1-difluoroethyl)cyclopentanes **72** (eq 26), while a similar reaction of benzocycloheptene **73**



71 **72**

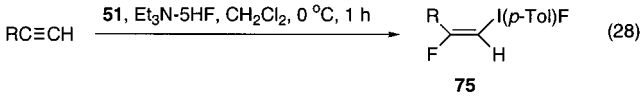
R = CO_2Me, C(O)Me, *t*-Bu, etc.



73 **74**

gives the respective difluoromethyl-substituted benzocyclohexane **74** in high yield (eq 27).[97]

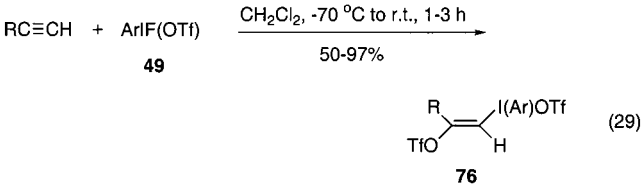
Iodoarene fluorides react with terminal alkynes with stereo- and regioselective formation of the synthetically useful (*E*)-2-fluoro-1-alkenyliodonium salts.[87,91,98−100] Hara, Yoneda, and co-workers developed a procedure for the preparation of various alkenyliodonium fluorides **75** by the addition of 4-(difluoroiodo)toluene **51** to terminal acetylenes (eq 28).[98−100]



75

R = MeC_9H_{18}, HOC_9H_{18}, ClC_9H_{18}, $MeO_2CC_8H_{16}$, *t*-BuC(O)C_8H_{16}, etc.

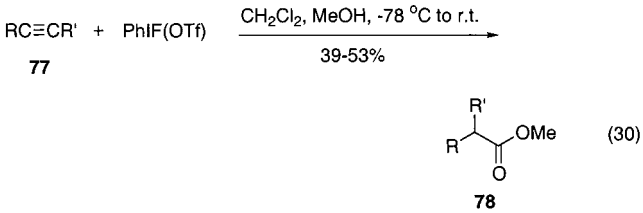
Zefirov, Brel, and co-workers reported a similar addition of [fluoro(sulfonyloxy)iodo]arenes **49** to alkynes with the stereoselective formation of alkenyliodonium sulfonates **76** (eq 29).[87,90] The chemistry of alkenyliodonium salts **75** and **76** will be further discussed in section I.3 of this review.



49 **76**

R = H, C_3H_7, C_4H_9, C_8H_{17}, CH_2OCH_3, CH_2OH, CH_2Cl
Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-$NO_2C_6H_4$

The reaction of PhIF(OTf) with nonterminal alkynes **77** in methanol results in an oxidative rearrangement leading to esters of carboxylic acids **78** in moderate yield (eq 30).[88]



77 **78**

R = Ph, 4-MeC(O)C_6H_4, Et, Pr; R' = Me, Et, Ph

Polyfluorophenyliodine(III) difluorides are useful reagents for the preparation of bis(polyfluorophenyl)-iodonium salts.[86,101,102]

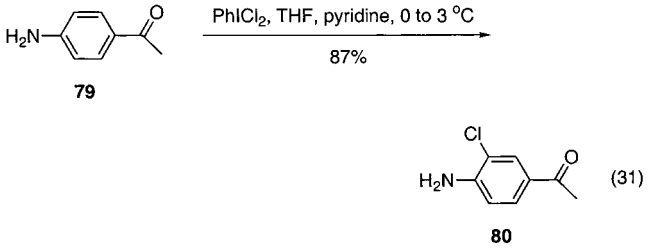
2. Chlorides

(Dichloroiodo)benzene has been known for more than 100 years.[1] It is a useful chlorinating reagent, but its practical application is limited due to its relatively low stability and commercial unavailability. Despite the low stability, a commercial process for a large-scale (20 kg) preparation of $PhICl_2$ has recently been developed by Zanka and co-workers.[103] This process is based on a direct chlorination of iodobenzene with chlorine in dichloromethane at low temperature. Skulski and co-workers reported several new procedures for the preparation of (dichloroiodo)arenes by chlorination of iodoarenes in aqueous hydrochloric acid in the presence of an appropriate

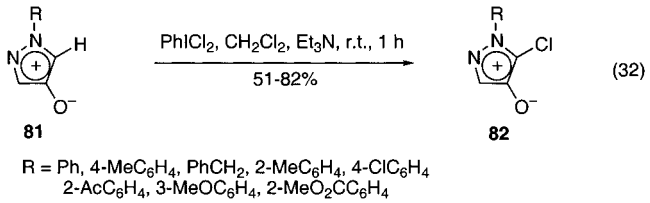
oxidant, such as $KMnO_4$, activated MnO_2, $KClO_3$, $NaIO_3 \cdot H_2O$, concentrated HNO_3, $NaBO_3 \cdot H_2O$, $Na_2CO_3 \cdot H_2O_2$, $Na_2S_2O_8$, CrO_3, and the urea$-H_2O_2$ complex.[104−107] For example, the chlorination of iodoarenes in a biphasic mixture of carbon tetrachloride and concentrated hydrochloric acid in the presence of $Na_2S_2O_8$ affords the corresponding (dichloroiodo)arenes in 60−100% crude yields.[105]

The first X-ray structure of $PhICl_2$ published in 1953 was imprecise by modern standards.[108] More recently, Chaloner and co-workers reported a good quality structure of $PhICl_2$ obtained at low temperature.[109] The molecule of $PhICl_2$ has the characteristic T-shape with primary I−Cl bond distances of 2.47 and 2.49 Å and Cl−I−C bond angles of 87.8° and 89.2°. In the solid state the molecules form an infinite zigzagged chain in which one of the chlorine atoms interacts with the iodine of the next unit with an intermolecular I···Cl secondary bond distance of 3.42 Å. The coordination of iodine is distorted square planar with the lone pairs occupying the *trans*-positions of a pseudooctahedron.[109] Protasiewicz reported the preparation and X-ray study of a sterically encumbered (dichloroiodo)arene $ArICl_2$ [Ar = 2,6-bis(3,5-dichloro-2,4,6-trimethylphenyl)benzene].[110] The geometry of this molecule is the expected T-shaped with Cl−I−C angles of 89.4(3)° and 92.1(3)° and I−Cl distances of 2.469(4) and 2.491(4) Å. The secondary I···Cl bond distance in this compound is 3.816 Å, which indicates a significant reduction of intermolecular association as compared to $PhICl_2$.[110] Recently, an X-ray structure of the $PhICl_2$ adduct with tetraphenylphosphonium chloride, $[Ph_4P]^+[PhICl_3]^-$, was reported.[111] The $[PhICl_3]^-$ anions in this structure have a planar coordination environment at the iodine atom. The I−Cl bond length of the chlorine atom trans to the Ph group is much longer (3.019 Å) than the bond distance to the cis Cl atoms (2.504 Å).[111]

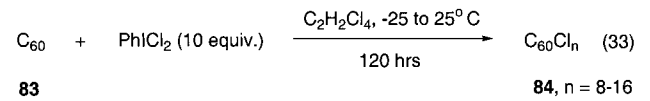
(Dichloroiodo)arenes have found some practical application as reagents for the chlorination and oxidation of various organic substrates. Recently, (dichloroiodo)benzene was applied for the chlorination of aminoacetophenone **79** on a large scale (eq 31). This process (eq 31) was successfully scaled up to afford 24.8 kg of product **80** with 94% purity.[103]



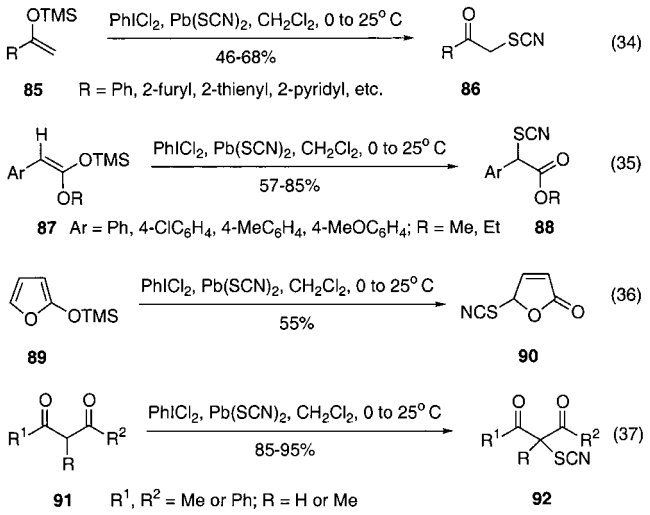
Turnbull and Ito used (dichloroiodo)benzene in the presence of triethylamine for the selective chlorination of 3-substituted sydnones **81** to form the 4-chloro-substituted products **82** in good yield (eq 32).[112]



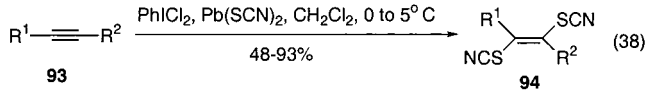
Fullerene C_{60} **83** smoothly reacts with (dichloro)iodobenzene in tetrachloroethane at −25 to 25 °C with the formation of polychlorinated fullerenes **84** (eq 33).[113] Laser desorption MS analysis of product **84** shows $C_{60}Cl_7$ and $C_{60}Cl_9$ as the most prevalent species, while elemental 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 1 day.



Moriarty, Prakash, and co-workers reported convenient procedures for the thiocyanation of organic substrates with the combination reagent $PhICl_2$/$Pb(SCN)_2$.[114−116] Various enol silyl ethers (**85**), ketene silyl acetals (**87**, **89**), and β-dicarbonyl compounds (**91**) can be effectively thiocyanated with this reagent to produce the respective thiocyanato derivatives of carbonyl and β-dicarbonyl compounds (eqs 34−37).[114,115] The mechanism of these reactions presumably involves the intermediate formation of unstable iodine(III) thiocyanate, $PhI(SCN)_2$.



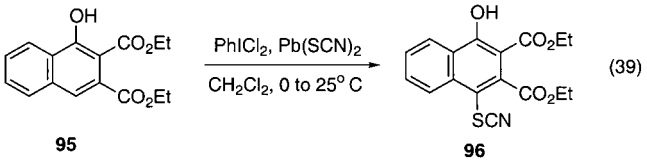
Under similar conditions, various alkynes **93** are stereoselectively converted into (*E*)-1,2-dithiocyanated alkenes **94** in generally good yield and with less than 5% of the corresponding (*Z*) isomers (eq 38).[116]



R1 = Ph, 4-MeC6H4, Pr, CH3(CH2)3, CH3(CH2)5, CH3(CH2)7, HO(CH2)4, 1-cyclohexenyl
R2 = H, Me, Ph, TMS

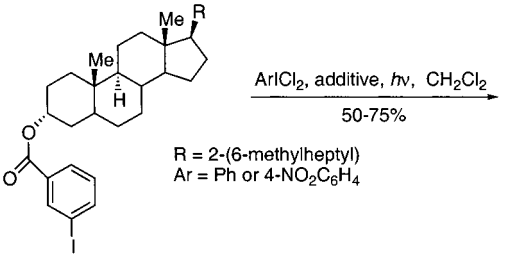
Kita and co-workers found that the $PhICl_2$/$Pb(SCN)_2$ combination is effective for the regioselective thiocyanation of various types of *para*-unsubstituted phenols and naphthols to give the appropriate

para-thiocyanatophenols and naphthols in good to quantitative yields.[117] Various functional groups, such as chloro, allyl, carbonyl, ester, amide, and primary hydroxyl groups, are shown to be compatible with this reaction. For example, the thiocyanation of naphthol **95** affords the respective thiocyanato derivative **96** in excellent yield (eq 39).[117]



95 **96** (39)

Wiedenfeld recently reported the remote functionalization of cholesterol derivatives at the 9α-carbon by tandem radical chain reactions directed by an attached *m*-iodobenzoate ester.[118] Normal radical relay chlorination of cholestan-3α-ol **97** with $PhICl_2$ affords a 9α-chloro steroid, but when the same reaction is conducted in the presence of an excess of CBr_4 or $(SCN)_2$ the product is the respective 9α-functionalized steroid **98** (eq 40).[118]



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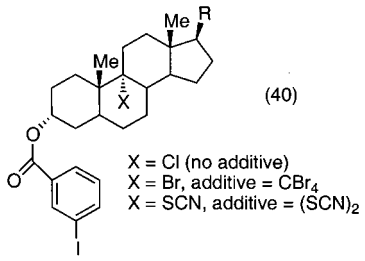
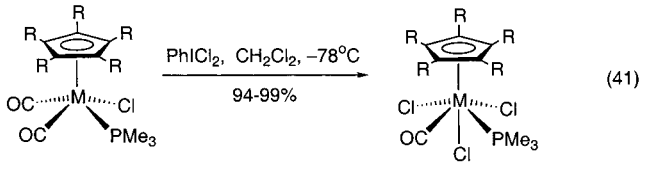


98 (40)

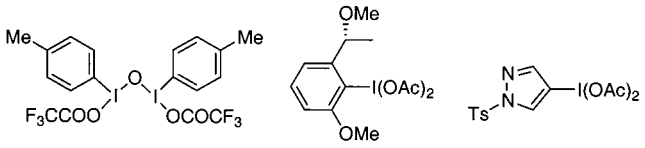
(Dichloroiodo)arenes are useful reagents for the chlorination or oxidation of organoelement compounds or complexes of transition metals.[119−125] Sulfides can be oxidized to the corresponding sulfoxides and sulfones by 3-(dichloroiodo)benzoic acid.[119] *N*-Chlorotriphenylphosphinimine, Ph_3PNCl, can be prepared in good yield by the reaction of $Ph_3PNSiMe_3$ with $PhICl_2$.[120] Organophosphorus(III) compounds can be oxidatively chlorinated to the respective organophosphorus(V) chlorides.[121] Numerous examples of oxidative chlorination of various molybdenum and tungsten complexes with $PhICl_2$ have recently been reported in the literature.[122−125] In a typical example, oxidative decarbonylation of the cyclopentadienyl complexes **99** with 1 equiv of $PhICl_2$ yields selectively the respective molybdenum(IV) or tungsten(IV) complexes **100** in excellent yield (eq 41).[125]



99 M = Mo or W, R = H or Me **100** (41)

C. Carboxylates

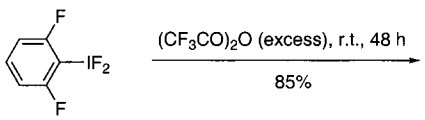
[Bis(acyloxy)iodo]arenes, $ArI(O_2CR)_2$, are the most important, well investigated, and practically useful organic derivatives of iodine(III).[1] Two of them, (diacetoxyiodo)benzene (DIB) and [bis(trifluoroacetoxy)iodo]benzene (BTI), are commercially available and commonly used as oxidizing reagents in organic synthesis. A large number of research papers and two reviews[21,22] dealing mainly with the synthetic application of DIB and BTI have been published in the last 5 years. The structural features of [bis(acyloxy)iodo]arenes were thoroughly discussed in earlier reviews and monographs. X-ray structural analysis of the new compounds **101**−**103** have been reported in the recent literature.[126−128]



101[126] **102**[127] **103**[128]

1. Preparation of New [Bis(acyloxy)iodo]arenes

Several new, potentially useful structural types of [bis(acyloxy)iodo]arenes have been prepared and investigated in the past few years.[86,127−137] The chiral diacetate **102** and several analogous products were prepared in 73−87% yield by the perborate oxidation of the appropriate aryliodides.[127] These acetates serve as important precursors to useful chiral [(hydroxy)tosyloxy]iodoarenes (see section II.D of this review). Several heteroaromatic derivatives of (diacetoxyiodo)arenes [i.e., *N*-tosyl-4-(diacetoxyiodo)pyrrazole (**103**), *N*-trifluoromethanesulfonyl-4-(diacetoxyiodo)pyrrazole, 2-(diacetoxyiodo)thiophene, and 3-(diacetoxyiodo)thiophene] were prepared similarly by using sodium perborate in acetic acid.[128] Naumann and coworkers prepared bis(trifluoroacetate) derivative **105** in high yield by the reaction of the appropriate (difluoro)iodoarene **104** with trifluoroacetic anhydride (eq 42).[86]



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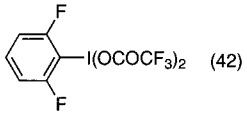
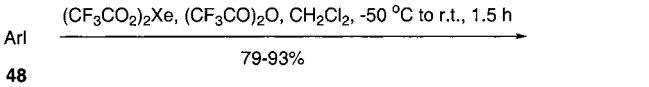


105 (42)

Zefirov, Brel, and co-workers developed a general procedure for the preparation of various [bis(trifluoroacetoxy)iodo]arenes **106** by the oxidation of iodoarenes **48** with xenon bis(trifluoroacetate), which can be generated in situ from XeF_2 and trifluoroacetic acid (eq 43).[129]



48

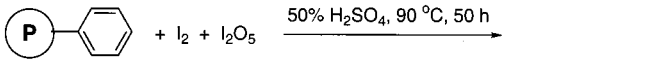
$ArI(OCOCF_3)_2$ (43)

106

Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 2-Me-4-$NO_2C_6H_3$

A general procedure for the preparation of (diacetoxyiodo)arenes by the oxidation of iodoarenes with chromium(VI) oxide in the anhydrous AcOH/Ac_2O/H_2SO_4 system was recently published by Skulski and Kazmierczak.[130]

Several very useful polymer-supported [bis(acyloxy)iodo]arenes have been developed in the past few years.[131−137] In contrast to the monomeric DIB and BTI, the polymeric analogues are reusable and convenient in handling and in the separation from the reaction mixture. Several groups recently utilized poly[styrene(iodosodiacetate)] **109**, which can be prepared in two steps from the commercial polystyrene **107** with an average molecular weight ranging from 45 000 to 250 000.[131−133] In the first step, polystyrene **107** is iodinated with iodine and iodine pentoxide in sulfuric acid to give poly(iodostyrene) **108** (eq 44). In the second step, poly(iodostyrene) is converted to diacetate **109** by treatment with peracetic acid (eq 45).[133]



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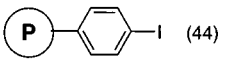

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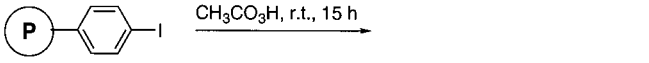

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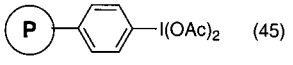


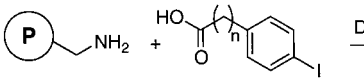
(45)

109

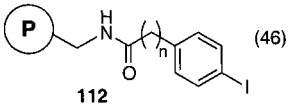
The composition (loading capacity) of the polymeric reagent **109** obtained by this procedure varies from 2.96 to 3.5 mmol/g as measured by iodometry and elemental analysis.[131−133] The reagent **109** prepared by Yokoyama, Togo, and co-workers is insoluble in organic solvents,[131,132] while Chen and Wang reported the preparation of soluble diacetate **109** from linear polystyrene (MW = 250 000).[133] An insoluble cross-linked poly[styrene(iodosodiacetate)] can be prepared by a similar procedure from commercially available 2% cross-linked polystyrene.[135]

Reagent **109** is very convenient in practical applications. After reaction with an organic substrate, the iodinated resin can be easily recovered from the reaction mixture by filtration and reoxidized with peracetic acid. Polymer-supported reagent **109** can be reused many times with no loss of activity.[134] Moreover, it can be used for the preparation of several other polymer-supported hypervalent iodine reagents, such as polymeric analogues of (difluoroiodo)benzene, [bis(trifluoroacetoxy)iodo]benzene, and [hydroxy(tosyloxy)iodo]benzene.[134,136] Kita and co-workers recently reported the preparation and synthetic application of polymer-supported BTI by the heating of diacetate **109** with trifluoroacetic acid or by the oxidation of polyiodostyrene **108** with 30% H_2O_2/$(CF_3CO)_2O$.[136] Compared to the diacetate **109**, the polymer-supported BTI is more soluble in dichloromethane and is a more effective oxidizer.[136]

An alternative polymer-supported BTI based on the commercially available aminomethylated polystyrene **110** was recently reported by Giannis and co-workers.[137] In the first step, the reaction of polymer **110** with 4-iodobenzoic acid or 4-iodophenylacetic acid **111** affords polymer-supported iodides **112** in excellent yields (eq 46). In the second step, iodide **112** is converted to diacetate **113** by treatment with peracetic acid at 40 °C overnight (eq 47).[137]

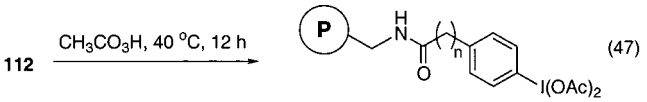


110 **111** n = 0, 1



(46)

112

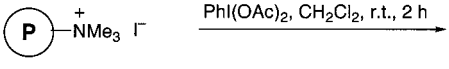


(47)

113, n = 0,1

Polymer-supported reagents **113** have a reactivity pattern similar to the polystyrene derivative **109**. Resins **113** are stable for storage and can be regenerated after their use without a measurable loss of activity.[137]

The preparation and synthetic application of several polymer-supported halogen−ate(I) complexes was reported by Kirschning and co-workers.[138−140] Specifically, the polymer-supported diacetoxyiodine−ate(I) complex **115** is prepared by the DIB-promoted oxidation of polystyrene-bound iodide **114** (eq 48).[138]



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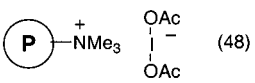


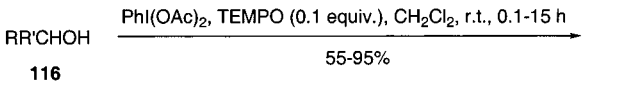
(48)

115

Complex **115** and similar polymer-supported reagents are especially useful for the electrophilic functionalization of alkenes and for the oxidation of alcohols to carbonyl compounds.[138−140]

2. Oxidation of Alcohols

[Bis(acyloxy)iodo]arenes normally have a very low reactivity toward alcohols. Only a few examples of catalytic oxidations of alcohols with DIB have been reported in the literature.[33,68,69,141,142] Piancatelli, Margarita, and co-workers found that catalytic amounts of 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) can be used in combination with DIB as a stoichiometric oxidant in the conversion of various primary and secondary alcohols **116** to carbonyl compounds **117** in generally high yields (eq 49).[141]

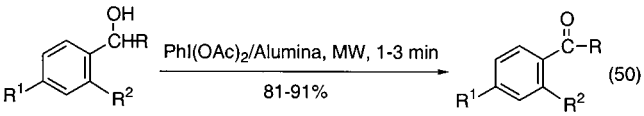


116 **117** (49)

R, R' = H, alkyl, aryl, alkenyl, etc.

This procedure 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.[141]

Benzylic alcohols **118** are rapidly oxidized to carbonyl compounds **119** using alumina-supported DIB as an oxidant under microwave irradiation (eq 50).[142] This environmentally benign solventless procedure involves mixing of the neat alcohols with 1.1 equiv of DIB doped on neutral alumina and irradiation of the reaction mixture in a microwave oven for 1−3 min. Primary alcohols are selectively oxidized under these conditions to the respective aldehydes.[142]



(50)

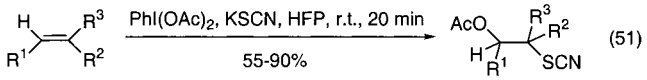
118 R = H, Et, C_6H_5CO, 4-MeC_6H_4CO; R^1 = H, Me, OMe; R^2 = H, CH_2OH **119**

Various primary and secondary allylic alcohols can be chemoselectively oxidized to the corresponding carbonyl compounds by (diacetoxyiodo)benzene in the presence of a (salen)Cr(III) complex as the catalyst (see eq 15 in section II.A.3).[68,69]

Polymer-supported DIB in the presence of KBr in water can oxidize primary and secondary alcohols analogous to the PhIO/KBr system (section II.A.2). The oxidation of primary alcohols affords carboxylic acids, while the oxidation of secondary alcohols under similar conditions results in the formation of the respective ketones in excellent yields.[33]

3. Oxidative Functionalization of Alkenes

The combination of DIB and thiocyanate anion in a polar, protic nonnucleophilic solvent is useful for the oxidative functionalization of alkenes **120** to acetoxy thiocyanate derivatives **121** with *anti*-stereoselectivity and with good regioselectivity (eq 51).[143]

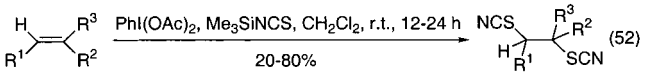


(51)

120 **121**

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 = CH_3 or $R^1 + R^2 = (CH_2)_4$, $(CH_2)_5$, R^3 = H
HFP = 1,1,1,3,3,3-hexafluoropropan-2-ol

A similar reaction of DIB with alkenes and trimethylsilyl isothiocyanate in dichloromethane affords 1,2-dithiocyanates **122** in moderate yields (eq 52). Cyclic alkenes, such as cyclohexene and 1-methylcyclohexene, react with this reagent system stereoselectively with the formation of the respective *trans*-adduct.[144]

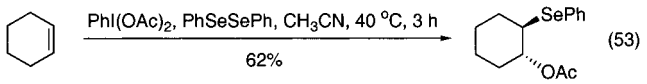


(52)

120 **122**

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

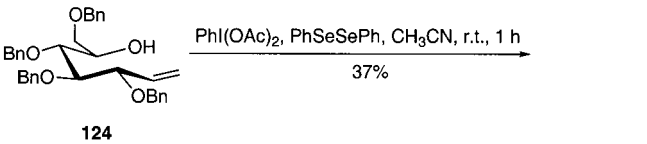
Various phenylselenated products are formed in good yields from the reaction of alkenes with diphenyl diselenide and DIB in acetonitrile. For example, cyclohexene under these conditions stereoselectively affords *trans*-1-acetoxy-2-(phenylseleno)cyclohexane **123** in good yield (eq 53).[145]



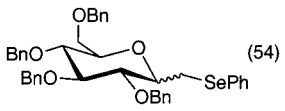
(53)

123

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 **124** reacts with diphenyl diselenide and DIB in acetonitrile with the formation of C-glycoside **125** in moderate yield (eq 54).[145]



124

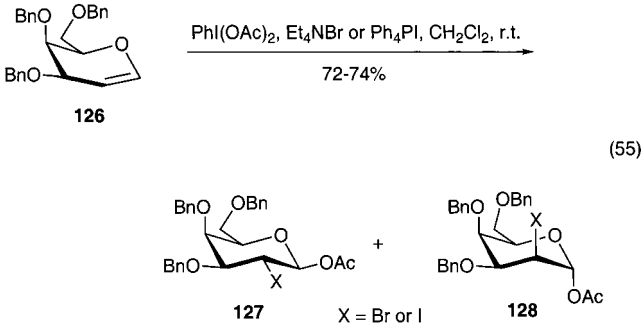


(54)

125
3:1 mixture of diastereoisomers

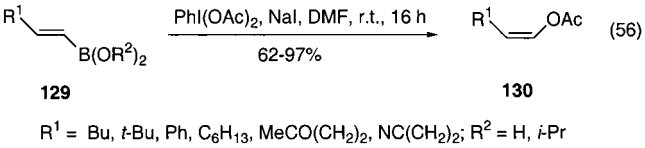
Kirschning and co-workers developed a mild method for the stereoselective bromoacetoxylation or iodoacetoxylation of alkenes by the reaction with DIB in the presence of the appropriate tetraalkylammonium or tetraphenylphosphonium salts.[146,147] This method, for example, can be applied to the synthesis of α-glycosyl acetates **127**, **128** from carbohydrate-derived enol ether **126** (eq 55). The actual reacting electrophilic species in these reactions (eq 55) are the

in situ generated diacetylhalogen(I) anions, $(AcO)_2I^-$ and $(AcO)_2Br^-$.[146,147]



(55)

Alkenylboronates **129** can be converted to the respective enol acetates **130** by treatment with DIB in the presence of sodium iodide (eq 56). This reaction (eq 56) stereoselectively affords products with inverted stereochemistry at the vinylic carbon. (*Z*)-Alkenylboronates under these conditions give stereochemically pure (*E*)-enol acetates in reasonable yields.[148]

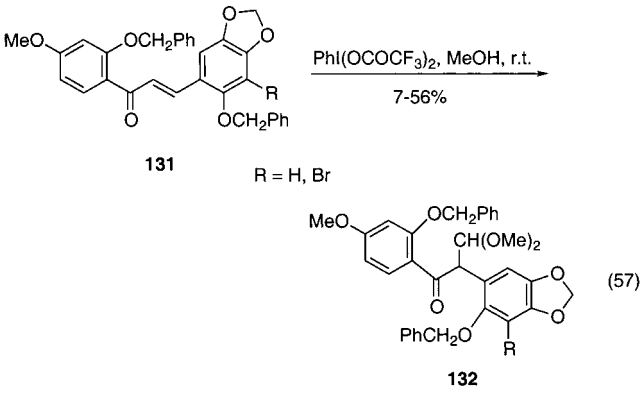


(56)

R^1 = Bu, *t*-Bu, Ph, C_6H_{13}, $MeCO(CH_2)_2$, $NC(CH_2)_2$; R^2 = H, *i*-Pr

4. Oxidative Rearrangements and Fragmentations

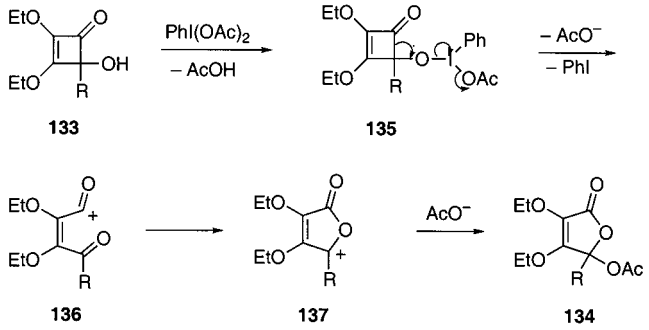
Numerous examples of DIB- or BTI-promoted rearrangements at electron-deficient centers have been reported in the literature. Reactions of [bis(acyloxy)-iodo]arenes with a double bond in some cases can give products of an oxidative, carbocationic rearrangement. Such a rearrangement of pentaalkoxychalcones **131** upon treatment with BTI was applied toward the preparation of the rearranged chalcones **132** (eq 57), which are key precursors in the synthesis of pterocarpins.[149]



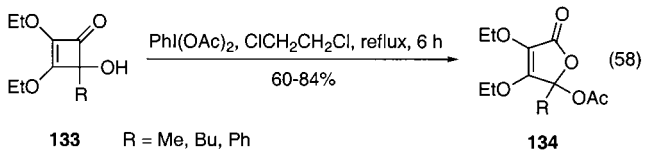
(57)

Reactions of 4-hydroxy-2-cyclobutenones **133** with DIB in 1,2-dichloroethane at reflux afford 5-acetoxy-2(5*H*)-furanones **134** as rearranged products (eq 58). The formation of these products is explained by ring cleavage of the hypervalent iodine intermediate **135**

Scheme 5



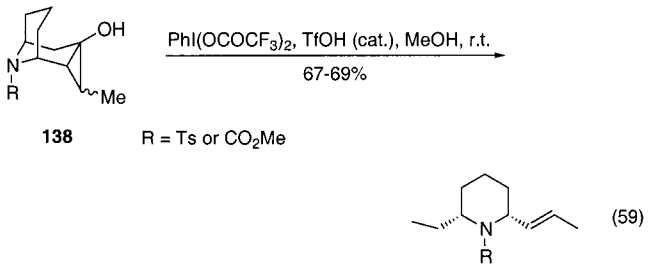
followed by recyclization of the resulting acyl cation **136** with a carbonyl oxygen (Scheme 5).[150]



(58)

In a similar procedure, 5-methoxy-2(5*H*)-furanones are obtained in good yields by using methanol as both a solvent and a nucleophile.[150]

Kirihara and co-workers reported a synthetically useful oxidative fragmentation of tertiary cyclopropyl silyl ethers with DIB or BTI which produced alkenoic acids or esters.[151,152] This fragmentation was successfully employed for the preparation of products **139** (eq 59), which are key precursors in the efficient asymmetric synthesis of the alkaloids pinidine and (+)-indolizidine 223AB.[152]

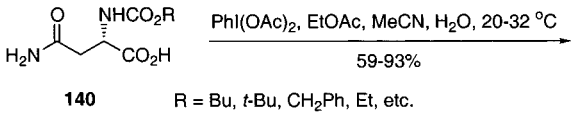


(59)

BTI and DIB are often used as reagents in the Hofmann rearrangement. Recently, Zhang and co-workers reported the application of DIB in a general synthetic procedure for the Hofmann rearrangement of protected asparagines.[153,154] After examination of many oxidizers (hypochlorite, hypobromide, *N*-bromosuccinimide, etc.), these authors found that DIB is a superior reagent for the preparation of *N*-protected *β*-amino-L-alanine derivatives **141** from *N*-protected asparagines **140** (eq 60).[153] This procedure was used for the preparation of optically pure N_α-*n*-Boc-L-α,*β*-diaminopropionic acid in hundred kilogram quantities.[154]

Another recent example includes the preparation of amine **143** by the BTI-induced Hofmann rearrangement of amide **142** (eq 61).[155]

Moriarty and co-workers recently developed a new synthetic approach to 2-benzimidazolones, 2-benzoxazolones, and related compounds based on the



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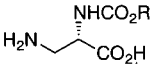
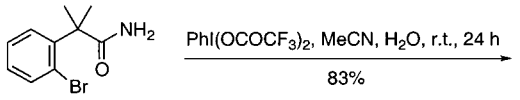


141 (60)



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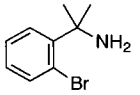
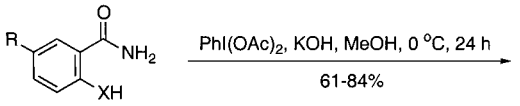


143 (61)

Hofmann-type rearrangement in the reaction of anthranilamides, salicylamides, and some β-substituted amides with DIB.[156] For example, a variety of 2-benzimidazolones (**145**, X = NR) and 2-benzoxazolones (**145**, X = O) were prepared by the treatment of amides **144** with DIB in a basic methanolic solution (eq 62). This reaction probably occurs via initial Hofmann-type rearrangement followed by intramolecular cyclization of the intermediate isocyanate.[156]



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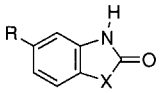
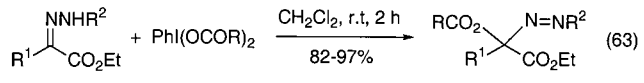


145 (62)

R = H or Cl; X = NH, NMe, NEt, NPr, N(*i*-Pr), NBu, O

Barton and co-workers reported the BTI- or DIB-induced oxidative transformations of various hydrazone derivatives of α-ketoesters.[157] The azo compounds **147** are formed in good isolated yields in the oxidation of hydrazones **146** by DIB in dichloromethane or methanol (eq 63).



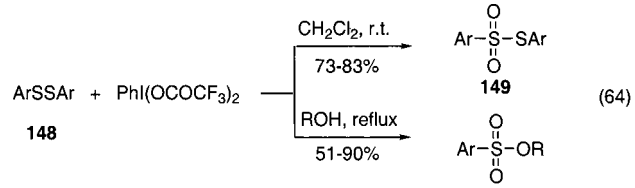
146 147 (63)

R = CH_3 or CF_3
R^1 = Me, Ph, $EtO_2C(CH_2)_2$; R^2 = Ph, Me, *t*-Bu

The α-hydroxy azo compounds, products of hydrolysis of **147**, are plausible intermediates in the BTI-induced oxidative hydrolysis of hydrazones in aqueous acetonitrile leading to the regeneration of the carbonyl group.[157]

5. Oxidations of Sulfur, Antimony, and Bismuth Compounds

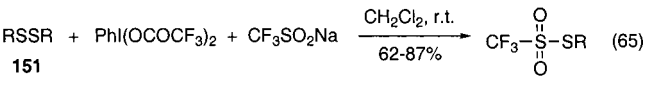
[Bis(acyloxy)iodo]arenes have been used for the oxidation of various organosulfur compounds.[132,133,158−164] Organic sulfides are selectively oxidized to sulfoxides by the solid reagent system DIB−alumina.[158] A mixture of sulfoxides and sulfones is formed upon the oxidation of sulfides by poly[styrene(iodosodiacetate)].[132,133] The reaction of diaryl disulfides **148** or thiophenols with BTI affords the corresponding thiosulfonic S-esters **149** in good yields under very mild conditions.[159] A similar reaction of diaryl disulfides with BTI in the presence of alcohols affords the respective arylsulfinic esters **150** (eq 64).[160]



148 149 150 (64)

Ar = 4-MeC_6H_4 or 4-ClC_6H_4; R = Me, Et, *i*-Pr, *t*-Bu

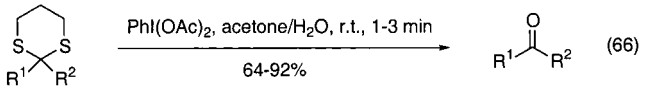
A similar oxidation of disulfides **151** with BTI in the presence of sodium trifluoromethanesulfinate provides a convenient synthetic approach to trifluoromethanethiosulfonates **152** (eq 65).[161] The analogous reaction of diselenides can be used for the preparation of trifluoromethaneselenosulfonates.[161]



151 152 (65)

R = Ph, 4-ClC_6H_4, $PhCH_2$, *t*-Bu, C_8H_{17}, *cyclo*-C_6H_{11}

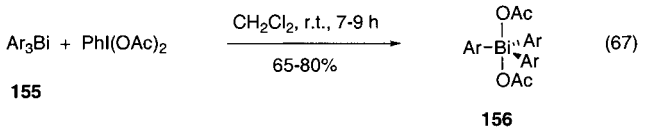
The oxidation of dithianes **153** with DIB leads to the formation of carbonyl compounds **154** (eq 66). This reaction is synthetically useful for the removal of the dithiane protecting group from aldehydes and ketones.[162] Similarly, monothioacetals can be deprotected by the treatment with BTI and sodium iodide in dichloromethane.[163]



153 R^1 = aryl, alkyl, vinyl; R^2 = H, alkyl 154 (66)

A recent paper reports the oxidation of several derivatives of tetrathiafulvalene [2-(1,3-dithiol-2-ylidene)-1,3-dithiole] with DIB leading to various cationic or radical cationic species.[164]

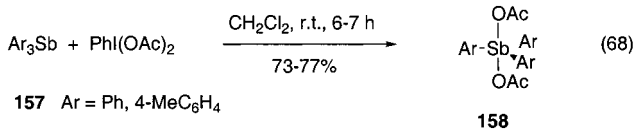
[Bis(acyloxy)iodo]arenes are useful for the oxidation of organic derivatives of bismuth and antimony.[165,166] Triarylbismuthanes **155** react with DIB in dichloromethane under mild, neutral conditions to afford pentavalent triarylbismuth diacetates **156**, which can be isolated in good yields (eq 67).[165]



155 156 (67)

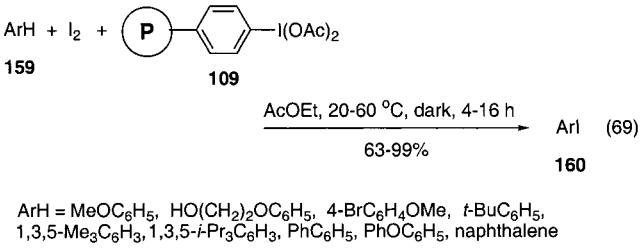
Ar = Ph, 2-MeC_6H_4, 4-MeC_6H_4, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-FC_6H_4

Triarylstibines **157** react with DIB under similar conditions to afford triarylantimony(V) diacetates **158** (eq 68).[166]

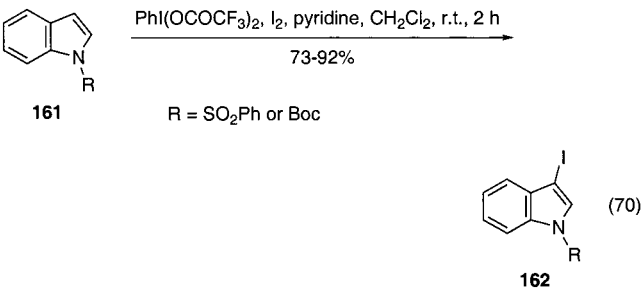


6. Oxidative Halogenation

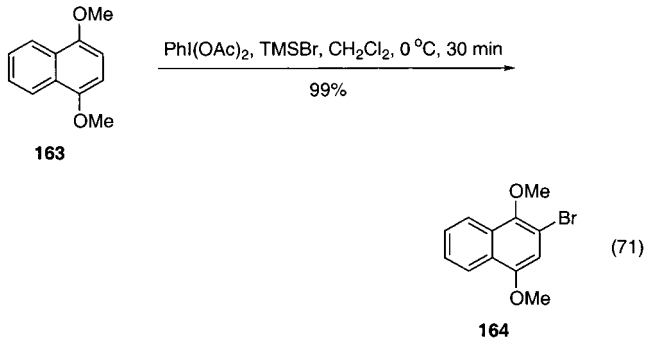
The iodination of aromatic compounds by the combination of BTI or DIB with iodine has been known for many years.[167] A recently reported improved procedure involves the treatment of activated arenes with the DIB−iodine system in a mixture of acetic acid and acetic anhydride in the presence of catalytic amounts of concentrated sulfuric acid at room temperature and within 15 min.[168] Several other [bis(acyloxy)iodo]arenes have recently been used as reagents for oxidative iodination of arenes.[128,131,132] The novel heteroaromatic derivatives of (diacetoxyiodo)arenes (see structure **103**) showed a reactivity similar to DIB in these reactions.[128] Poly-[styrene(iodosodiacetate)] **109** is an especially convenient reagent for the oxidative iodination since it can be regenerated and reused many times. This polymer-supported reagent gives the best results for the iodination of electron-rich arenes **159** with the predominant formation of the *para*-substituted products **160** (eq 69).[131,132]



Benhida and co-workers recently reported a mild and effective procedure for the iodination of electron-deficient heterocyclic systems using the BTI−iodine system. The usefulness of this procedure is best illustrated by the preparation of 3-iodoindole derivatives **162** (eq 70), which are difficult to obtain by other methods due to their chemical instability.[169] Sensitive protecting groups such as acetyl and *tert*-butyldimethylsilyl are stable under these iodination reaction conditions.[169]

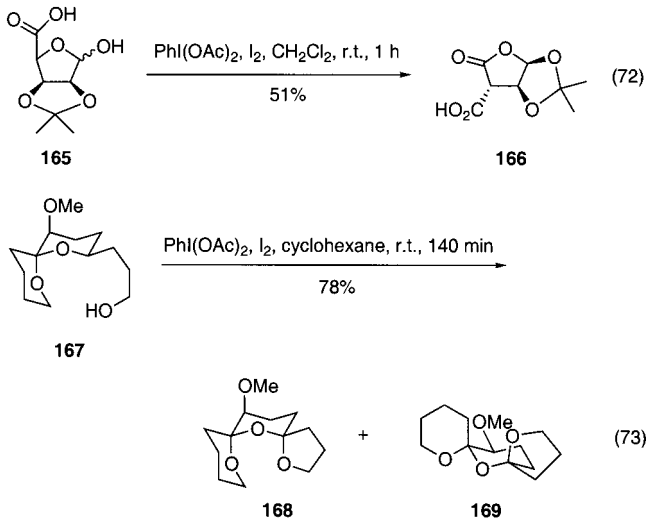


Evans and Brandt reported the oxidative halogenation of 1,4-dimethoxynaphthalenes with DIB and trimethylsilyl chloride or bromide with the formation of the corresponding halogenated or haloacetoxylated products. For example, the treatment of naphthalene derivative **163** with DIB and trimethylsilyl bromide affords 3-bromo-1,4-dimethoxynaphthalene **164** in 99% yield (eq 71).[170,171]



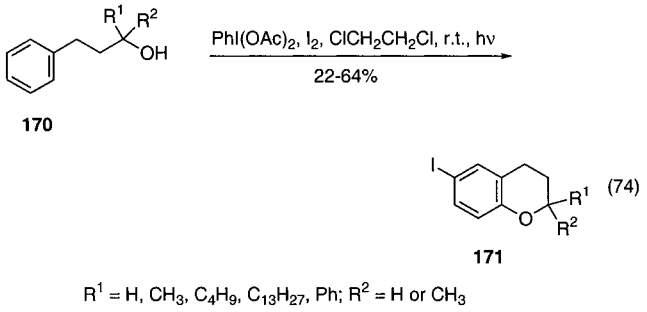
7. Generation of Oxygen- and Nitrogen-Centered Radicals

There has been significant recent interest in the development of new synthetic methodologies based on the generation of the alkoxy radicals in the reaction of alcohols with [bis(acyloxy)iodo]arenes or other hypervalent iodine reagents in the presence of iodine (see section II.A.2). Suàrez and co-workers applied this methodology in the synthesis of various carbohydrate derivatives.[37,38,172−175] Recent examples include the preparation of alduronic acid lactones **166** (eq 72)[172,173] and the synthesis of chiral dispiroacetals **168** and **169** (eq 73).[174]

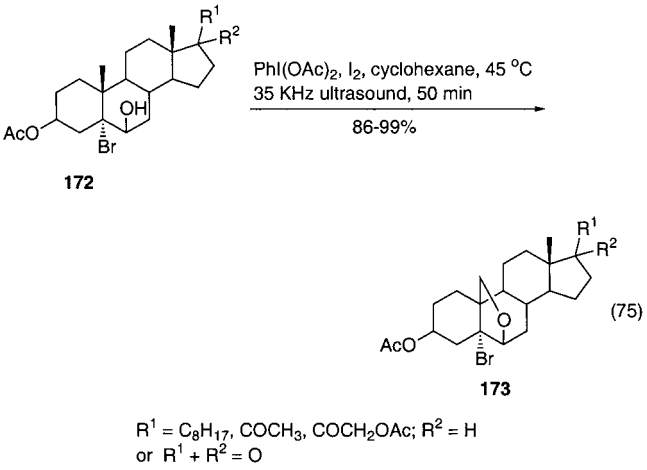


This methodology, based on the generation of the alkoxy radicals, has also been used for the oxidative cyclization of various alcohols. For example, the irradiation of alcohols **170** with DIB and iodine affords the chroman derivatives **171** in moderate to good yields (eq 74).[176]

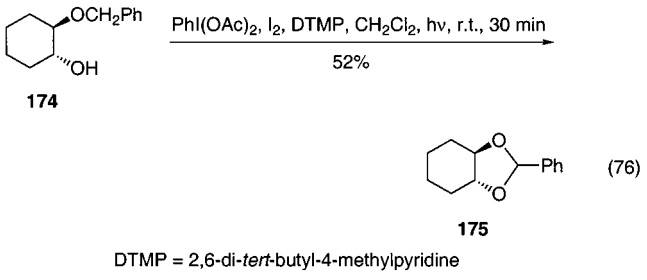
The oxidative cyclization of steroidal bromohydrins **172** selectively affords tetrahydrofurans **173** in very good yields (eq 75).[177] This reaction can be promoted either by photolysis or by ultrasonic irradiation. The



yields of products **173** are much better under the ultrasound-assisted conditions.[177]

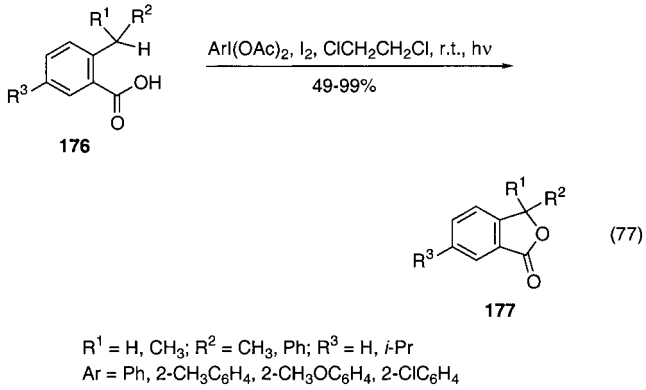


A similar oxidative cyclization initiated by the irradiation of the substrate in the presence of DIB and iodine can be used for the deprotection of benzyl ethers situated next to the hydroxyl in the α-, *β*-, or *γ*-position.[178] Depending on the substrate, the corresponding benzylidene derivatives of diols (such as **175**) are isolated (eq 76).

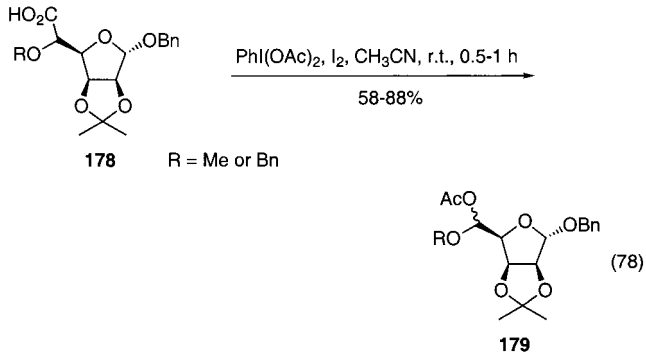


Several useful synthetic methodologies are based on the generation of the oxygen-centered radicals from carboxylic acids and the DIB−iodine system.[179−184] Togo, Yokoyama, and co-workers reported a direct conversion of 2-substituted benzoic acids **176** to lactones **177** (eq 77) via oxidative cyclization induced by [bis(acyloxy)iodo]arene/iodine.[179,180]

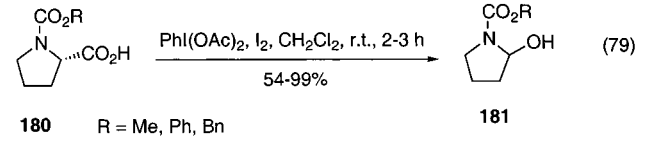
The reaction of carboxylic acids with the DIB−iodine system may result in a decarboxylation leading to the intermediate formation of a carbon-centered radical, which can be further oxidized to a carbocation and trapped by a nucleophile. This process has been utilized in several recent syntheses.[181−184] In a typical example, the oxidative decarboxylation of



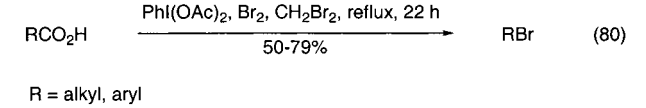
uronic acid derivatives **178** in acetonitrile under mild conditions affords acetates **179** in good yields (eq 78).[181]



A similar oxidative decarboxylation can be used for the synthesis of 2-substituted pyrrolidines **181** from the cyclic amino acid derivatives **180** (eq 79).[182,183]

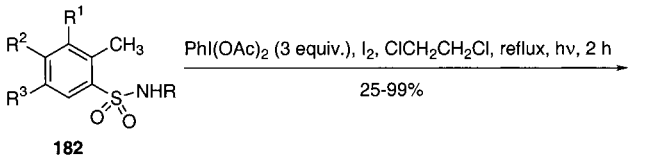


Carboxylic acids are bromodecarboxylated in moderate to good yields on reaction with DIB and bromine under irradiation with a tungsten lamp (eq 80).[184] The reaction works very well with carboxylic acids having a primary, secondary, or tertiary α-carbon atom, although diphenylacetic acid gives benzophenone. Benzoic acid derivatives are bromodecarboxylated in moderate yields if electron-withdrawing substituents are present in the benzene ring, while they are recovered mostly unchanged if the substituents are electron donating.[184]



Nitrogen-centered radicals can be generated from amides by treatment with the DIB−iodine system. Recently, Suàrez and co-workers applied this methodology in the synthesis of homochiral 7-oxa-2-azabicyclo[2.2.1]heptane derivatives from the respective phosphoramidate derivatives of carbohydrates (see eqs 9 and 10 in section II.A.2).[39] Togo, Yokoyama, and co-workers developed a useful synthetic proce-

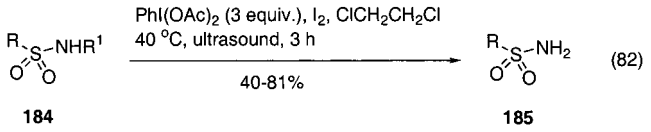
dure for the preparation of nitrogen heterocycles based on the *N*-radical cyclization onto an aromatic ring.[185−188] Specifically, various *N*-alkylsaccharins **183** are easily prepared in moderate to good yields by the reaction of arenesulfonamides **182** with DIB in the presence of iodine under irradiation with a tungsten lamp (eq 81).[185]



182 **183** (81)

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

A similar procedure was applied to the synthesis of 1,2,3,4-tetrahydroquinoline derivatives[186,187] and 3,4-dihydro-2,1-benzothiazine 2,2-dioxides.[188] Under conditions of ultrasonic irradiation in the presence of DIB and iodine, *N*-alkylsulfonamides **184** are dealkylated to afford sulfonamides **185** in moderate to good yields (eq 82).[189]

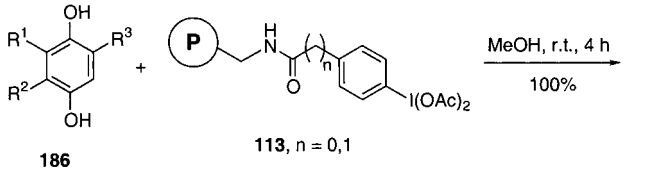


184 **185** (82)

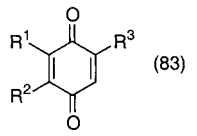
R = alkyl, aryl; R^1 = Et, Pr, Bu, $CH_2CH_3CH_2Ph$

8. Oxidation of Phenols

The reaction of [bis(acyloxy)iodo]arenes with phenols can lead to a variety of synthetically useful products. The oxidation of various *o*-substituted phenols or *o*- and *p*-hydroquinones usually affords

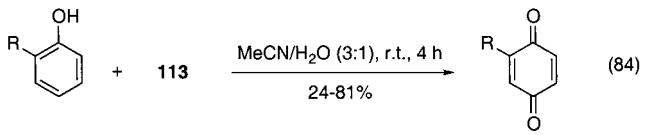


186 **113**, n = 0,1



187 (83)

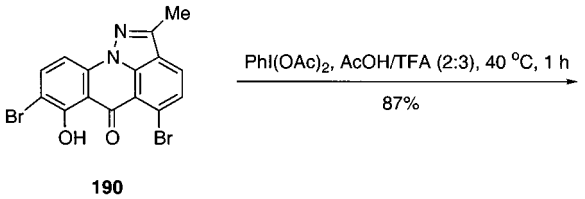
R^1 = H, Cl, Me; R^2 = H or Me; R^3 = H or Me



188 R = H, Cl, CH_2OH **189** (84)

the corresponding benzoquinones in excellent yields.[134,137,190−193] Giannis and co-workers recently reported the use of the polymeric reagents **113** (see section II.C.1) for the oxidation of polysubstituted *p*-hydroquinones **186** (eq 83) and phenols **188** (eq 84) to benzoquinones **187** and **189**.[137] These reactions (eqs 83 and 84) proceed under mild conditions, and resins **113** can be regenerated without a measurable loss of activity. The polystyrene-supported reagent **109** (see section II.C.1) oxidizes various substituted *p*-hydroquinones to benzoquinones in quantitative yields under similar conditions.[134]

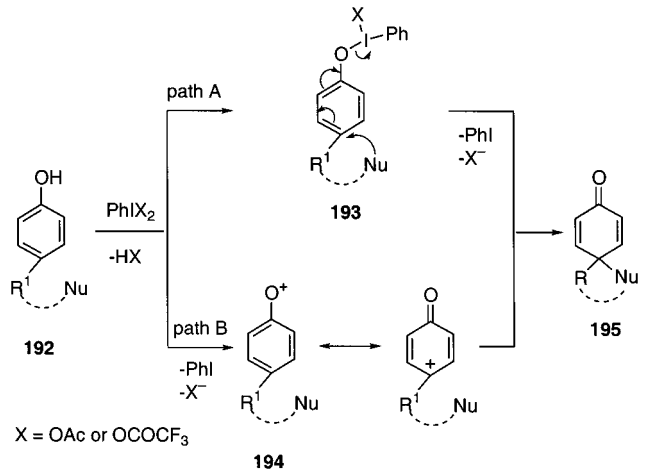
DIB is the reagent of choice for the oxidation of various phenols and hydroquinones to benzoquinones.[190,191] The oxidation of phenol **190** with DIB was recently used for the preparation of quinone **191** (eq 85), which is a key intermediate in the synthesis of a novel class of antitumor agents.[191]



190 **191** (85)

BTI can selectively oxidize polychlorinated phenols to the respective benzoquinones in aqueous media.[192] This reaction can be applied in the sensitive electrochemical determination and identification of pentachlorophenol, one of the most toxic polychlorinated phenols. Especially interesting and synthetically useful is the oxidation of the *para*-substituted phenols **192** in the presence of an appropriate external or internal nucleophile (Nu) leading to the respective spiro dienones **195** according to Scheme 6. It is assumed that this reaction proceeds via concerted addition−elimination in the intermediate product **193** or via phenoxenium ions **194**.[194−197] The recently

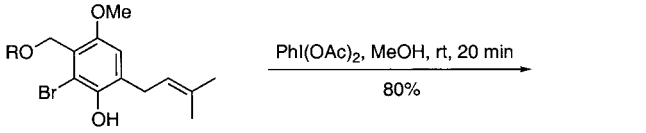
Scheme 6



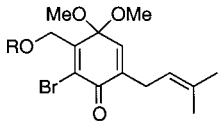
192 **193** **194** **195**

reported lack of chirality induction in the phenolic oxidation in the presence of dibenzoyltartaric acid supports the hypothesis of the mechanism proceeding via phenoxenium ions **194**.[194]

Ortho-substituted phenols can be oxidized similarly with the formation of the respective 2,4-cyclohexadienone derivatives. Various nucleophiles, such as alcohols, fluoride ion, amides, allylsilane, and electron-rich aromatic rings, have been successfully used in this reaction (Scheme 6) in either an inter- or intramolecular mode.[194−214] Recent examples of the synthetic application of this reaction in the intermolecular mode include the preparation of dimethoxyketal **197** (eq 86), which is an essential precursor in the enantioselective synthesis of the potent antifungal agent (−)-jesterone,[198] various dimethoxyketals of *para*- and *ortho*-benzoquinones,[199−201] the nucleophilic *para*-fluorination of binaphthol **198** (eq 87)[202] or 4-substituted phenols,[203] and the preparation of 2,4-cyclohexadienone derivatives **202** (eq 88)[204] by the oxidation of 2-alkoxynaphthols in the presence of an allylsilane or a silyl enol ether as a carbon-based nucleophile.

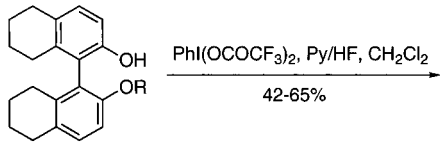


196 R = TBDPS

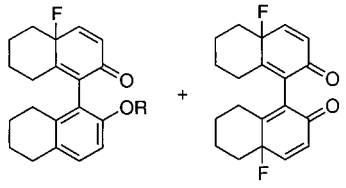


(86)

197

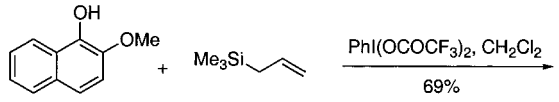


198 R = H or Ac



(87)

199 **200**



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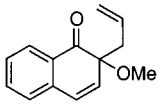
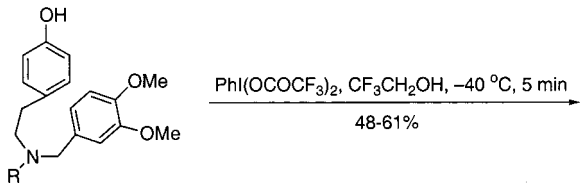


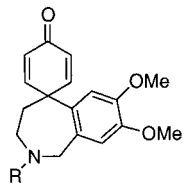
(88)

202

The phenolic oxidation in the intramolecular mode has been widely exploited as a powerful synthetic tool for the construction of a spirodienone fragment. Kita and co-workers applied the oxidative coupling of various phenolic derivatives toward the synthesis of several pharmacologically interesting natural products.[11,197,205,206] Specifically, spirodienone compounds **204**, which are intermediates for the synthesis of an amaryllidaceae alkaloid, (+)-maritidine, were selectively obtained by the reaction of **203** and BTI (eq 89).[206] More recently, Ley and co-workers applied the polymer-supported reagent **109** in this spirocyclization.[207]



203

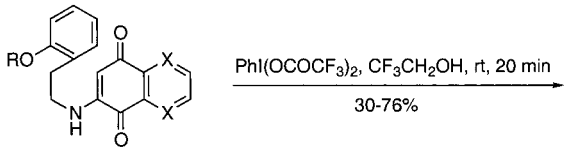


(89)

204

R = $COCF_3$, CO_2t-Bu, TEOC, CO_2Et, COC_6F_5, Me, H

A similar oxidation of the phenol derivatives **205** bearing aminoquinones at the ortho positions affords the respective azacarbocyclic spirodienones **206** (eq 90).[205]



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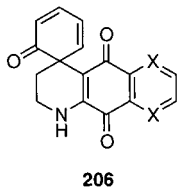
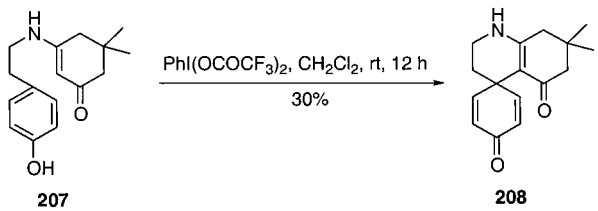


(90)

206

R = H, TMS, TBDM; X = C or N

Spyroudis, Varvoglis, and co-workers used the analogous oxidation of phenolic enaminone derivatives **207** for the preparation of spirocyclohexadienones **208** (eq 91).[208]

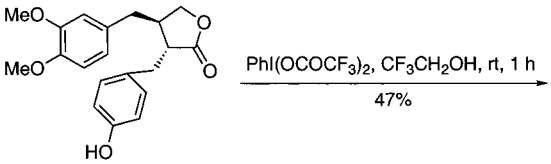


207 **208**

(91)

Treatment of the dibenzylbutyrolactone **209** with BTI in trifluoroethanol for 1 h gives as the major

product spirodienone **210**, which has been postulated as an intermediate in the biosynthesis of tetrahydrodibenzocyclooctene lignans.[209]



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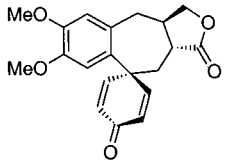
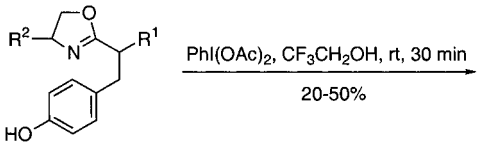


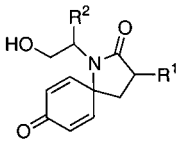
(92)

210

The BTI-induced intramolecular phenolic coupling reaction was recently used in the synthesis of galanthamine, a natural alkaloid isolated from the Amaryllidaceae family.[210] The oxidative spirocyclization of phenolic substrates containing an internal nitrogen nucleophile provides a useful tool for the construction of nitrogen heterocycles.[211−214] Ciufolini and co-workers reported the oxidative cyclization of phenolic oxazolines **211** affording the synthetically useful spirolactams **212** (eq 93).[211−213]



211



(93)

212

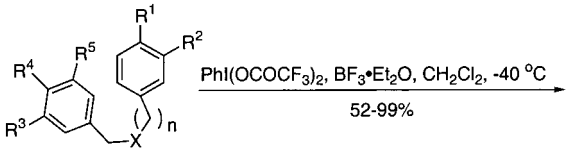
R^1 = H, NHTs, NHBoc; R^2 = H, Bn

Recently, this methodology was applied in the total synthesis of tricyclic azaspirane derivatives of tyrosine, FR901483 and TAN1251C.[214]

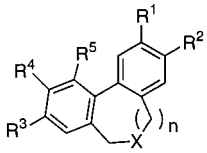
9. Oxidation of Phenol Ethers

The oxidation of phenol ethers **213** by BTI in the presence of external or internal nucleophiles affords products of nucleophilic substitution **215** via the intermediate formation of the cation radical intermediate **214** according to Scheme 7.[11,136,197,215−217]

In the intermolecular mode, this reaction has been utilized for the preparation of the products **215** from N_3^-, AcO^-, ArS^-, SCN^-, β-dicarbonyl compounds, and other external nucleophiles.[11] A similar reaction in the intramolecular mode provides a powerful synthetic tool for the preparation of various heterocyclic compounds via oxidative biaryl coupling.[136,197,215−219] Kita and co-workers reported the preparation of various dibenzoheterocyclic compounds **217** by the oxidation of phenol ether derivatives **216** with BTI in the presence of $BF_3{\cdot}Et_2O$ in dichloromethane (eq 94).[136,215,216]



216



(94)

217

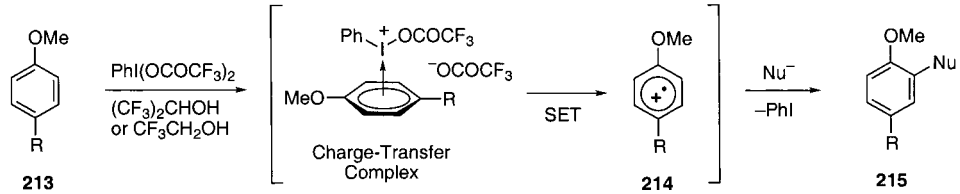
X = CH_2, $NCOCF_3$, O, S; n = 1, 2
R^1 = OMe; R^2 = H, OMe or $R^1 + R^2 = OCH_2O$
R^3 = OMe; R^4 = OMe, OTBS, OAc or $R^3 + R^4 = OCH_2O$
R^5 = H, OMe

Under similar conditions, the phenanthro-fused thiazoles **219** (eq 95), isoxazoles, and pyrimidines **221** (eq 96) can be prepared by oxidative coupling of the respective phenol ethers **218** and **220**.[218,219]

Recently, Kita and co-workers reported a novel BTI-induced direct intramolecular cyclization of α-(aryl)alkyl-β-dicarbonyl compounds **222** (eq 97).[217] Both *meta*- and *para*-substituted phenol ether derivatives containing acyclic or cyclic 1,3-dicarbonyl moieties at the side chain undergo this reaction in a facile manner affording spirobenzannulated compounds **223** that are of biological importance.[217]

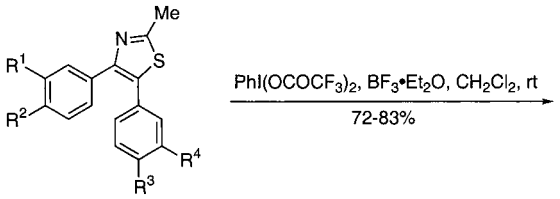
The oxidation of phenol ethers containing the azido group as an internal nitrogen nucleophile provides a useful tool for the construction of nitrogen heterocycles.[220−222] Kita and co-workers reported an efficient synthesis of quinone imine ketals **225** from the substituted phenol ethers **224** bearing an alkyl azido side chain (eq 98).[220]

Scheme 7

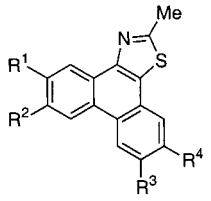


213 **214** **215**

R = alkyl, alkoxy, halogen, etc.
Nu = N_3, OAc, SAr, SCN, etc. or internal nucleophilic group



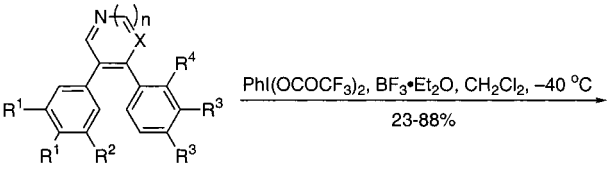
218



(95)

219

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



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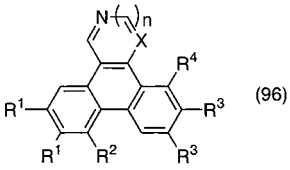


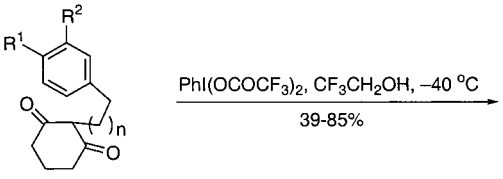
(96)

221

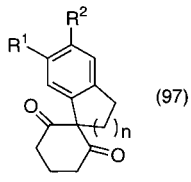
X = O, n = 0; X = N, n = 1
R^1, R^2, R^3, R^4 = H or OMe

A similar intramolecular cyclization of 3-(azidoethyl)indole derivatives **226** provides an efficient route to the pyrroloiminoquinone system **227** (eq 99), which is an essential component of a number of recently isolated marine alkaloids such as makaluvamines, isobatzelline C, and discorhabdins**,** which possess potent biological activities.[221]

The oxidation of phenol ethers **228** bearing an alkyl sulfide side chain followed by treatment with aqueous



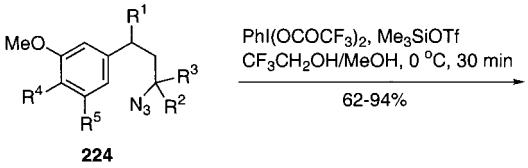
222



(97)

223

R^1 = OMe, R^2 = H, n = 1
R^1 = OMe, R^2 = OMe, n = 1 or 2
R^1 = H, R^2 = OMe, n = 1 or 2



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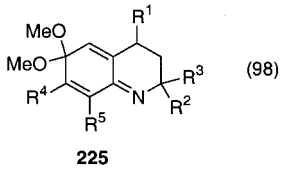
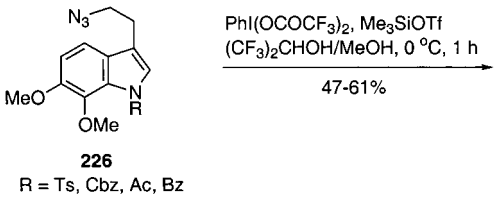


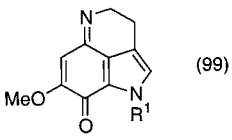
(98)

225

R^1, R^2, R^3 = H or Me; R^4, R^5 = H or OMe



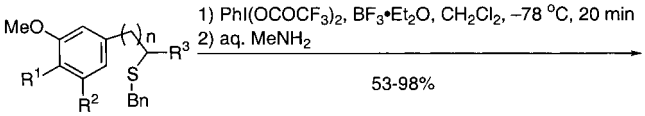
226
R = Ts, Cbz, Ac, Bz



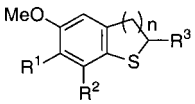
(99)

227
R^1 = Ts, Cbz, or H

methylamine selectively affords various dihydrobenzothiophenes **229** (eq 100) without yielding any sulfoxides as byproducts.[222]



228



(100)

229

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

This procedure was applied in the total synthesis of the potent cytotoxic makaluvamine F, a sulfur-containing pyrroloiminoquinone marine product.[223]

D. Derivatives of Strong Acids

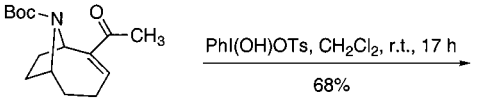
[Hydroxy(organosulfonyloxy)iodo]arenes, ArI(OH)-OSO_2R, are the most common, well investigated, and practically useful iodosyl derivatives of strong acids.[1] The most important of them, [hydroxy(tosyloxy)iodo]-benzene (HTIB or "Koser's Reagent"), is commercially available and is commonly used as an oxidizing reagent in organic synthesis.[13] The structural features of HTIB and similar sulfonates were thoroughly discussed in earlier reviews and monographs. In a recent paper, Richter, Koser, and co-workers characterized the species present in aqueous solutions of [hydroxy(mesyloxy)iodo]benzene and [hydroxy(tosyloxy)iodo]benzene.[27] Specifically, it was found that

upon solution in water, both PhI(OH)OMs and PhI(OH)OTs undergo complete ionization to give the hydroxy(phenyl)iodonium ion (PhI^+OH) and the corresponding sulfonate anion (RSO_3^-) as fully solvated species, i.e., free ions, which do not form ion pairs with each other. In addition, the μ-oxo dimer, $[Ph(HO)I-O-I^+(OH_2)Ph]$, is present at significant levels even in relatively dilute solutions.[27]

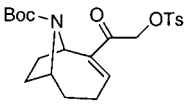
Numerous iodosyl derivatives of other strong inorganic acids, such as sulfuric, trifluoromethanesulfonic, perchloric, and others, have also been reported in the literature. In general, these derivatives lack stability and typically are generated and used in situ, at low temperature, under absolutely dry conditions.

1. [Hydroxy(tosyloxy)iodo]benzene

A large number of research papers dealing with the synthetic application of HTIB and other similar sulfonates such as mesylate and nosylate have been published in the last five years.[224−248] The functionalization of carbonyl compounds at an α-carbon represents the most typical reaction of [hydroxy(organosulfonyloxy)iodo]arenes.[224−232] HTIB was recently used for the functionalization of the azabicyclic alkaloid anatoxin-a, which is one of the most potent nicotinic antagonists. Reaction of *N*-Boc anatoxin-a **230** with HTIB is the method of choice for the preparation of the synthetically versatile α-tosyloxy ketone **231** (eq 101).[224]



230



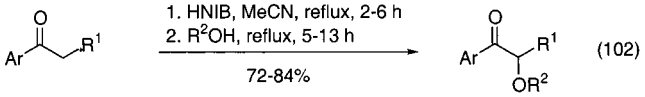
(101)

231

The tosyloxylation of the appropriate ketones was recently used in the syntheses of 2-aroylbenzo[*b*]furans, 3-aryl-5,6-dihydroimidazo[2,1-*b*][1,3]thiazoles, (1*S*,2*R*)-indene oxide, 2-mercaptothiazoles, triazolo[3,4-*b*]-1,3,4-thiadiazines, and other important heterocycles.[225−228]

Lee and co-workers used the reaction of various ketones with [hydroxy(*p*-nitrobenzenesulfonyloxy)iodo]benzene (HNIB) and subsequent treatment with the appropriate nucleophile for a one-pot preparation of secondary α-alkoxy or α-acetoxy aromatic ketones **233** (eq 102),[229] α-iodoketones **235** (eq 103),[230] and α-azidoketones **237** (eq 104)[231] in high yields.

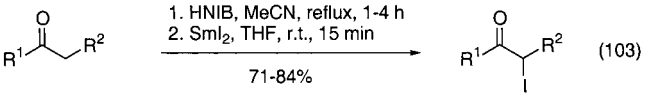
Recently, Koser and co-workers reported a novel functionalization of carboxylic anhydrides at α-carbon with [hydroxy(organosulfonyloxy)iodo]arenes. The treatment of carboxylic anhydrides **238** with reagents **239** at about 100 °C and esterification of the reaction mixture with methanol affords 2-sulfonyloxycarboxylate esters **240** (eq 105) in moderate to good yields.



(102)

232 **233**

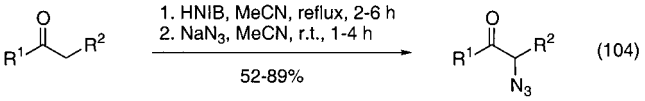
HNIB = $PhI(4\text{-}NO_2C_6H_4SO_3)OH$
Ar = Ph, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}MeC_6H_4$, etc.
$R^1 = C_2H_5$, C_3H_7, etc.; $R^2 = CH_3$, C_2H_5, Ac



(103)

234 **235**

HNIB = $PhI(4\text{-}NO_2C_6H_4SO_3)OH$
R^1 = aryl, alkyl, cyclopropyl; R^2 = H, CH_3
or $R^1 + R^2$ = cycloalkyl

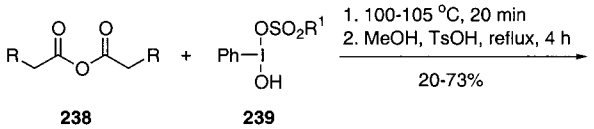


(104)

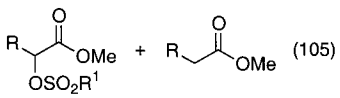
236 **237**

HNIB = $PhI(4\text{-}NO_2C_6H_4SO_3)OH$
R^1 = aryl, heteroaryl, alkyl; R^2 = H, CH_3
or $R^1 + R^2$ = cycloalkyl

This reaction is consistent with enolic behavior in carboxylic anhydrides.[232]



238 **239**

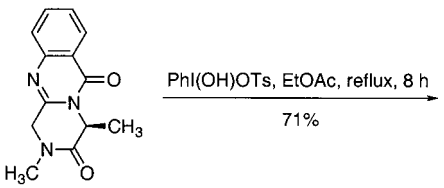


(105)

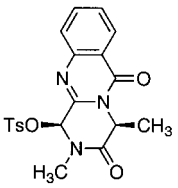
240

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

Pyrazino[2,1-*b*]quinazoline-3,6-dione **241** can be selectively converted into a *cis*-tosylate **242** by treatment with HTIB in ethyl acetate (eq 106).[233−235] This reaction was used as the key step in the synthesis of the didehydro analogues of *N*-acetylardeemin, which is an important fungal metabolite, one of the most potent known inhibitors of multidrug resistance to antitumor agents.[235]



241

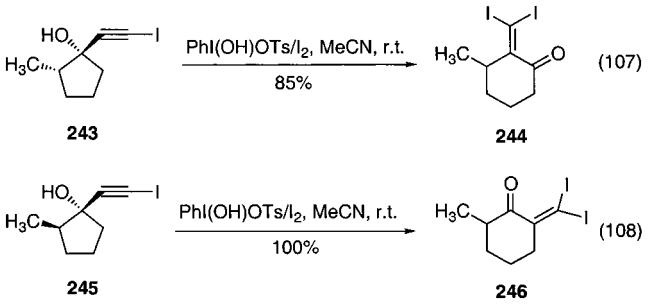


(106)

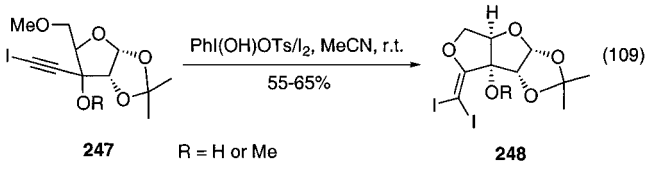
242

HTIB has been used in various oxidative rearrangements and fragmentations. McNelis and Herault reported stereoselective ring expansions in

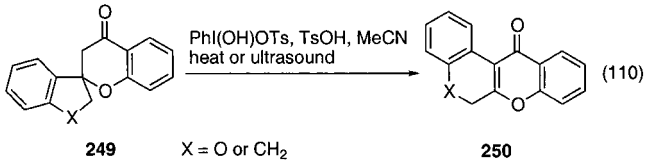
1-haloethynyl-2-methylcyclopentanols **243** and **245** upon treatment with HTIB and iodine.[236] Depending on the relative stereochemistry of the methyl and the hydroxyl groups in the starting cyclopentanol, the products are 2-(dihalomethylidene)-3-methylcyclohexanone **244** from *cis*-cyclopentanol **243** (eq 107) and 2-(dihalomethylidene)-6-methylcyclohexanone **246** from *trans*-cyclopentanol **245** (eq 108).[236]



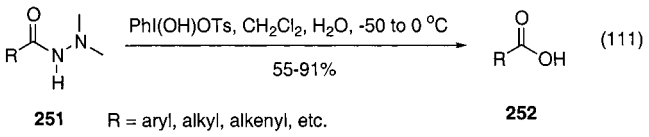
The treatment of iodoalkynol derivatives of xylose **247** with HTIB and iodine under similar conditions affords *β*,*β*-diiodoenol ethers **248** contained in furo[3,4-*b*]furan cores (eq 109).[237]



Gabbutt and co-workers reported a convenient synthesis of rotenoid derivatives **250** by the novel oxidative ring expansion of spiro-substituted chroman-4-ones **249** upon treatment with HTIB (eq 110).[238]

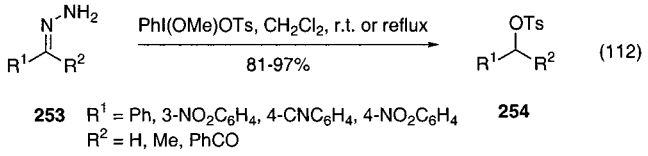


HTIB can also be used in the oxidative rearrangements and fragmentations of various nitrogen-containing compounds.[239−242] *N*,*N*-Dimethylhydrazides **251** are efficiently cleaved to give the carboxylic acid **252** upon treatment with HTIB in water or aqueous dichloromethane (eq 111).[239]

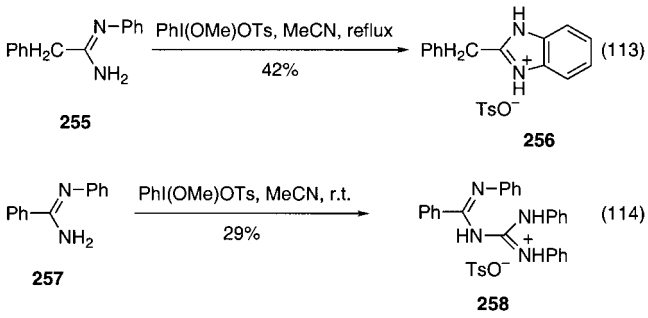


Aromatic hydrazones **253** are converted to the corresponding tosylates **254** in high yield upon the reaction with [methoxy(tosyloxy)iodo]benzene (MTIB) in dichloromethane (eq 112).[240]

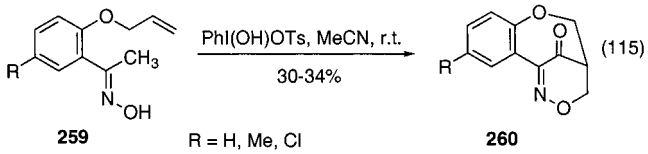
N-Substituted amidines react with MTIB with the formation of cyclization products or the products of oxidative rearrangement. *C*-Alkyl-*N*-arylamidines **255** cyclize in high yield giving benzimidazoles **256**



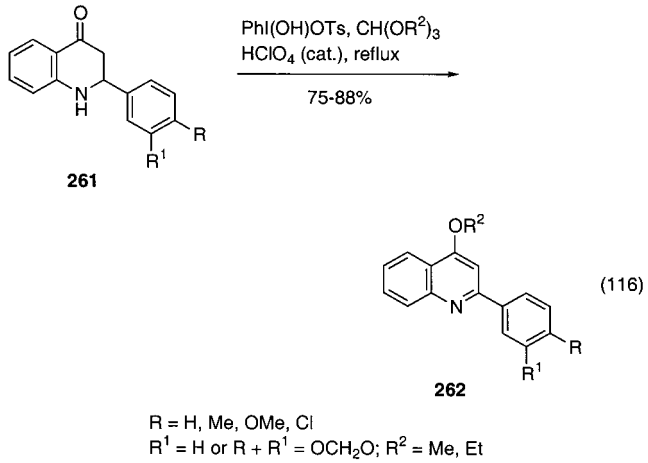
(eq 113), but *C*,*N*-diarylamidines **257** rearrange to give products **258** (eq 114) derived from an intermediate carbodiimide.[241]



Ketoximes generally react with HTIB affording the corresponding ketones as deoximation products.[242] However, the treatment of oximes of *o*-allyloxyacetophenones **259** with HTIB gives tricyclic products **260** (eq 115) due to the intramolecular cyclization of an intermediate nitrosoalkene generated from the oxime and HTIB.[242]

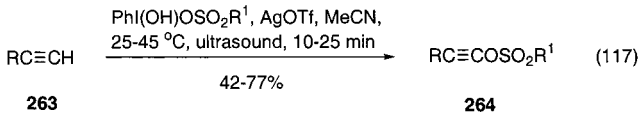


Quinolones **261** are readily oxidized by HTIB to the corresponding quinolines **262** in high yield (eq 116), thus providing a concise route to an important class of naturally occurring alkaloids.[243]

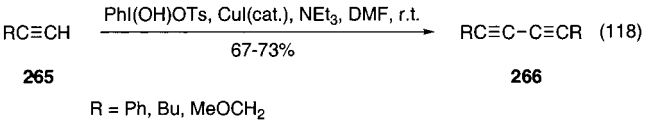


Alkynyl sulfonate esters **264** can be prepared in one pot from terminal alkynes **263** and the appropriate [hydroxy(organosulfonyloxy)iodo]benzene under ultrasonic irradiation conditions (eq 117).[244]

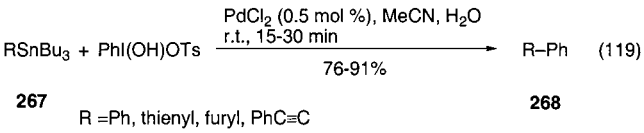
In the presence of HTIB, catalytic amounts of CuI and a base terminal alkyne couple smoothly affording



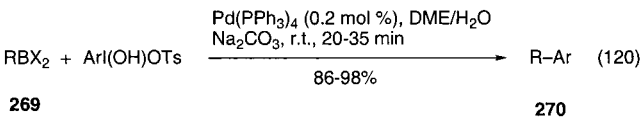
conjugated diynes **266** (eq 118).[245] This coupling can also be promoted by (diacetoxyiodo)benzene.



The coupling of organostannanes **267** with HTIB in the presence of a palladium catalyst is accomplished at room temperature under aqueous conditions to afford phenyl-substituted products **268** (eq 119).[246] The μ-oxo-bridged triflate (Zefirov's reagent) can also be used in this cross-coupling reaction.

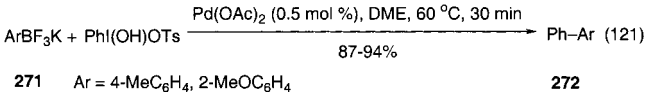


Organoboron compounds can also be used in the palladium-catalyzed cross-coupling reaction with HTIB.[247,248] Coupling of boronic acids, boronates, and trialkylboranes **269** with ArI(OH)OTs in the presence of $Pd(PPh_3)_4$ or $Pd(OAc)_2$ under aqueous conditions affords biphenyls and aryl-substituted alkenes **270** in almost quantitative yield (eq 120).[247]



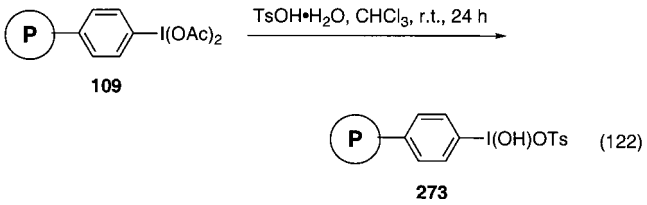
Potassium aryltrifluoroborates **271** react smoothly with HTIB under mild conditions in the presence of a palladium catalyst to afford biaryls **272** in excellent yields (eq 121).[248]

HTIB and other sulfonate derivatives of iodosylbenzene have also found wide application for the preparation of various iodonium salts (see section II.I).

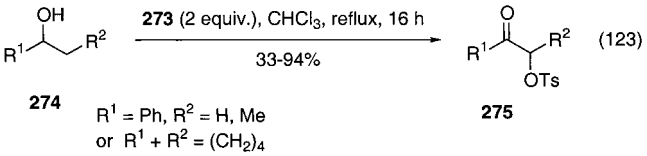


2. Other Reagents—Derivatives of Strong Acids

Several new, potentially useful organosulfonate derivative of iodosylarenes have been reported in the recent literature.[127,249,250] Togo and co-workers reported the preparation of novel polymer-supported [hydroxy(tosyloxy)iodo]arenes **273** from the respective poly[(diacetoxy)iodo]styrenes **109** (eq 122).[249] According to analytical data, 100% of the (diacetoxy)-iodo groups of polymer **109** were converted to the corresponding hydroxy(tosyloxy)iodo groups in product **273** under these reaction conditions.

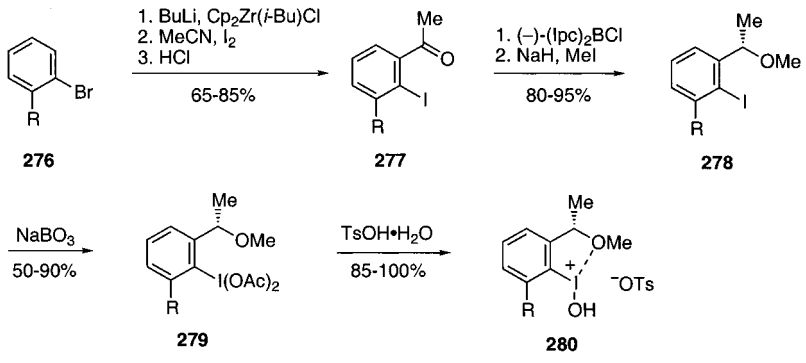


Poly[hydroxy(tosyloxy)iodo]styrenes **273** show the same reactivity as HTIB in the reaction of α-tosyloxylation of ketones. In addition, the polymeric reagents **273** show excellent reactivity in the direct conversion of alcohols to α-tosyloxyketones **275** (eq 123), while HTIB has a low reactivity toward alcohols.[249]



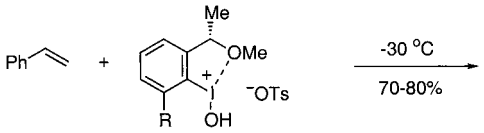
Wirth and co-workers reported the preparation of a series of *ortho*-substituted chiral hypervalent iodine reagents **280** starting from the corresponding arylhalides as shown in Scheme 8.[127,250] The structure of compound **280** (R = H) was established by X-ray analysis.[127] In contrast to HTIB, the two oxygen atoms nearest to the iodine atom in **280** are the oxygen atom of the hydroxy group (I−OH, 1.94 Å)

Scheme 8

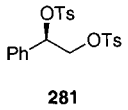


and the methoxy oxygen atom (I−OMe, 2.47 Å), while the tosylate oxygen atom is further away from the iodine atom (I−OTs, 2.82 Å).

The new compounds **280** were evaluated as enantioselective electrophilic reagents toward alkenes and ketones. Enantioselectivities as high as 65% have been achieved in the dioxytosylation of styrene (eq 124) and of up to 40% in the oxytosylation of propiophenone (eq 125). The maximum selectivity is observed in the reactions of *ortho*-ethyl compounds **280**, with lower selectivity being observed for reagents **280** bearing both smaller and larger substituents R. X-ray structure analysis and ab initio calculations have been used to develop a model for rationalizing the stereoselectivities in the reactions of chiral hypervalent iodine reagents **280**. 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.[250]



280

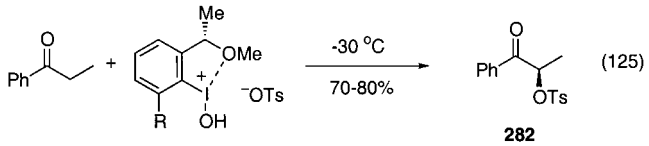


(124)

281

up to 65% ee
(when R = Et)

R = Me, Et, *i*-Pr, Ph, OMe, OBn, OEt,
O*i*-Pr, O*t*-Bu, OMOM, Naphthyl



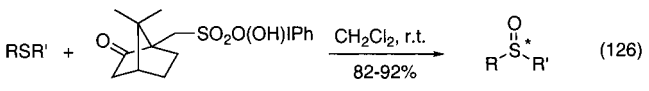
(125)

280 **282**

up to 40% ee
(when R = Et)

R = Me, Et, *i*-Pr, Ph, OMe, OBn, OEt,
O*i*-Pr, O*t*-Bu, OMOM, Naphthyl

Chen and Xia reported the oxidation of alkyl and aryl sulfides **283** with [hydroxy(((+)-10-camphorosulfonyl)oxy)iodo]benzene **284** as chiral oxidant (eq 126). This reaction afforded the corresponding sulfoxides **285** in excellent yields but with low enantioselectivity.[251]

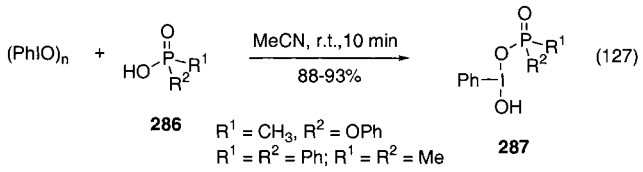


(126)

283 **284** **285**, 3-14% ee

Moriarty and co-workers reported the preparation of new [hydroxy(phosphoryloxy)iodo]benzenes **287** by the reaction of iodosylbenzene with the appropriate phosphonic or phosphinic acid **286** (eq 127).[252]

These reagents (**287**) are useful for the introduction of the corresponding phosphonate or phosphinate

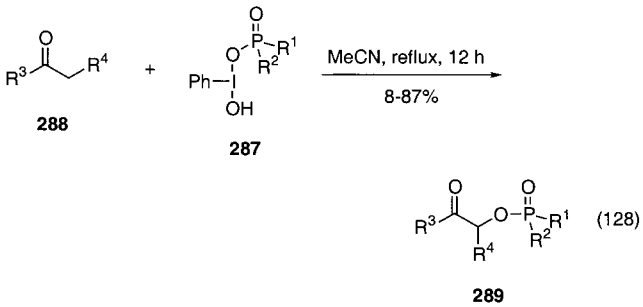


(127)

286 $R^1 = CH_3$, $R^2 = OPh$
$R^1 = R^2 = Ph$; $R^1 = R^2 = Me$

287

groups in the α-position to ketone and ester carbonyl groups of carbonyl compounds **288** (eq 128).[252]



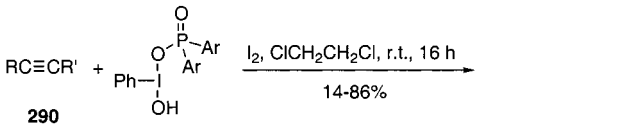
288 **287**

(128)

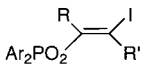
289

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

Recently, Togo and co-workers demonstrated the utility of these reagents for iodophosphoryloxylation of alkynes and alkenes.[253] Specifically, alkynes **290** were converted to the corresponding 1,2-iodophosphoryloxylated compounds **291** in moderate to good yields upon treatment with reagents **287** in the presence of iodine (eq 129).



290 **287**

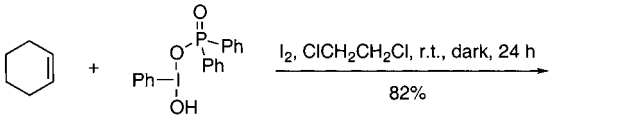


(129)

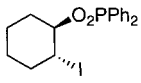
291

Ar = Ph or OPh; R = Ph, Pr, Bu; R' = H, Me, Pr, Ph

Under similar conditions, cyclohexene is converted to the corresponding adduct **292** in excellent yield (eq 130).[253]



287



(130)

292

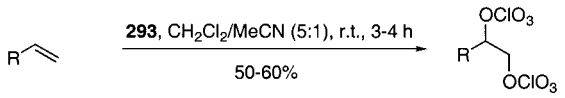
Piancatelli and co-workers reported the preparation of an unusual iodosylbenzene derivative of perchloric acid, diperchlorate **293**, by the reaction of DIB with magnesium perchlorate (eq 131).[254] The structure of product **293** was suggested on the basis of NMR and HPLC-MS data; however, this structure is inconsistent with the previously reported μ-oxo-

bridged structures for the iodosylbenzene derivatives of strong acids including perchloric acid.[1,23]

$$PhI(OAc)_2 + Mg(ClO_4)_2 \xrightarrow{EtOAc,\ r.t.,\ 30\ min} PhI(ClO_4)_2 \quad (131)$$

293

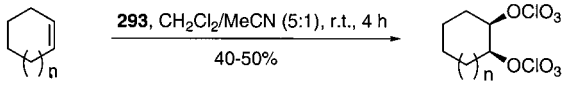
The reaction of alkenes **294** and cycloalkenes **296** with reagent **293** generated in situ from DIB and magnesium perchlorate affords 1,2-diperchlorates **295** and **297** (eqs 132 and 133).[254]



(132)

294 **295**

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



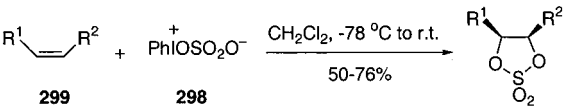
(133)

296, n = 1, 2, 3 **297**

Taylor and co-workers reported a new procedure for the preparation of phenyliodosulfate **298** by the reaction of iodosylbenzene and trimethylsilyl chlorosulfonate followed by removal of the solvent and trimethylchlorosilane (eq 134).[255] This reagent can be used to prepare cyclic sulfates **300** from alkenes and vinylsilanes **299** (eq 135).

$$(PhIO)_n + 2Me_3SiOSO_2Cl \xrightarrow[-2Me_3SiCl]{CH_2Cl_2,\ -78\ ^\circ C} PhIOSO_2O^- \quad (134)$$

298



(135)

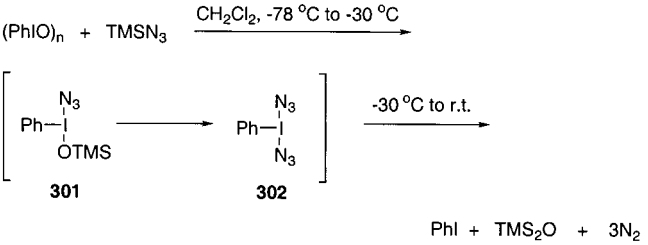
299 **298** **300**

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

E. Azidoiodanes

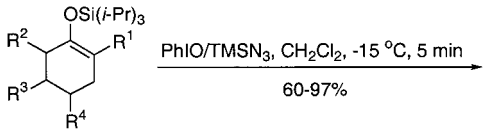
Azidoiodanes **301** or **302** can be conveniently generated by a low-temperature reaction of iodosylbenzene and azidotrimethylsilane in dichloromethane (Scheme 9).[1] Above −30 °C azidoiodanes decompose with the formation of iodobenzene and dinitrogen; however, low-temperature spectroscopy and chemical reactions in situ provided experimental evidence toward the existence of these species.[1] A recent isolation and X-ray structural analysis of the stable 1-azidobenziodoxoles (see section II.F) further support the structure of azidoiodanes **302**.[256]

Scheme 9

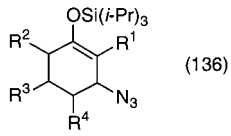


301 **302**

Azidoidanes **301** and **302** generated in situ from $PhIO/TMSN_3$ have found some practical application as efficient reagents for the introduction of the azido function into organic molecules. Magnus and co-workers recently reported several useful azidonations utilizing this reagent system.[257−263] Various triisopropylsilyl enol ethers **303** and **305** react with this reagent at −15 to −18 °C to give the β-azido adducts **304** and **306** in excellent yields (eqs 136 and 137).[257]



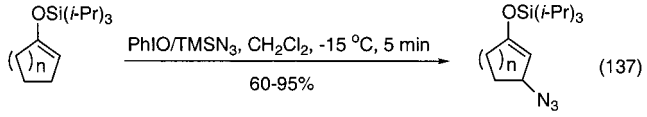
303



(136)

304

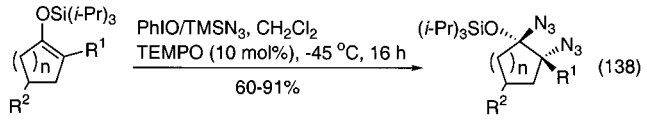
R^1, R^2 = H or Me; R^3 = H, *i*-Pr or 2-propenyl
R^4 = H, Me, Et, *i*-Pr, *t*-Bu, etc.



(137)

305 n = 1 - 6, 8 **306**

A similar reaction of silyl ether **307** with PhIO/$TMSN_3$ at lower temperatures and in the presence of catalytic amounts of the stable radical TEMPO stereoselectively affords vicinal *trans*-diazides **308** as the major products (eq 138).[257] The effect of TEMPO on the outcome of this reaction (eqs 136−138) was explained by the change of the mechanism from ionic dehydrogenation to a radical addition process in the presence of TEMPO.[257]



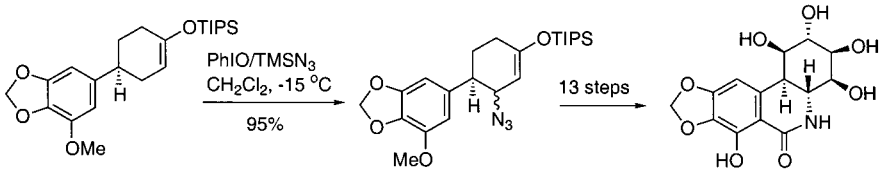
(138)

307 **308**

n = 1 or 2; R^1 = H or Ph; R^2 = H, *t*-Bu, etc.
TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl

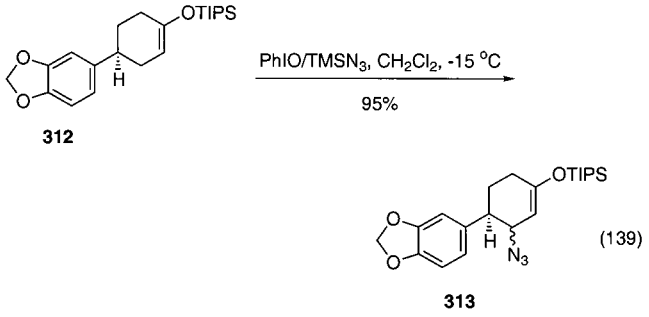
The β-azidonation reaction of triisopropylsilyl enol ethers (eqs 136 and 137) has been effectively utilized in organic synthesis.[258−261] Magnus and co-workers developed a mechanistically different enone synthesis that involves treatment of β-azido TIPS enol ethers **304** and **306** with fluoride anion to effect desilylation and concomitant β-elimination to give an α,β-enone.[258] Alternatively, the β-azido group in **304** or **306** can be ionized with Me_3Al or Me_2AlCl and the intermediate enonium ion trapped by a variety of nucleophiles such as an allylstannane, electron-rich aromatics, trimethylsilyl enol ethers, etc., to give various β-substituted triisopropylsilyl enol ethers. Reduction of the β-azido TIPS enol ether provides access to the synthetically useful β-amino TIPS enol ethers.[258]

Scheme 10

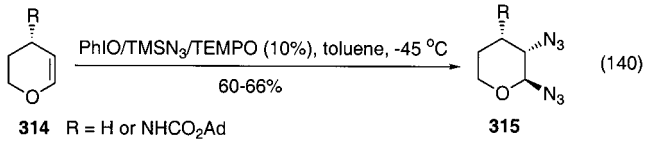


The β-azidonation of the TIPS derivative **309** was used in the total synthesis of the antitumor alkaloid (+)-pancratistatin **311**. Azide **310**, the key intermediate product in this synthetic scheme, was obtained with 95% yield as a mixture of *trans*- and *cis*-diastereomers in a 3.5:1 ratio and was further converted to pancratistatin **311** in 13 steps (Scheme 10).[259,260]

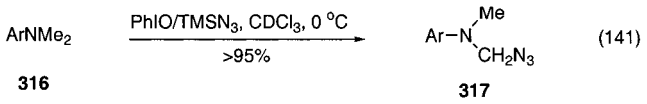
Likewise, the β-azidonation reaction was applied to the enantioselective synthesis of the core structure of Lycorane Amaryllidaceae alkaloids. **T**he key intermediate (**313**) in this synthesis was obtained by the β-azidonation of the TIPS derivative **312** as a mixture of *trans*- and *cis*-diastereomers in a 3.5:1 ratio (eq 139).[261]



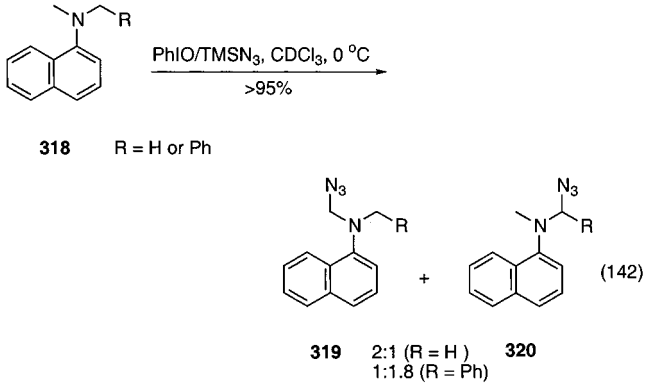
The azidonation reaction of triisopropylsilyl enol ethers leading to the vicinal *trans*-diazides (eq 138) has also been utilized in organic synthesis.[262] Dihydropyrans **314** react with the $(PhIO)_n$/$TMSN_3$/TEMPO system to give 2,3-bis-azido adducts **315** (eq 140), which can be further elaborated into amino pyrans.[262]



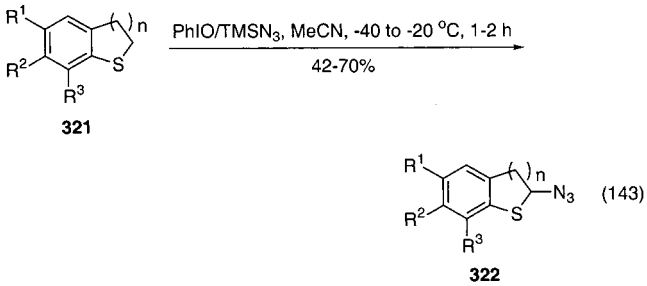
The treatment of *N*,*N*-dimethylarylamines **316** with the PhIO/$TMSN_3$ reagent system results in the functionalization of one of the methyl groups to give *N*-azidomethyl derivatives **317** (eq 141). The same reaction with an excess of the PhIO/$TMSN_3$ reagent (2.6−4 equiv) affords the respective bis(*N*,*N*-azidomethyl) derivatives. The azidonation of the unsymmetrical substrates **318** gives a mixture of products **319** and **320** (eq 142).[263]



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.



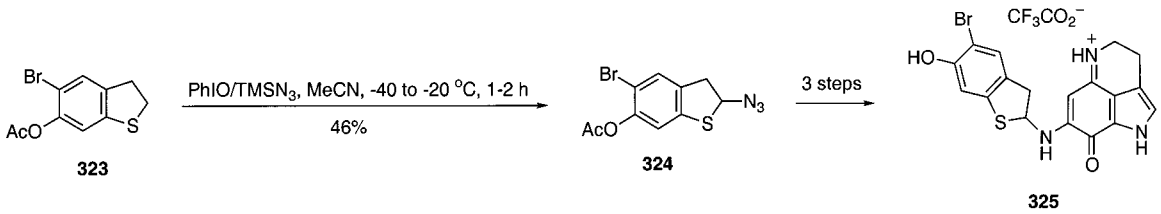
Kita and co-workers reported the direct α-azidation of cyclic sulfides using the PhIO/$TMSN_3$ reagent system.[264] This method is applicable to substrates which are easily aromatized under oxidative conditions, such as mono- and bicyclic sulfides **321**, to give the corresponding α-azido sulfides **322** in moderate to good yields (eq 143).



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

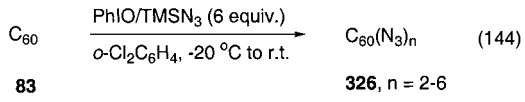
A similar α-azidation of cyclic sulfide **323** was recently used in the total synthesis of the strongly

Scheme 11

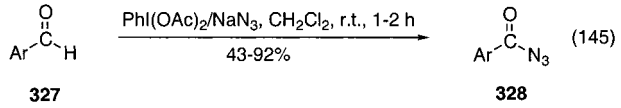


cytotoxic marine alkaloid (±)-makaluvamine F **325** (Scheme 11).[223,265]

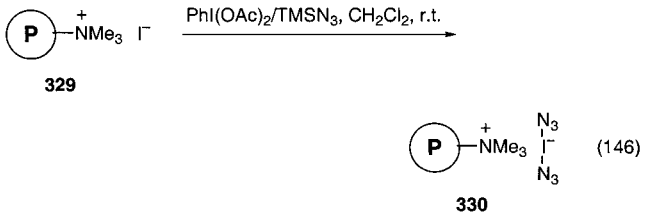
Fullerene C_{60} **83** smoothly reacts with the PhIO/$TMSN_3$ reagent system under typical azidonation conditions with the formation of the explosive polyazidofullerenes **326** (eq 144).[113]



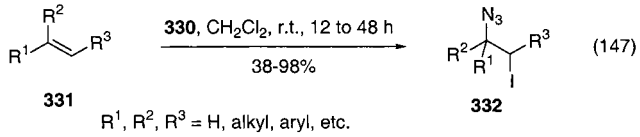
The combination of DIB and sodium azide, which presumably generates (diazidoiodo)benzene **302** as the principal reagent, readily reacts with aryl aldehydes **327** to afford aroyl azides **328** in generally high yields (eq 145).[266]



Kirschning and co-workers reported the preparation of novel reagent systems generated in situ from (diazidoiodo)benzene and tetraalkylammonium halides.[267] Especially useful is a stable polymer-bound bis(azido)iodate **330**, which can be readily prepared by the reaction of polystyrene-bound iodide **329** with (diazidoiodo)benzene generated from DIB and azidotrimethylsilane (eq 146).[267a]



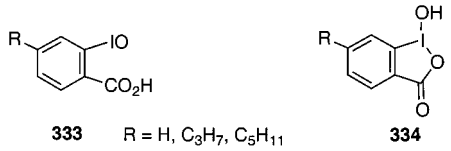
Reagent **330** reacts with alkenes **331** to give the corresponding products of β-azido-iodination **332** (eq 147). These reactions predominantly afford products of *anti*-addition with Markovnikov regioselectivity.[267a]



The preparation, structure, and reactions of stable azidobenziodoxoles will be discussed in section II.F.

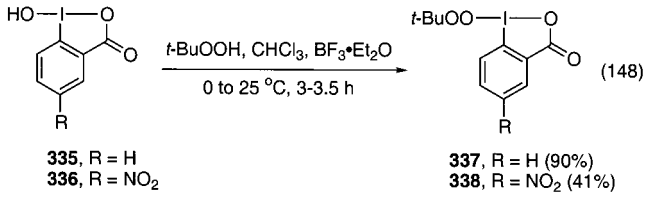
F. Benziodoxoles

The most important and best investigated representative of benziodoxoles is the commercially available 1-hydroxy-1,2-benziodoxole-3(1*H*)-one (**334**, R = H)—the cyclic tautomer of 2-iodosylbenzoic acid.[1,20,23] Recently, Moss and co-workers[268] reported the results of a structural reinvestigation of 4-alkyl-2-iodosylbenzoic acids, for which an open tautomeric form **333** was previously assigned by others. Contrary to the previous report, only the closed, iodoxolone form **334** of 4-alkyl-2-iodosobenzoic acid can be isolated; the previously assigned open (iodoso) form is actually 4-pentanoyl-2-iodobenzoic acid.[268]

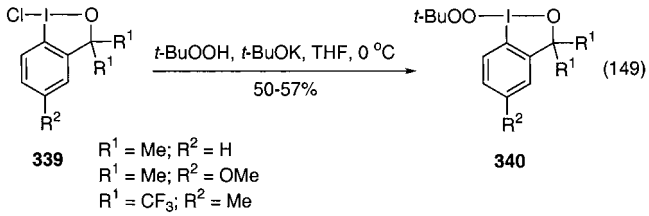


In the last 15 years 1-hydroxy-1,2-benziodoxole-3(1*H*)-one and its derivatives have attracted considerable research interest due to their excellent catalytic activity in the cleavage of toxic phosphates and reactive esters. An excellent, comprehensive review by Moss and Morales-Rojas on the phosphorolytic activity of *o*-iodosylcarboxylates and related nucleophiles appears in this issue of *Chemical Reviews*.[269]

The distinctive feature of cyclic iodanes is a considerably higher stability than that of their acyclic analogues. This stabilization is usually explained by the bridging of an apical and an equatorial position by a five-membered ring and also by better overlap of the lone pair electrons on the iodine atom with the p-orbitals of the benzene ring. The greater stability of heterocyclic iodanes enables the isolation of otherwise unstable iodine(III) derivatives with I−OOR, $I-N_3$, I−CN, and other bonds. Ochiai and co-workers reported the preparation of 1-(*tert*-butylperoxy)benziodoxoles **337** and **338** by treatment of the appropriate benziodoxoles (**335**, **336**) with *tert*-butyl hydroperoxide in the presence of BF_3·etherate (eq 148).[270] Peroxides **337** and **338** are stable, crystalline products which can be safely stored at room temperature for an indefinite period of time.



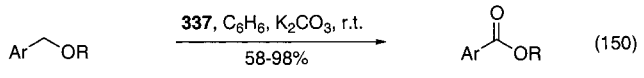
An alternative preparation of 1-(*tert*-butylperoxy)-benziodoxoles **340** from the corresponding chloroiodanes **339** and *tert*-butyl hydroperoxide in the presence of potassium *tert*-butoxide in THF (eq 149) was reported by Dolenc and Plesnicar.[271]



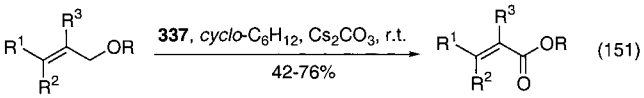
In a series of papers, Ochiai and co-workers demonstrated that peroxyiodane **337** is a useful reagent acting as a strong oxidizer toward a variety of organic substrates, such as ethers, organic sulfides, amides, and phenols.[270,272−275]

Peroxyiodane **337** oxidizes various benzyl and allyl ethers (**341**, **343**) to the respective esters (**342**, **344**) under mild conditions in the presence of alkali-metal carbonates (eqs 150 and 151).[270] Since this reaction is compatible with other protecting groups such as MOM, THP, TBDMS ethers, and acetoxy groups and

because esters are readily hydrolyzed under basic conditions, this new method provides a convenient and effective alternative to the usual reductive deprotection.

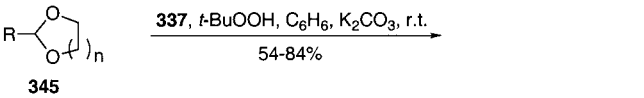


341 **342** (150)

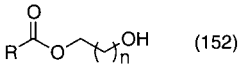


343 **344** (151)

Under similar mild conditions, peroxyiodane **337** oxidatively cleaves cyclic acetals **345** to glycol monoesters **346** (eq 152).[272]



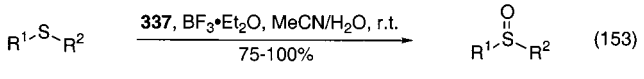
345



346 (152)

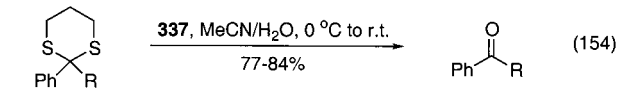
n = 1, 2; R = Ph, 4-MeC6H4, 4-ClC6H4, 3-ClC6H4, 2-furyl, PhCH2, PhCH=CH, C9H19, *cyclo*-C6H11, etc.

Sulfides **347** can be oxidized with peroxyiodane **337** under mild conditions to afford sulfoxides **348** in high yields (eq 153).[273] A similar oxidation of dithioacetals **349** leads to the regeneration of the parent carbonyl function (eq 154) and thus can be useful as a method for selective deprotection.[273]



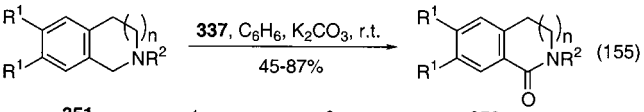
347 **348** (153)

R1 = Bu, *i*-Bu, *s*-Bu, PhCH2, Me(CH2)4, CH2=CHCH2, 4-MeC6H4, 4-MeOC6H4, 4-ClC6H4, Ph; R2 = PhCH2, Ph, Me, CH2P(O)(OEt)2



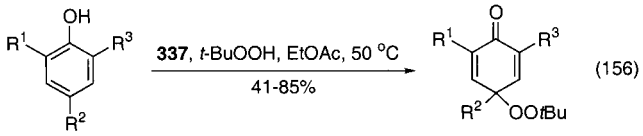
349 **350** (154)

Amides **351** are oxidized by peroxyiodane **337** at the α-methylene carbon yielding imides **352** as major products (eq 155).[274a] A similar oxidation of secondary amines affords the respective imines.[274b]



351 n = 0, 1; R1 = H or OMe; R2 = Ac, Ts, Boc **352** (155)

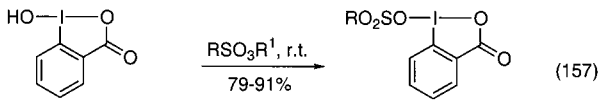
The oxidation of 4-alkylphenols **353** by peroxyiodane **337** in the presence of *tert*-butyl hydroperoxide affords selectively 4-(*tert*-butylperoxy)-2,5-cyclohexadien-1-ones **354** in good yields (eq 156).[275]



353 **354** (156)

R1, R3 = H or *t*-Bu; R2 = Me, *i*-Pr, *t*-Bu, CH2Ph, OMe, etc.

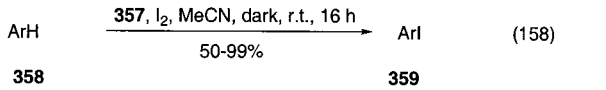
A variety of new, stable benziodoxole derivatives can be prepared from the commercially available 1-hydroxybenziodoxole by ligand exchange on iodine. Specifically, the sulfonate derivatives **355** can be conveniently prepared in a simple, one-step procedure by the treatment of 1-hydroxybenziodoxole **335** with the corresponding sulfonic acids or trimethylsilyltriflate (eq 157).[276] Sulfonates **355**−**357** were isolated as moderately hygroscopic, but thermally stable, crystalline solids.



335 R1 = H or TMS (157)

355, R = CF_3
356, R = CH_3
357, R = 4-MeC_6H_4

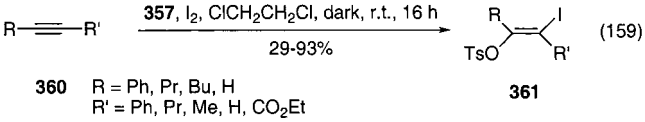
Muraki, Togo, and Yokoyama recently demonstrated that tosyloxybenziodoxole **357** can be used as an effective reagent for the oxidative iodination of aromatic compounds.[277,278] Treatment of various aromatic compounds **358** with reagent **357** and I_2 gives the corresponding iodinated compounds **359** in good yields (eq 158). Similarly, both chlorination and bromination proceed effectively. As compared with other trivalent iodine compounds, the tosylate **357** shows the best reactivity as a halogenation reagent.[277]



358 **359** (158)

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-$Me_2C_6H_4$, $MeOC_6H_5$, *t*-BuC_6H_5, $AcOC_6H_5$, naphthalene, 2,3-benzothiophene, etc.

Likewise, the reagent **357**/iodine system can be used for the iodotosyloxylation of alkynes **360** to give the addition products **361** in good yields (eq 159).[278] These reactions presumably proceed via the intermediate formation of arenesulfonyl hypoiodites.

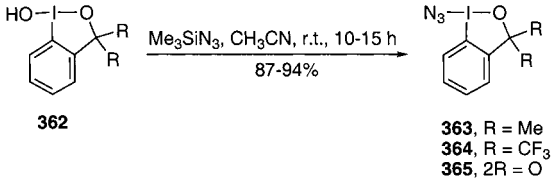


360 R = Ph, Pr, Bu, H
R' = Ph, Pr, Me, H, CO_2Et

361 (159)

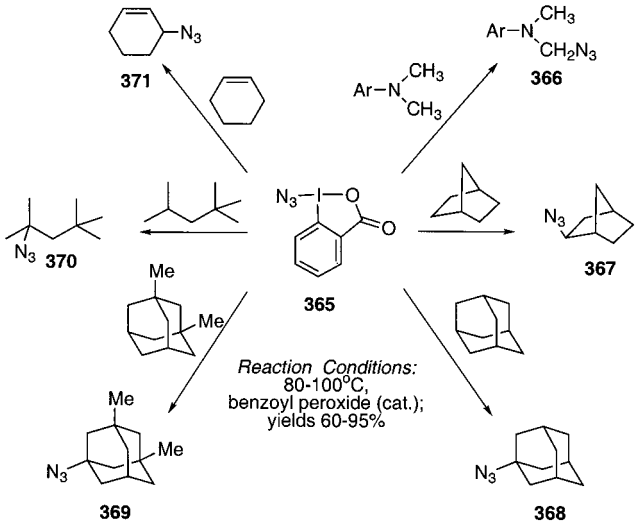
Stable azidobenziodoxoles **363**−**365** can be synthesized in one step by the reaction of hydroxybenziodoxoles **362** with trimethylsilyl azide in acetonitrile (eq 160).[279] In an alternative procedure, Kita and coworkers used acetoxybenziodoxole as starting material for the preparation of azidobenziodoxole **365**.[280] All three azides (**363**−**365**) are thermally stable, nonexplosive crystalline solids; the molecular struc-

ture of compound **364** was unambiguously established by a single-crystal X-ray analysis.[279]

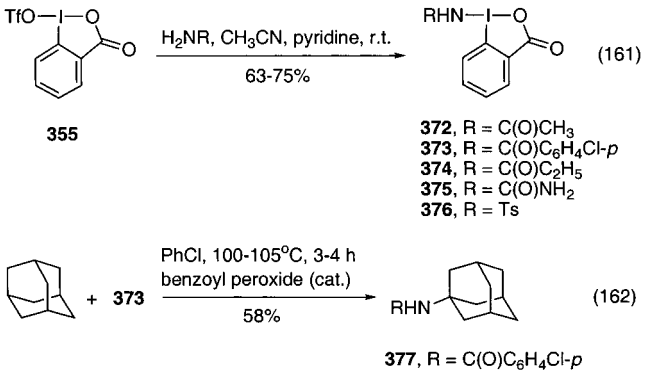


Azidobenziodoxoles can be used as efficient azidating reagents toward various organic substrates (Scheme 12). In a typical example, reagent **365** reacts with *N*,*N*-dimethylanilines in dichloromethane at reflux in 30 min to afford the respective *N*-azidomethyl-*N*-methylanilines **366** in excellent yields. The main advantage of reagent **365** over the known, unstable PhIO/$TMSN_3$ reagent combination is high thermal stability allowing its use at higher temperatures. In particular, azidobenziodoxoles **364** and **365** can even be used for direct azidation of hydrocarbons at high temperatures and in the presence of radical initiators (Scheme 12). Reagent **365** selectively reacts with isooctane upon reflux in 1,2-dichloroethane in the presence of catalytic amounts of benzoyl peroxide to afford tertiary azide **370** and 2-iodobenzoic acid as the only products. Under similar conditions, reactions of azidobenziodoxoles **364** or **365** with bicyclic and tricyclic hydrocarbons afford the respective alkyl azides **367**−**369**.[279]

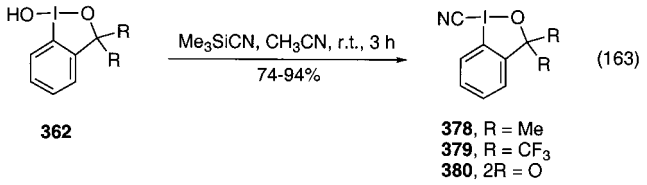
Scheme 12



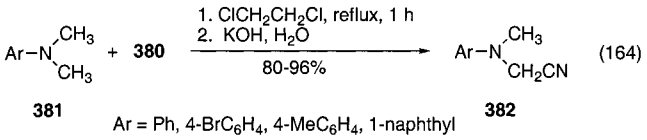
Amidobenziodoxoles **372**−**376** can be conveniently prepared in one step from hydroxybenziodoxole **335**, trimethylsilyltriflate, and the appropriate amide, RNH_2 (eq 161).[281] All five adducts **372**−**376** were isolated as thermally stable, white, nonhygroscopic, microcrystalline solids. Their reactivity is generally similar to the reactivity of azidobenziodoxoles. In particular, amidobenziodoxoles **372**−**376** can be used as amidating reagents toward polycyclic alkanes under radical conditions. For example, reagent **373** reacts with adamantane in chlorobenzene at 100−105 °C in the presence of a catalytic amount of benzoyl peroxide to afford 1-amidoadamantane **377** in moderate yield (eq 162).[281]



The stable cyanobenziodoxoles **378**−**380** can be prepared in one step by the reaction of cyanotrimethylsilane with the respective hydroxybenziodoxoles **362** (eq 163)[282,283] or from acetoxybenziodoxole and cyanotrimethylsilane.[280] The structures of products **379** and **380** were unambiguously established by single-crystal X-ray analysis.[280,283]

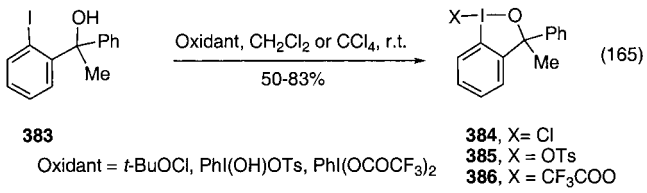


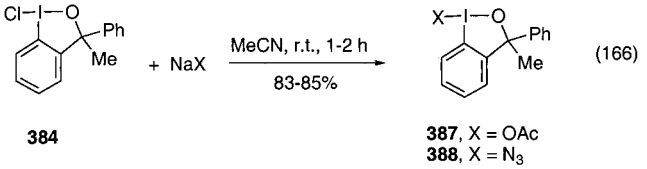
The chemical reactivity of cyanobenziodoxoles **378**−**380** is generally similar to that of azidobenziodoxoles, and they can be used as efficient cyanating reagents toward *N*,*N*-dialkylarylamines. In a typical example, reagent **380** reacts with *N*,*N*-dimethylanilines **381** in 1,2-dichloroethane at reflux to afford the respective *N*-cyanomethyl-*N*-methylanilines **382** in good yield (eq 164).[282]



In a recent paper, Hanzlik and co-workers applied cyanobenziodoxole **380** to the synthesis of *N*-cyanomethyl-*N*-cyclopropylamine, which is an important metabolite of the cyclopropylamine-derived drugs.[284]

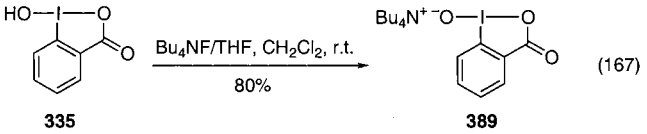
Koser and Rabah reported the synthesis of a series of optically active 1,3-dihydro-3-methyl-3-phenyl-1,2-benziodoxoles **384**−**388** containing chloro, tosyloxy, acetoxy, trifluoroacetoxy, and azido ligands (eqs 165





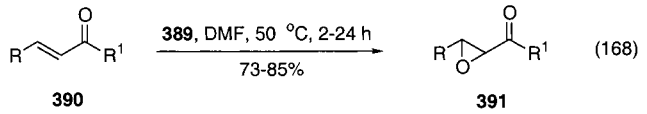
and 166).[285] These homochiral benziodoxoles are potentially useful reagents for asymmetric functionalization reactions.

Ochiai and co-workers reported the preparation of the tetrabutylammonium derivative of benziodoxole **389** by the reaction of hydroxybenziodoxole **335** with tetrabutylammonium fluoride (eq 167).[286]



(167)

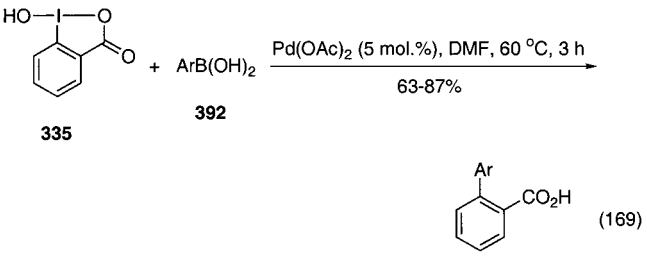
Reagent **389** reacts with α,β-unsaturated carbonyl compounds **390** yielding *trans*-epoxides **391** with high stereoselectivity (eq 168). This reaction probably involves a nucleophilic attack of the oxyanion of **389** on the electron-deficient double bond.[286]



(168)

R = PhC(O), R^1 = Ph; R = Me, R^1 = Ph; R = Ph, R^1 = Ph; etc.

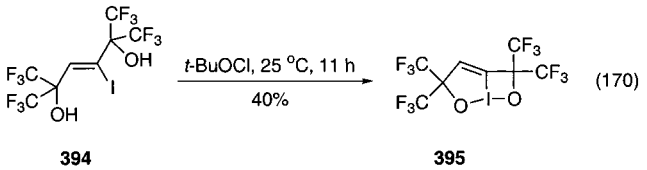
Chen and Xia reported the palladium-catalyzed coupling reaction of hydroxybenziodoxole **335** with arylboronic acids **392** affording biaryl-2-carboxylic acids **393** in good yields under mild conditions (eq 169).[287]



(169)

Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-MeC_6H_4, 2-$MeOC_6H_4$, 1-naphthyl

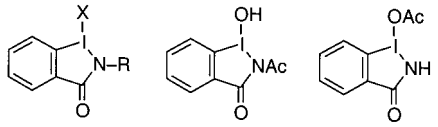
Kawashima and co-workers reported the synthesis of a novel benziodoxole **395** by the oxidative cyclization of the corresponding 3-iodo-3-hexene-2,5-diol **394** with neat *t*-BuOCl (eq 170).[288,289] The structure of product **395** was confirmed by X-ray analysis. Compound **395** can oxidize benzyl alcohol to give benzaldehyde in moderate yield.[289]



(170)

G. Benziodazoles

In contrast to benziodoxoles, the analogous five-membered iodine−nitrogen heterocycles, benziodazoles **396**, have received much less attention and, moreover, their structural assignment in some cases was not reliable.[1] The most important and readily available derivative of benziodazole, acetoxybenziodazole, was first prepared in 1965 by the peracetic oxidation of 2-iodobenzamide.[290] On the basis of IR spectroscopy, the authors of this paper incorrectly assigned the structure of *N*-acetyl-1-hydroxy-3-(1*H*)-1,2-benziodazole-3-one (**397**) for this compound. Structure **397** was also adopted in several other studies.[280,291,292] X-ray crystal analysis of acetoxybenziodazole (as a solvate with acetic acid) revealed its actual structure as **398**, which was different from the previously adopted **397**.[293] The structural data for **398** showed the expected distorted T-shaped geometry with a N−I−O bond angle of 162.1°. The lengths of the bonds to the iodine atom, I−N (2.101 Å), I−O (2.34 Å), and I−C (2.106 Å), are all within the range of typical single covalent bonds in organic derivatives of polyvalent iodine and are in good agreement with the previously reported structures of chlorobenziodazoles.[294] The results of ab initio molecular orbital calculations show that structure **398** is 6.31 kcal/mol more stable than **397** at the Hartree−Fock level of theory.[295]

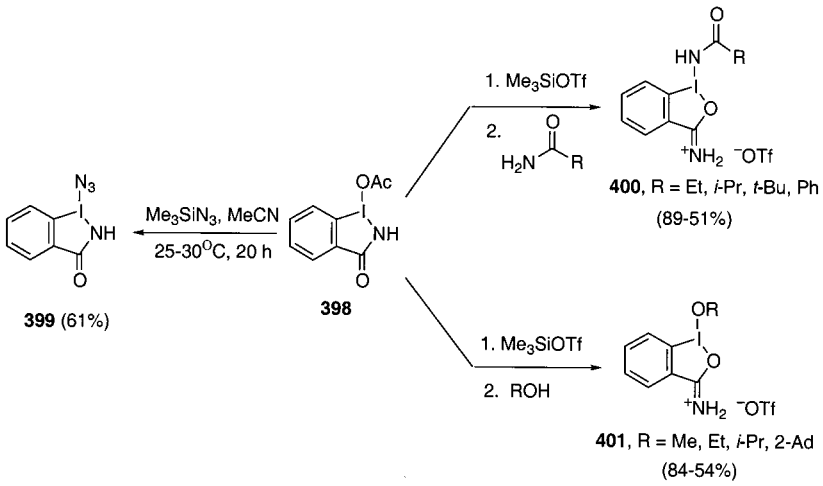


The reactions of acetoxybenziodazole **398** with azidotrimethylsilane, amides, and alcohols are summarized in Scheme 13.[294,295] Acetoxybenziodazole **398** reacts at room temperature with azidotrimethylsilane to afford a novel azide **399** in the form of a yellow, microcrystalline precipitate.[294] Azide **399** has a reactivity similar to that of azidobenziodoxoles and can be used as an efficient azidating reagent toward dimethylanilines.[294] Amides and alcohols react with acetate **398** at room temperature after activation with trimethylsilyltriflate to afford the rearranged products **400** and **401** (Scheme 13), the structures of which were established by X-ray analysis.[295] A plausible mechanism of this rearrangement most likely includes ring opening and ring closure in the protonated benziodazole. Molecular orbital calculations indicate that the driving force of this novel rearrangement of benziodazoles to 3-iminiumbenziodoxoles is the greater thermodynamic stability of the *N*-protonated 3-iminobenziodoxoles (**400** and **401**) relative to the respective *O*-protonated benziodazole-3-ones by about 15 kcal/mol.[295]

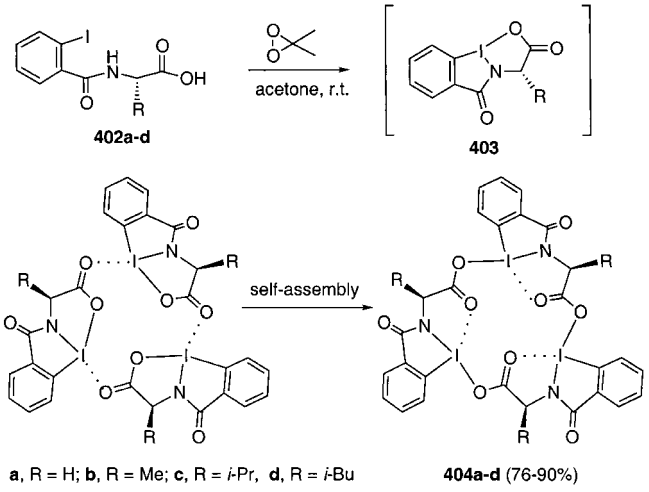
A novel self-assembly of the amino acid-derived benziodazoles into chiral and optically pure hypervalent iodine macrocycles **404** (Scheme 14) was recently reported.[296] Macrocyclic products **404** were prepared by the oxidation of the corresponding *N*-(2-iodobenzoyl) amino acids **402** with dimethyldioxirane in 76−90% yields. It is assumed that the initial products in this reaction are the monomeric amino acid-derived benziodazoles **403**, subsequent trimerization of which affords the final products **404** (Scheme 14).

The structures of macrocycles **404c** and **404d** were established by X-ray analysis. Molecule **404** consists of a slightly distorted planar macrocyclic system with

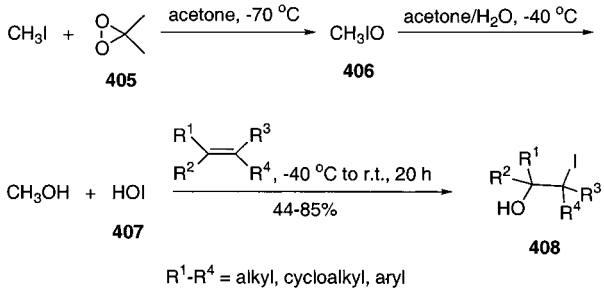
Scheme 13



Scheme 14



Scheme 15



three oxygens of the amino acid carboxyls inside the ring and all three alkyl groups above the plane. Each iodine atom is covalently bonded to carbon (I−C = 2.092 Å) and nitrogen (I−N = 2.064 Å) and has three longer intramolecular contacts with oxygen atoms (I−O = 2.368, 2.524, and 2.877 Å). With the consideration of primary and secondary bonds, the iodine atoms in **404** have a pentagonal-planar geometry, which is analogous to that found in the solid state for $PhI(OAc)_2$.[297] Secondary bonding between iodine and oxygen atoms of the neighboring molecular subunits provides the driving force for self-assembly of monomeric benziodazoles **403** into macrocyclic molecules **404**. As a result of the central oxygens, the electron-rich cavity of macrocycles **404** is suitable for complexation of metal cations. Specifically, ESI-MS data indicate that macrocycles **404** can selectively form complexes with sodium cations in the presence of K^+, Li^+, Ag^+, or Pb^{2+}.[296]

H. Alkyl and Fluoroalkyl Iodosyl Derivatives

Derivatives of polyvalent iodine with an alkyl substituent at iodine, RIX_2, generally are highly unstable and can exist only as short-lived reactive intermediates in the oxidations of alkyliodides. Recently, Asensio and co-workers reported a low-temperature oxidation of iodomethane with dimethyldioxirane **405** affording a pale yellow precipitate of iodosylmethane **406** (Scheme 15).[298] Upon raising the temperature to −40 °C, iodosylmethane decomposes with the formation of hypoiodous acid **407**, which can be trapped in situ by an alkene to afford iodohydrins **408** in good yields (Scheme 15).

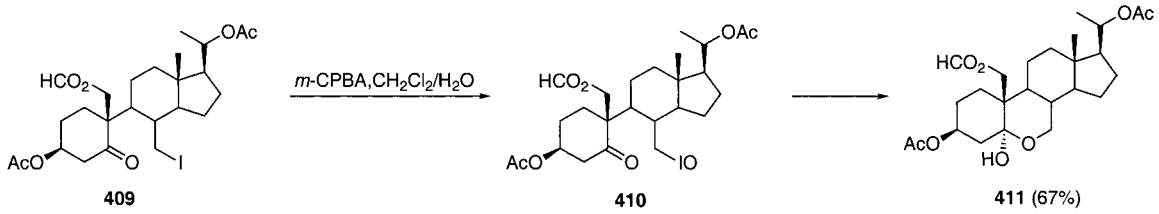
The dioxirane oxidation of iodocyclohexane under similar conditions affords *trans*-2-iodocyclohexanol via the intramolecular elimination of hypoiodous acid, which then adds to the alkene generated in the elimination step.[299]

Burton and co-workers utilized the oxidative deiodination reaction in the synthesis of steroidal products.[300,301] For example, the steroidal iodo ketone **409** can be converted to cyclic hemiketal **411** by oxidation with *m*-CPBA via the intermediate formation of the respective iodosyl derivative **410** (Scheme 16). Spontaneous cyclization of this intermediate affords the final hemiketal **411**.[301]

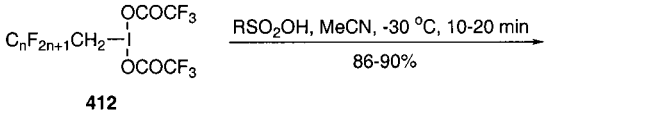
The thermal stability of alkyliodosyl derivatives can be substantially increased by steric or electronic modification of the alkyl moiety preventing decomposition of the molecule by either elimination or nucleophilic substitution pathways. Most commonly such a stabilization is achieved by the introduction of an electron-withdrawing substituent, such as perfluoroalkyl or sulfonyl groups, into the alkyl moiety.[1] For example, the relatively stable iodosylperfluoroalkanes $C_nF_{2n+1}IO$ can be prepared by the hydrolysis of the respective bis(trifluoroacetates) $C_nF_{2n+1}I(CO_2CF_3)_2$.[302]

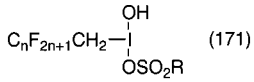
Trifluoroacetates **412** can be converted to sulfonates **413** and **414** (eq 171) by treatment with *p*-toluenesulfonic or methanesulfonic acid, respec-

Scheme 16



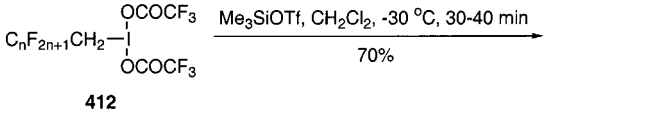
tively.[303] In contrast to the starting trifluoroacetates **412**, sulfonates **413** and **414** have a substantially higher thermal stability with a melting point of about 124 °C without decomposition. Both tosylate **413** and mesylate **414** are not water sensitive, can be purified by crystallization from acetonitrile, and can be stored for several months in a refrigerator.

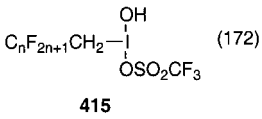




(171)

The analogous triflate **415** was prepared in a 70% yield by the reaction of trifluoroacetate **412** with trimethylsilyltriflate in dichloromethane (eq 172) and isolated as a colorless, stable, nonhygroscopic solid.[303]

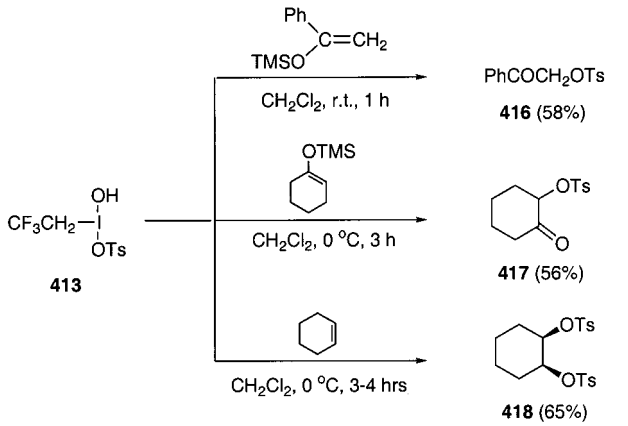




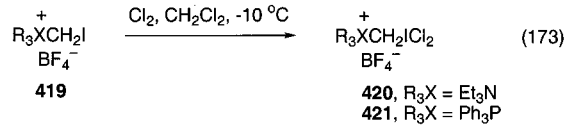
(172)

The reactivity pattern of sulfonates **413**−**414** is analogous to Koser's reagent, PhI(OH)OTs. Similar to its phenyl-substituted analogue, compound **413** is highly reactive toward electron-rich organic substrates, such as silyl enol ethers and alkenes. Reactions of tosylate **413** with silyl enol ethers of acetophenone and cyclohexanone afford α-tosyloxyketones **416** and **417** as major products, while the reaction of cyclohexene under similar conditions gives *cis*-1,2-bis(tosyloxy)cyclohexane **418** (Scheme 17).[303] Sulfonates **413**−**415** are useful reagents for the preparation of fluoroalkyliodonium salts (see section II.I.1).[303,304]

Scheme 17



The novel alkyliodine(III) dichlorides **420** and **421** and bis(trifluoroacetate) **423**, which are stabilized due to the presence of the electron-withdrawing trialkylammonium or triphenylphosphonium groups, can be prepared from readily available iodomethyl phosphonium and ammonium salts **419** (eqs 173 and 174).[305]



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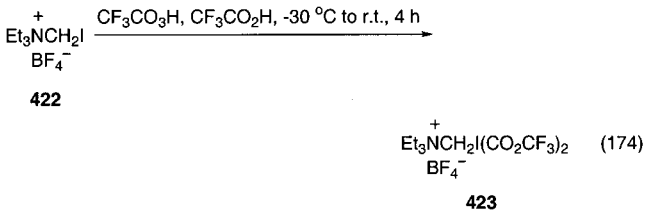
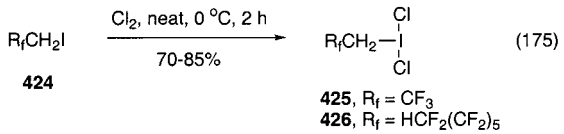
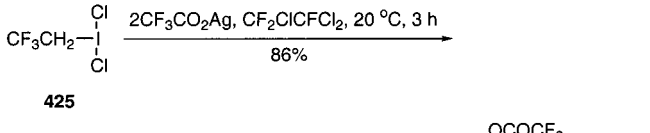


(174)

Recently, Montanari, DesMarteau, and Pennington reported the preparation and X-ray structural analysis of several fluoroalkyliodonium derivatives **425**−**427** (eqs 175 and 176).[306,307] The structures of products **425**−**427** are heavily influenced by secondary bonding involving the iodine(III) center and oxygen or chlorine. The chlorides **425** and **426** have complicated structures in which weak interactions between chains, coupled with aggregation of perfluoroalkyl groups, result in the formation of layers in the solid state. Compound **427** has a T-shaped coordination similar to other known dicarboxylates but forms a previously unknown tetrameric array of molecules due to strong intermolecular I···O contacts.[306]



(175)



(176)

In a series of recent papers, Minkwitz and co-workers reported the preparation and crystal structures of several novel trifluoromethyliodine(III) derivatives.[308−315] Specifically, (trifluoromethyl)iodine difluoride, CF_3IF_2, was synthesized by the reaction of trifluoromethyl iodide, CF_3I, with trifluoromethyl hypochlorite, CF_3OCl, at 223 K. This product has a T-shaped molecular structure with a disordered CF_3 group.[308] A similar reaction of CF_3I with CF_3OCl at −78 °C affords the mixed dihalide, $CF_3I(Cl)F$, which is unstable even at low temperatures and decomposes to the symmetrical halides, CF_3IF_2 and CF_3ICl_2.[309] (Trifluoromethyl)iodine dichloride, CF_3ICl_2, can be obtained in high purity and yield by the reaction of $CF_3I(Cl)F$ with trimethylchlorosilane at −40 °C.[310] CF_3ICl_2 is, in contrast to iodine trichloride, monomeric, and its molecular structure is T-shaped with the CF_3 group in the equatorial position.[310] The mixed trifluoroacetate $CF_3I(Cl)O_2CCF_3$ was prepared by the reaction between $CF_3I(Cl)F$ and $Me_3SiO_2CCF_3$ at −50 °C. The molecule of $CF_3I(Cl)O_2CCF_3$ was characterized by vibrational spectra, NMR, and a crystal structure analysis.[311] The bis-trifluoroacetate $CF_3I(OCOCF_3)_2$ was obtained by a similar reaction between CF_3IF_2 and $Me_3SiO_2CCF_3$ and was characterized by X-ray analysis.[312] Likewise, the reactions of $CF_3I(Cl)F$ and CF_3IF_2 with Me_3SiOMe lead to the analogous methoxy derivatives, $CF_3I(Cl)OMe$ and $CF_3I(OMe)_2$, respectively, both of which were characterized by X-ray analysis, Raman, IR, and NMR spectroscopy.[313] Three novel nitrates $CH_3I(ONO_2)_2$, $(CH_3)_3SiI(ONO_2)_2$ and $NCI(ONO_2)_2$ were prepared by the oxidation of the respective iodides with excess $ClONO_2$ and characterized by vibrational and NMR spectra.[314,315]

A study of the respective ^{19}F NMR and ^{13}C NMR spectra of CF_3IF_2 and CF_3IF_4 was recently reported by Naumann and co-workers.[316]

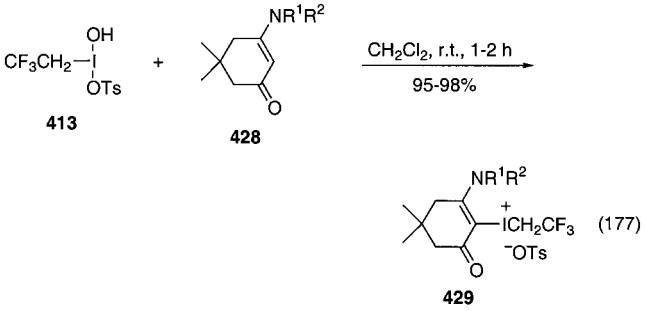
I. Iodonium Salts

According to conventional classification, iodonium salts are defined as positively charged 8-I-2 species with two carbon ligands and a negatively charged counterion, $R_2I^+ X^-$. X-ray structural data for the overwhelming majority of iodonium salts show a significant secondary bonding between the iodine atom and the anion with average bond distances within a range of 2.3−2.7 Å.[1] With consideration of the anion, iodonium salts have a T-shaped geometry consistent with other λ^3-iodanes. The most common and well investigated class of these compounds are diaryliodonium salts, known for over 100 years and extensively covered in previous reviews.[23] In recent years significant research activity was focused on aryliodonium derivatives bearing alkynyl, alkenyl, or fluoroalkyl groups as the second ligand.

1. Alkyl- and Fluoroalkyliodonium Salts

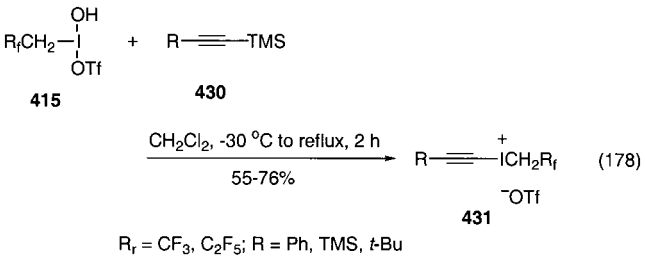
Iodonium salts with one or two nonsubstituted aliphatic alkyl groups generally lack stability. However, several examples of these unstable species were generated and investigated by NMR spectroscopy at low temperatures.[317]

The presence of electron-withdrawing groups in the alkyl group of iodonium salts has a pronounced stabilizing effect. The most stable and important derivatives of this type are fluoroalkyl(aryl)iodonium salts. The preparation of fluoroalkyl(aryl)iodonium salts and their application as electrophilic fluoroalkylating reagents was reviewed by Umemoto.[19] Recently, the preparation and chemistry of several new fluoroalkyliodonium salts has been reported.[303,304,306,307] The reaction of tosylate **413** with cyclic enaminones **428** affords stable iodonium salts **429** (eq 177).[304] Mild thermolysis of salts **429** in boiling acetonitrile cleanly affords 2,2,2-trifluoroethyl tosylate and the respective iodoenaminone.[304]



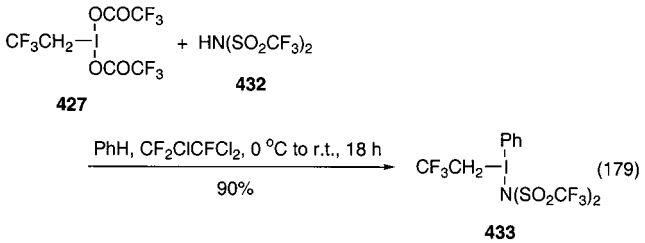
R^1 = H or Me; R^2 = H or Bu

Likewise, fluoroalkyl(alkynyl)iodonium triflates **431** can be prepared by the reaction of triflates **415** and (trimethylsilyl)acetylenes **430** (eq 178).[303]



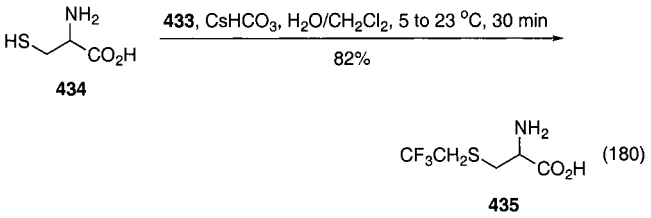
R_f = CF_3, C_2F_5; R = Ph, TMS, *t*-Bu

DesMarteau and co-workers recently reported the preparation, X-ray structure, and chemistry of the novel trifluoroethyliodonium salt **433** (eq 179).[306,307]



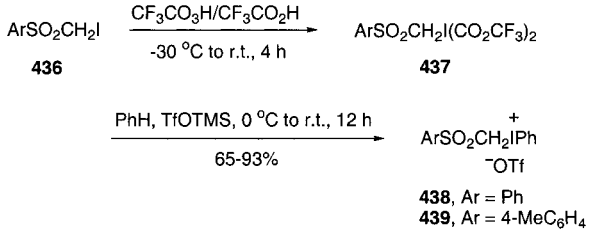
In contrast to the other known fluoroalkyliodonium salts, compound **433** is stable to water and can be used for fluoroalkylations in aqueous media. It is especially useful as a reagent for fluoroalkylation of amino acids and peptides. For example, the reaction of iodonium salt **433** with cysteine **434** under aqueous conditions selectively affords *S*-trifluoroethyl-cysteine **435** in good yield (eq 180).[307]

The novel (arylsulfonylmethyl)iodonium salts **438** and **439** can be conveniently prepared in two steps starting from the readily available iodomethyl sul-



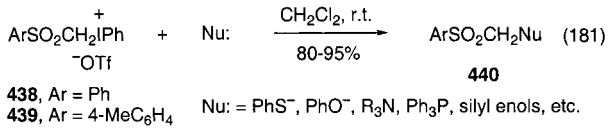
fones **436** (Scheme 18).[318] In the first step, starting iodides **436** are oxidized with peroxytrifluoroacetic acid to trifluoroacetates **437** in almost quantitative yield. The subsequent treatment of trifluoroacetates **437** with benzene and trimethylsilyltriflate in dichloromethane affords products **438** and **439** in good yields. Both iodonium salts **438** and **439** are not moisture sensitive, can be purified by crystallization from acetonitrile, and can be stored for several months in a refrigerator.

Scheme 18



The structure of iodonium triflate **439** was unambiguously established by a single-crystal X-ray analysis.[318] The structural data revealed the expected geometry for iodonium salts with a C−I−C bond angle of 91.53°. The I−C bond distances of 2.131 and 2.209 Å are longer than the typical bond length in diaryliodonium salts (2.0−2.1 Å). The distance between the iodine atom and the nearest oxygen of the triflate anion, I···O, is 2.797 Å.

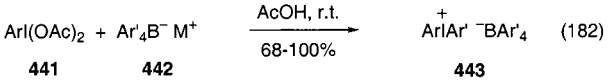
Similar to fluoroalkyl(aryl)iodonium salts, iodonium salts **438** and **439** are efficient electrophilic alkylating reagents toward a variety of organic nucleophiles (thiophenolate anion, amines, pyridine, triphenyl phosphine, and silyl enol ethers). All these reactions proceed under mild conditions and selectively afforded the appropriate product of alkylation (**440**) along with iodobenzene as the byproduct (eq 181).[318]



2. Aryl- and Heteroaryliodonium Salts

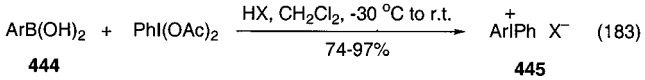
Aryl- as well as heteroaryliodonium salts belong to the most common, stable, and well investigated class of polyvalent iodine compounds.[1,2,23] The chemistry of aryliodonium salts was extensively covered in previous reviews, so in this section we will concentrate only on the important recent developments in this area.

Several new approaches to the preparation of aryliodonium salts were developed in the past few years.[319−327] Ochiai and co-workers reported an efficient regioselective synthesis of diaryliodonium tetraarylborates **443** by the reaction of (diacetoxyiodo)arenes **441** with sodium or potassium tetraarylborates **442** in acetic acid (eq 182).[319]



Ar =Ph, 3-NO$_2$C$_6$H$_4$, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-MeOC$_6$H$_4$
Ar' = Ph, 4-FC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$

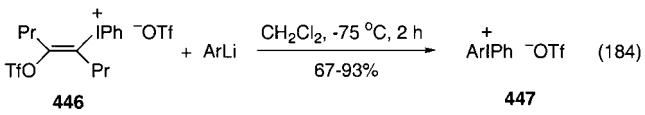
Likewise, a variety of diaryliodonium and heteroaryliodonium sulfonates **445** were prepared, in a regioselective manner, from readily available arylboronic acids **444** and (diacetoxyiodo)benzene (eq 183).[320]



Ar = Ph, 4-PhC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-MeC$_6$H$_4$,
2-thienyl, 2-furyl, 3-furyl, etc.; HX = HOTs or HOTf

Various unsymmetrically functionalized diaryliodonium salts have been synthesized by the direct reaction of (diacetoxyiodo)arenes with arenes in a trifluoromethanesulfonic or trifluoroacetic acid medium[321] or by the treatment of aryltributylstannanes with Koser's reagent [hydroxy(tosyloxy)iodo]benzene.[322]

Kitamura and co-workers developed a selective approach to aryl- and heteroaryl(phenyl)iodonium triflates **447** by the ligand-transfer reaction between vinyliodonium salt **446** with aryllithiums (eq 184).[323] A similar reagent was recently applied by Zefirov, Brel, and co-workers for the selective preparation of various aryl(phenyl)- and alkynyl(phenyl)iodonium triflates in high yields.[324]



Ar = Ph, 2-MeC$_6$H$_4$, 2-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$, 2-thienyl, 2-benzothienyl

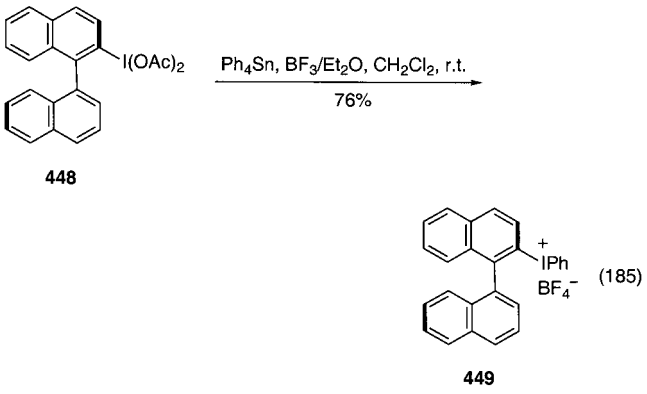
Tykwinski and co-workers applied a similar ligand transfer reaction between thienyltributylstannanes and phenyl(cyano)iodonium triflate, PhI(CN)OTf, for the preparation of thienyl and bithienyl iodonium salts, which are potentially useful as nonlinear optical materials.[325]

Peacock and Pletcher reported a simple, one-step procedure for the synthesis of diaryliodonium salts by the electrochemical oxidation of aryl iodide at a carbon felt anode in acetic acid in the presence of an arene.[326]

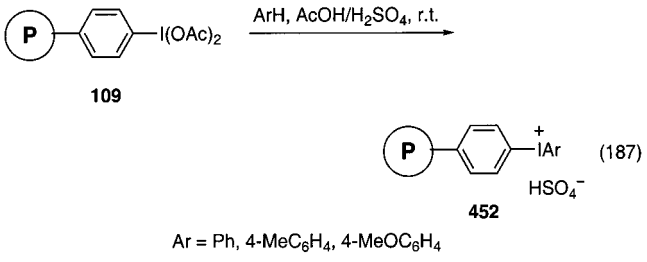
Kazmierczak and Skulski developed a useful procedure for the oxidative anion exchange in diaryliodonium iodides and chlorides. Specifically, the oxidation of diaryliodonium iodides with hydrogen peroxide in the presence of an appropriate acid affords the corresponding hydrogensulfates, nitrates, tetrafluoroborates, triflates, tosylates, as well as bromides and chlorides in 54−86% yields.[327] Neckers and co-workers recently reported the preparation of

several iodonium tetrakis(perfluorophenyl)gallate salts by the anion exchange of diaryliodonium hexafluoroantimonates with lithium tetrakis(pentafluorophenyl)gallate.[328] Preliminary evaluation showed that the new iodonium tetrakis(perfluorophenyl)gallates are useful UV photoinitiators for the polymerization of epoxy silicon monomers and other acid susceptible compounds.[328]

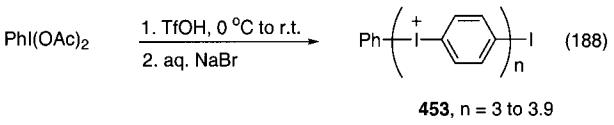
Several interesting, new structural types of aryliodonium salts have been reported in the last 5 years.[329−335] Ochiai and co-workers reported the preparation of the chiral iodonium salt **449** (eq 185) and several analogous mono- and bis(iodonium) salts by the BF_3-catalyzed tin−iodane exchange. Both the structure and the absolute configuration of (*S*)-(−)-**449** were unambiguously established by X-ray analysis. Iodonium salt **449** can be used in the asymmetric phenylation of 1-oxo-2-indancarboxylates **450** with moderate enantioselectivity (eq 186).[329]



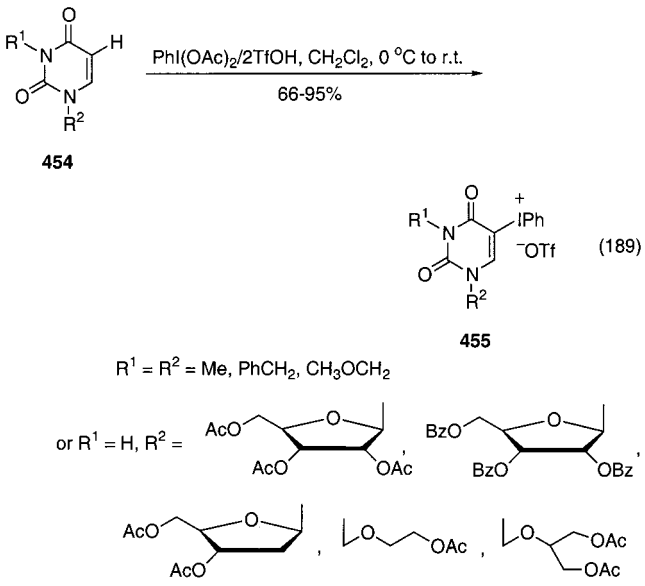
The polymer-supported diaryliodonium salts **452** can be prepared by the treatment of diacetate **109** (see section II.C.1) with arenes in the presence of sulfuric acid (eq 187).[330] Polymers **452** are useful aryl transfer reagents in the Pd(II)-catalyzed cross-coupling reactions with aromatic aldehydes.



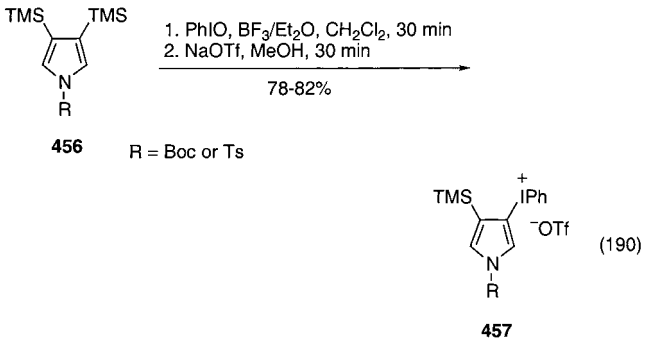
Kitamura and co-workers reported the preparation of several oligomeric iodonium salts by the treatment of (diacetoxyiodo)arenes with an excess of trifluoromethanesulfonic acid. For example, the reaction of (diacetoxyiodo)benzene with trifluoromethanesulfonic acid followed by quenching with aqueous NaBr gives the hypervalent iodine oligomer **453** (eq 188) with an average degree of polymerization of 3.0−3.9.[331]



Kim and co-workers reported the preparation of phenyliodonium triflate-substituted uracil nucleosides **455** by the reaction of uracil nucleosides **454** with (diacetoxyiodo)benzene in the presence of trifluoromethanesulfonic acid.[332] Alternatively, iodonium salts **455** can be prepared by iodine transfer reaction between the appropriate tributylstannylated uracil derivatives and phenyl(cyano)iodonium triflate.[332] Uracil-5-iodonium triflates **455** were used in a new palladium-catalyzed cross-coupling reaction with alkenyl boronic acids or unsaturated stannanes.[333]

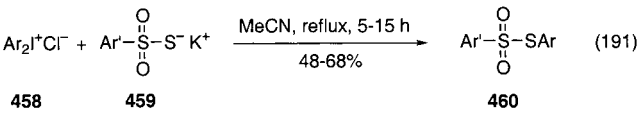


Pyrrolyliodonium triflates **457** were prepared by the reaction of bis(trimethylsilyl)pyrroles **456** with iodosylbenzene in the presence of BF_3·etherate (eq 190).[334] Iodonium salts **457** were employed as key precursors to generate a highly strained and reactive five-membered cyclic cumulene, namely, 1-*tert*-butoxycarbonyl-3,4-didehydro-1*H*-pyrrole.[334]

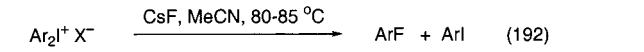


Likewise, a novel [*o*-(trimethylsilyl)carboranyl]-iodonium acetate, an efficient 1,2-dehydro-*o*-carborane precursor, was prepared by the reaction of [*o*-(trimethylsilyl)carboranyl]lithium with (diacetoxyiodo)benzene.[335]

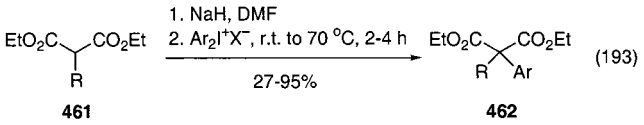
Diaryliodonium salts have found synthetic application as arylating reagents in reactions with various organic substrates under polar, catalytic, or photochemical conditions. Recent examples of arylations of nucleophiles under polar, noncatalytic conditions include the reactions of diaryliodonium salts with thiosulfonate anion **459** (eq 191),[336] fluoride anion (eq 192),[337,338] malonates **461** (eq 193),[339] and silyl enol ethers **464** (eq 194).[340]



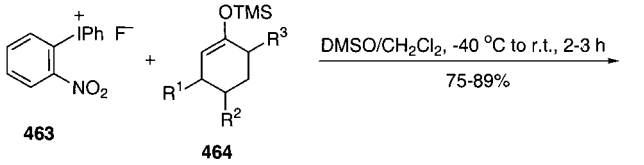
Ar = Ph, 4-ClC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 4-MeC$_6$H$_4$
Ar' = Ph, 4-MeC$_6$H$_4$, 2-MeC$_6$H$_4$, 4-ClC$_6$H$_4$

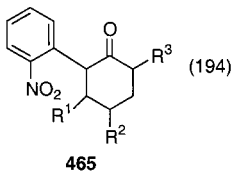


Ar = Ph, 2-MeC$_6$H$_4$, 4-MeC$_6$H$_4$, 2-furyl, 2-thienyl, etc.
X = TfO$^-$, CF$_3$CO$_2^-$, TsO$^-$



R = H, CH$_3$, CH$_2$CH=CH$_2$; Ar = Ph, 4-MeC$_6$H$_4$; X = BF$_4$, OTf



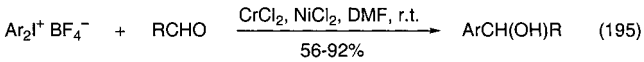


R^1, R^2, R^3 = H, Me, or OMe

Arylations with aryliodonium salts can be effectively catalyzed by transition metals.[341−347] The arylation of the lithium enolates of cyclic ketones with diphenyliodonium triflate in the presence of stoichiometric quantities of copper cyanide afford the corresponding α-phenylated ketones in moderate yields.[341] Likewise, the copper-catalyzed arylation of tetrahydrothiophene selectively affords cyclic *S*-phenyl sulfonium salt, a key precursor to the important oxosulfonium ylides.[342]

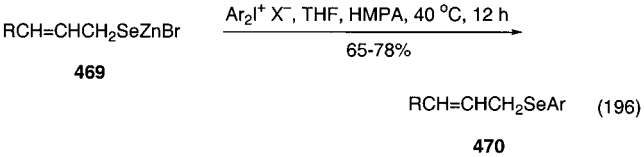
Diaryliodonium salts **466** react with aldehydes **467** in the presence of chromium dichloride and nickel dichloride with the formation of benzyl alcohols **468** (eq 195).[343,344] The mechanism of this reaction involves the generation of organochromium(III) species via reaction of iodonium salts with chromium dichloride, followed by their nucleophilic addition to aldehydes to yield alcohols.

Diaryliodonium triflates react with metallic ytterbium giving benzene almost quantitatively, while the same reaction in the presence of methylphenylsilane affords arylmethylphenylsilanes.[345]

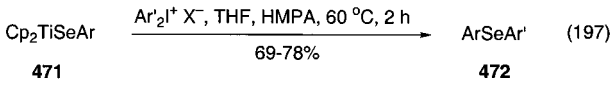


Ar = Ph, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$
R = Ph, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-MeC$_6$H$_4$, C$_{10}$H$_{21}$, Me$_2$CH, (*E*)-MeCH=CH, (*E*)-PhCH=CH

Zinc allyl selenoate **469** reacts with diaryliodonium salts to afford the allyl aryl selenides **470** in high yields (eq 196).[346] Likewise, unsymmetrical diarylselenides **472** were prepared from the reaction of diaryliodonium salts and arylselenium complexes of titanocene **471** (eq 197).[347]

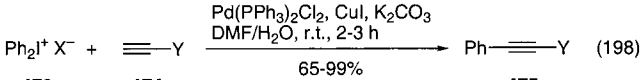


R = H, 1-cyclohexenyl
Ar = Ph, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$



Ar = 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 3-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$
Ar' = Ph, 4-MeC$_6$H$_4$

There has been substantial recent interest in the palladium-catalyzed cross-coupling reaction of diaryliodonium salts.[247,248,333,348−380] Palladium salts and complexes are efficient catalysts in the cross-coupling reaction of diaryliodonium salts with secondary amines,[348,349] benzotriazoles,[350,351] amidoximes,[352] uracil nucleosides,[333] organoboron compounds,[247,248,353,354] organostannanes,[355−358] silanes,[359,360] organolead triacetates,[361] organobismuth(V) derivatives,[362] organozirconium compounds,[363] *O,O*-dialkyl phosphites,[364] mercaptans,[365] alcohols and carbon monoxide,[366] allylic alcohols,[367] functionalized allenes,[368−370] β-substituted α,β-enones,[371] Grignard reagents,[372] 2,3-dihydrofuran,[373] alkenes,[374−376] and terminal alkynes.[377−381] A recent example of the synthetic application of the palladium-catalyzed coupling is illustrated by the reaction of diaryliodonium sulfonates **473** with enynes and electron-deficient alkynes **474** affording aryl alkynes **475** in good yields in a convenient single-pot procedure (eq 198).[381]

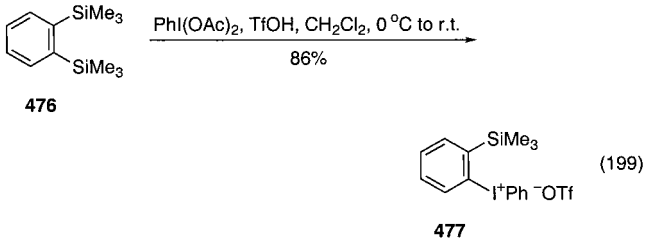


X = OTs or OTf
Y = CO$_2$Et, COPh, CO-cyclohexyl, CO-adamantyl, MeC=CH$_2$

Recently, Kang and co-workers found that cross-coupling of iodonium salts with terminal alkynes or organostannanes can be effectively catalyzed by CuI, MnCl$_2$·4H$_2$O, or Ni(acac)$_2$.[382−385]

In a series of recent papers, Kitamura and coworkers reported the preparation and uses of several efficient benzyne precursors based on aryliodonium salts.[386−390] Specifically, iodonium triflate **477** is readily prepared by the reaction of 1,2-bis(tri-

methylsilyl)benzene **476** with the $PhI(OAc)_2$/TfOH reagent system (eq 199).[386]

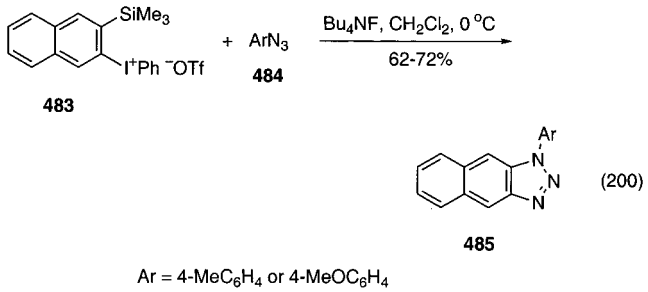


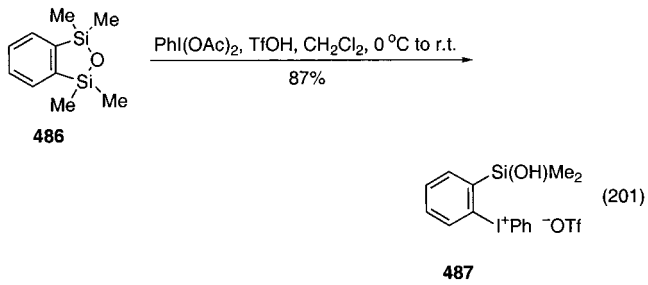
The treatment of reagent **477** with Bu_4NF in dichloromethane at room temperature gives high yields of the benzyne adducts **478**−**482** in the presence of a trapping agent such as furan, 2-methylfuran, anthracene, tetraphenylcyclopentadienone, 1,3-diphenylisobenzofuran, or thiobenzophenones (Scheme 19).[386,387] Similarly, 3- and 4-methylbenzynes are efficiently generated from the corresponding methyl-substituted (trimethylsilyl)phenyliodonium triflates.[386]

The analogous (trimethylsilyl)naphthyliodonium triflate **483** can be prepared by the reaction of 2,3-bis(trimethylsilyl)naphthalene with $PhI(OAc)_2$.[388] Addition of Bu_4NF to **483** results in the generation of 2,3-didehydronaphthalene, which can be trapped with furans, tetraphenylcyclopentadienone, or aryl azides **484** (eq 200).[388]

A new benzyne precursor iodonium triflate **487** was prepared from benzoxadisilole **486** and the $PhI(OAc)_2$/TfOH reagent system (eq 201).[389] The treatment of reagent **487** with Bu_4NF in dichloromethane at room temperature generates benzyne, which can be trapped with furans or tetraphenylcyclopentadienone.[389]

Under photochemical conditions diaryliodonium salts can decompose by a variety of pathways, which usually involve radical or radical cation intermediates.[390,391] Due to this property they have found some practical application as photoinitiators for radical polymerizations.[392−403]



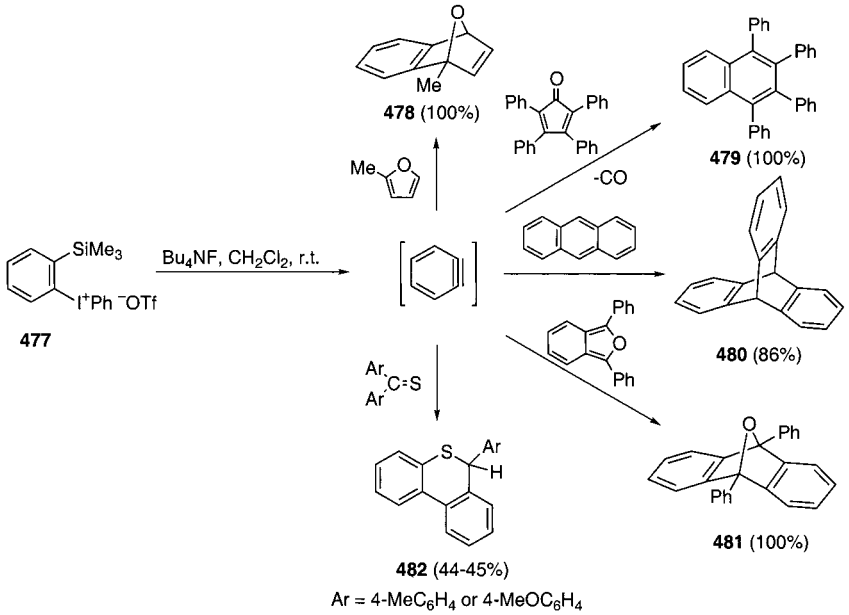


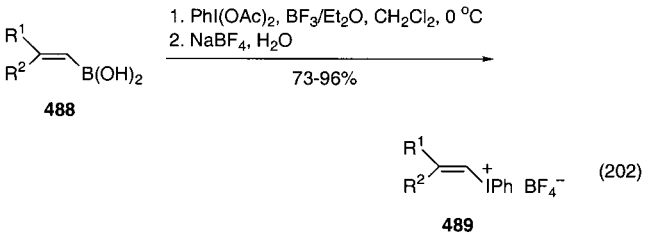
3. Alkenyliodonium Salts

The chemistry of alkenyliodonium salts was extensively covered in several recent reviews by Ochiai,[14] Okuyama,[15] and Zefirov and co-workers.[17] This section of our review will summarize the important recent developments in the preparation and synthetic application of alkenyliodonium salts.

Several new approaches to the synthesis of alkenyliodonium salts were developed in the past few years.[87,90,98,404−407] Ochiai and co-workers reported an efficient synthesis of vinyl(phenyl)iodonium tetrafluoroborates **489** by the reaction of vinylboronic acids **488** or esters with (diacetoxyiodo)benzene in the presence of $BF_3 \cdot Et_2O$ (eq 202).[404] The reaction proceeds under mild conditions yielding vinyl(phenyl)-iodonium tetrafluoroborates stereoselectively with retention of configuration.

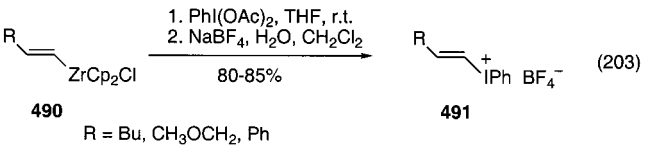
Scheme 19





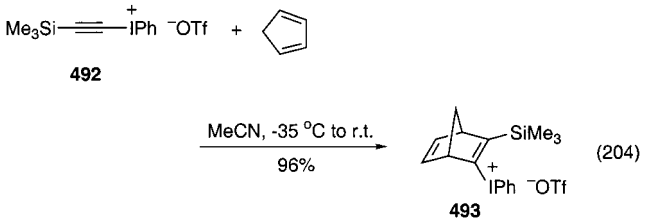
R^1 = Bu, C_8H_{17}, $Ph(CH_2)_3$, $Cl(CH_2)_3$, $NC(CH_2)_3$, *cyclo*-$C_5H_9CH_2$, $Me_2CH(CH_2)_2$, *t*-Bu, Ph
R^2 = H, Me, Ph

Likewise, the reaction of vinylzirconium derivatives **490** with (diacetoxyiodo)benzene followed by anion exchange affords alkenyl(phenyl)iodonium salts **491** stereoselectively with retention of configuration (eq 203).[405]



R = Bu, CH_3OCH_2, Ph

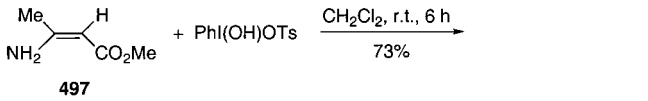
Several types of functionalized alkenyl iodonium salts have been prepared by the addition of hypervalent iodine reagents to alkynes.[87,90,98] Zefirov, Brel, and co-workers developed a procedure for the stereoselective preparation of (*E*)-[*β*-(triflyloxy)alkenyl]-(aryl) iodonium triflates **76** by the addition of (aryl)-fluoroiodonium triflates **49** to terminal alkynes (eq 29, section II.B.1).[87,90] Likewise, Hara, Yoneda and co-workers prepared various alkenyliodonium fluorides **75** by the addition of 4-(difluoroiodo)toluene **51** to terminal acetylenes (eq 28, section II.B.1).[98−100]

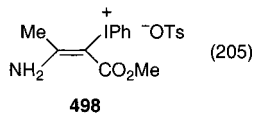


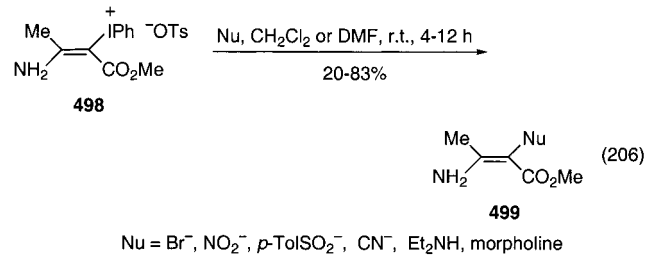
Kitamura and co-workers reported the preparation of norbornadienyl iodonium salt **493** by the Diels−Alder reaction of alkynyliodonium salt **492** with cyclopentadiene (eq 204).[406]

Iodonium triflate **493** is useful for the generation of a highly strained cyclic alkyne, bicyclo[2.2.1]hept-2-en-5-yne **494**, which can be efficiently trapped with tetraphenylcyclopentadienone or 1,3-diphenylisobenzofuran (Scheme 20).[406]

Papoutsis, Spyroudis, and Varvoglis reported the preparation of a new alkenyl(phenyl)iodonium tosylate **498** from methyl 3-aminocrotonate **497** (eq 205). Iodonium salt **498** reacts with various nucleophiles affording substituted enamine derivatives of crotonic acid **499** (eq 206).[407]





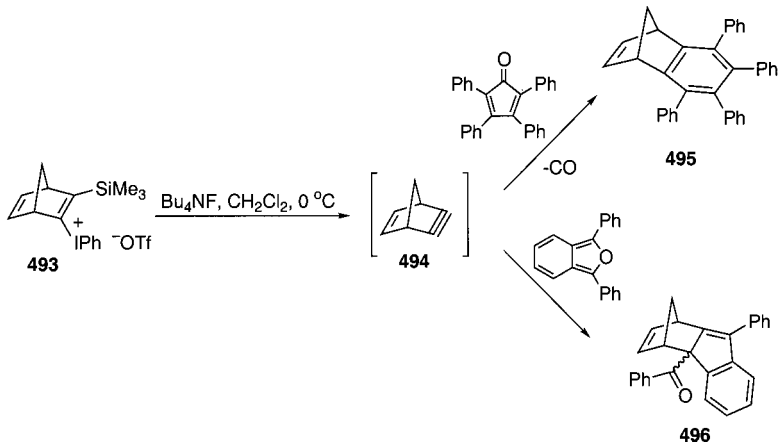


Nu = Br^-, NO_2^-, *p*-$TolSO_2^-$, CN^-, Et_2NH, morpholine

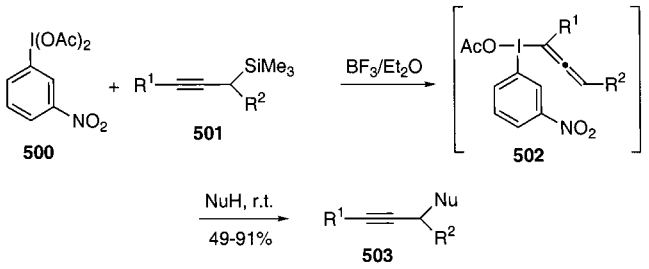
Ochiai and co-workers reported the generation of the allenyl(aryl)iodonium salt **502** by the reaction of (diacetoxyiodo)arene **500** and alkyne **501** (Scheme 21).[408] The unstable iodonium salt **502** can be trapped with a nucleophilic solvent to afford the respective product of nucleophilic substitution **503** in generally high yields.

The preparation and X-ray structure of new phosphorane-derived iodonium salts from the stabilized phosphonium ylides and iodosylbenzene sulfonates was recently reported.[409] These compounds represent a potentially useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt.

Scheme 20



Scheme 21



$R^1 = C_5H_{11}$, R^2 = H; R^1 = *cyclo*-C_6H_{11}, R^2 = H
$R^1 = C_{10}H_{21}$, R^2 = H; R^1 = H, $R^2 = C_{10}H_{21}$

NuH = MeOH, EtOH, PrOH, AcOH, MeCN, etc.

Alkenyl(phenyl)iodonium salts have found synthetic application as alkenylating reagents in the reactions with various organic substrates. Recent examples of alkenylations of nucleophiles under noncatalytic conditions include the reactions of alkenyliodonium salts with thioamides **505** (eq 207),[410] sodium dithiocarbamates and potassium carbonotrithioates **508** (eq 208),[411] sodium tellurolates and selenolates **510** (eq 209),[412,413] potassium phosphorothioates, phosphorodithioates, and phosphoroselenoates (eq 210),[414−416] group 15 element nucleophiles **515** (eq 211),[417] dicarbonyl compounds (eq 212),[418] formamides (eq 213),[419] and tetrafluoroborate anion upon thermolysis (eq 214).[420]

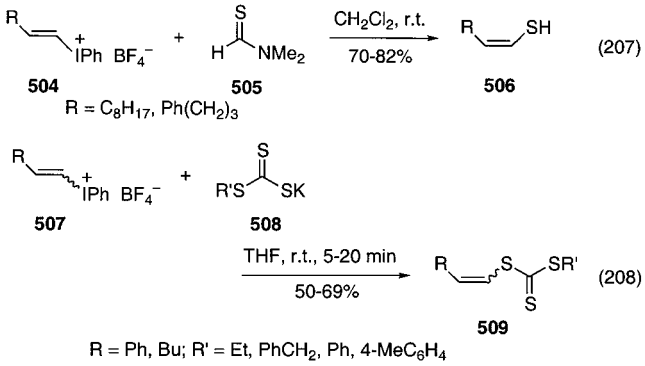
Several research groups have been intensely involved in the mechanistic studies of nucleophilic substitution in alkenyliodonium salts.[421−442] A variety of mechanisms, including S_N1, S_N2, and ligand coupling, have been observed in these reactions. The mechanistic aspects of the reactions of vinylic iodonium salts with nucleophiles have recently been reviewed by Okuyama[15] and by Ochiai.[14,421]

Alkenyliodonium salts have been utilized in several cross-coupling reactions. Hinkle and co-workers reported the cross-coupling reaction of benzylic organozinc reagents **524** with alkenyl(phenyl)iodonium triflates **523** affording single stereoisomers of trisubstituted olefins **525** in excellent yields under very mild conditions (eq 215).[443]

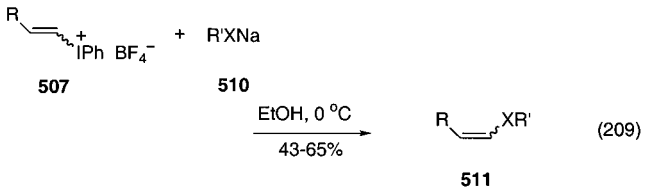
Zefirov and co-workers developed a method for the stereospecific synthesis of conjugated alkenynes **527** by the reaction of (*E*)-[*β*-(trifluoromethanesulfonyloxy)-1-alkenyl](phenyl) iodonium triflates **526** with terminal alkynes in the presence of catalytic amounts of dichloro(triphenylphosphine)palladium(II) and CuI in aqueous medium (eq 216).[444]

Likewise, a variety of bicyclic enediynes **529** were synthesized by the palladium(II)- and copper(I)-cocatalyzed cross-coupling of bis-iodonium salts **528** and alkynylstannanes (eq 217).[445] This coupling reaction was recently utilized in the synthesis of novel dinuclear complexes with a photochromic bridge.[446]

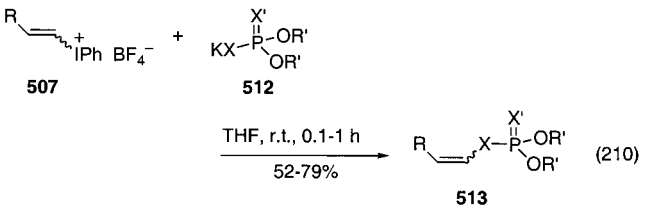
Transition-metal catalysts were used in the cross-coupling reactions of alkenyliodonium salts with uracil nucleosides,[333] organoboron compounds,[247,383] organostannanes,[357,383−385] Grignard reagents,[405] alcohols and carbon monoxide,[366] and allylic alcohols.[367]



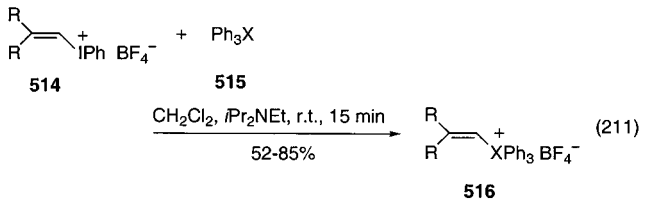
R = Ph, Bu; R' = Et, $PhCH_2$, Ph, 4-MeC_6H_4



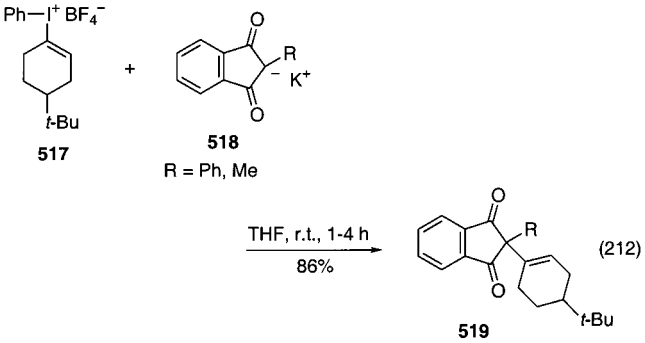
X = Se or Te; R = Ph, Bu; R' = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, etc.

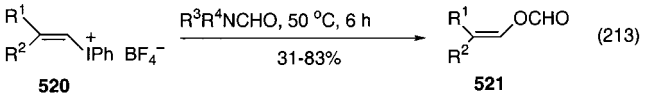


X = Se, X' = O; X = S, X' = O; X = X' = S
R = Ph, Bu; R' = Me, Et, Pr, Bu, *i*-Pr

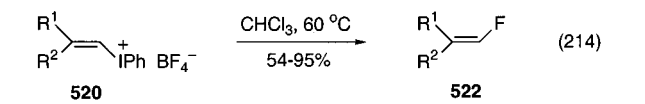


R = Me or 2R = $(CH_2)_5$; X = P, As, Sb

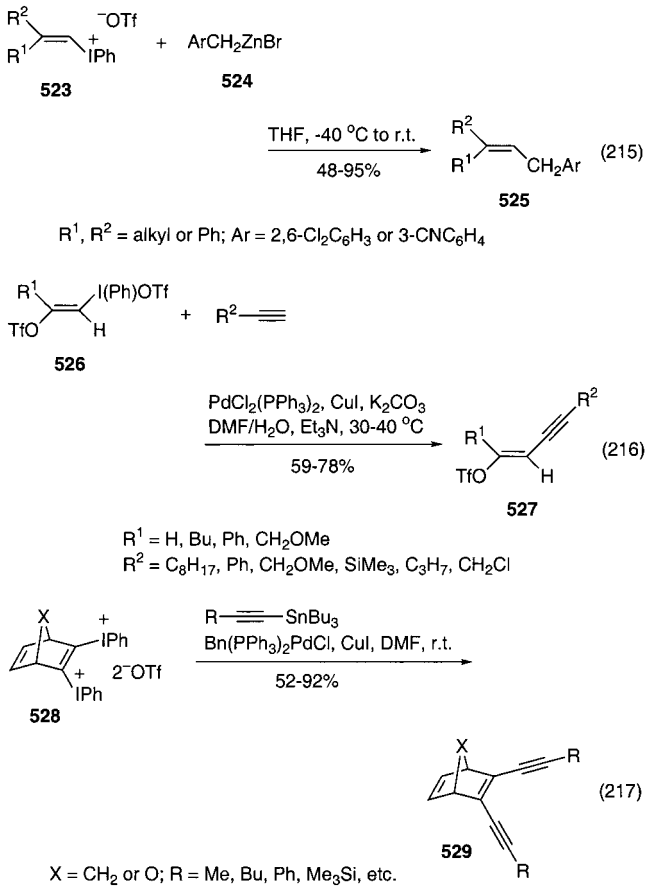




$R^1 = C_6H_{17}$, R^2 = H; $R^1 = Me_2CH(CH_2)_2$, R^2 = H; $R^1 = Ph(CH_2)_3$, R^2 = Me, etc.
R^3, R^4 = alkyl, aryl



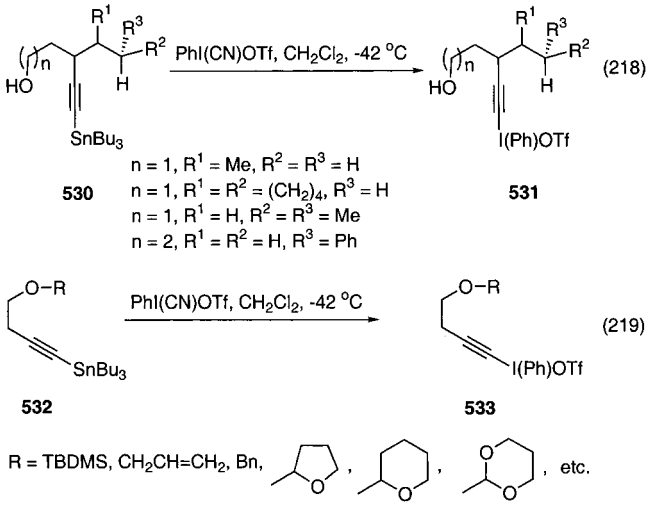
$R^1 = C_8H_{17}$, R^2 = H; R^1 = Me, R^2 = H; R^1 = Ph, R^2 = Me, etc.



4. Alkynyliodonium Salts

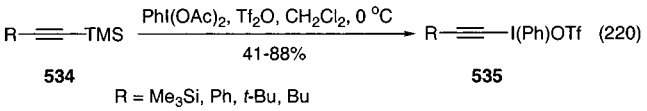
The chemistry of alkynyliodonium salts was exhaustively covered in our comprehensive review published in 1998.[16] Therefore, this section will only summarize the important recent developments in the preparation and synthetic application of alkynyliodonium salts.

The most general approach to alkynyliodonium salts under very mild conditions involves the ligand exchange reaction of stannylated alkynes with phenyl(cyano)iodonium triflate.[1,16] Recently, this approach was utilized by Feldman and co-workers for the preparation of functionalized iodonium salts **531** and **533** (eqs 218 and 219), which were then used as key

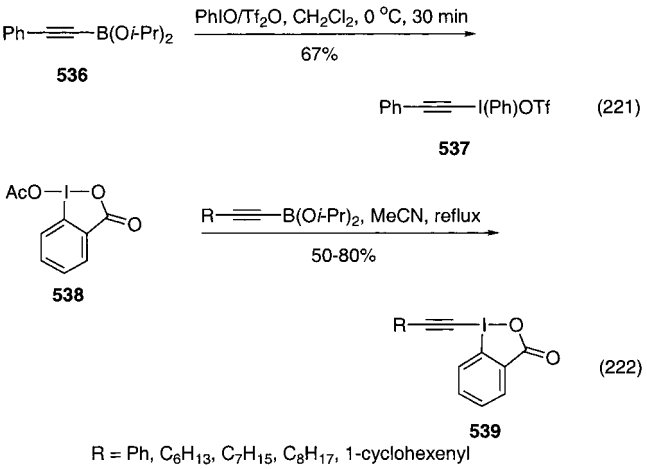


intermediates in carbene cyclizations leading to substituted dihydrofurans and cyclopentannelated tetrahydrofurans.[447,448] Iodonium salts **531** and **533** have low stability and typically decompose above 0 °C; therefore, their preparation and handling should be conducted at low temperatures with final solvent removal at below 0 °C in vacuo.[448]

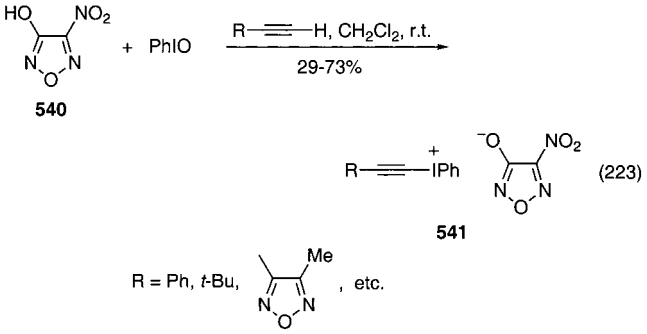
Several new approaches to the synthesis of alkynyliodonium salts were developed in the past few years.[449,450] Kitamura and co-workers proposed a new procedure based on the reaction of trimethylsilylated alkynes **534** with(diacetoxyiodo)benzene in the presence of trifluoromethanesulfonic acid or trifluoromethanesulfonic anhydride (eq 220).[449]



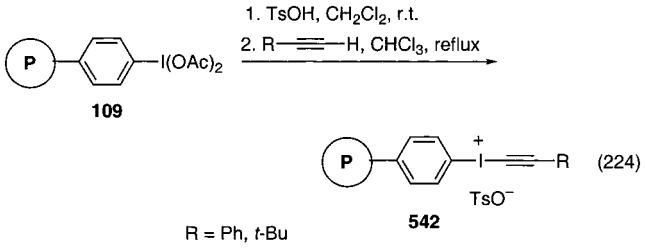
Alkynyliodonium triflates **537** can be obtained from the reaction of alkynylboronates **536** with iodosylbenzene and trifluoromethanesulfonic anhydride (eq 221).[450] Likewise, alkynylbenziodoxoles **539** can be conveniently prepared by the reaction of alkynylboronates with acetoxybenziodoxole **538** under mild conditions (eq 222).[450]



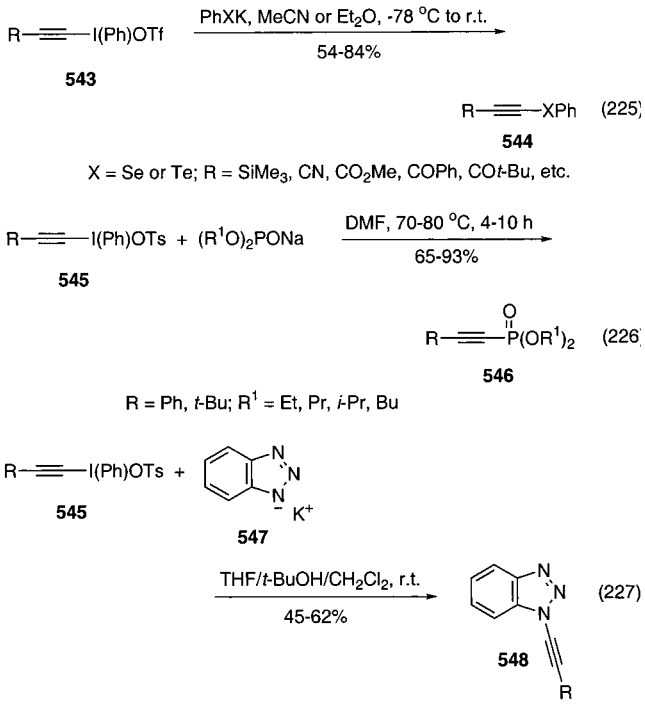
The novel alkynyl(phenyl)iodonium salts with nitrofurazanylate as a counterion **541** were prepared by the reaction of nitrofurazan **540** with iodosylbenzene and terminal alkynes (eq 223).[451]

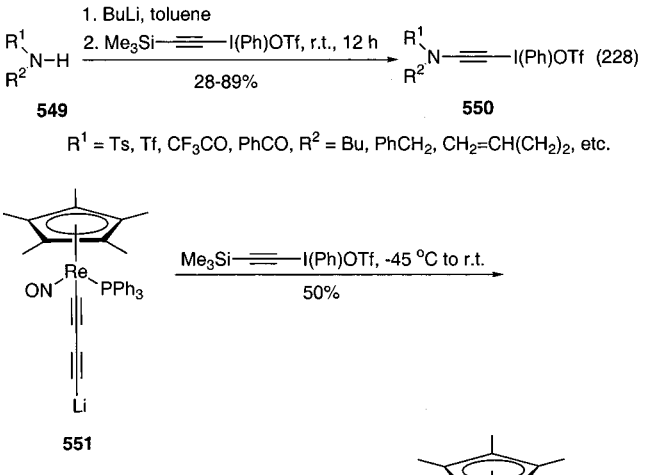


Polymer-supported alkynyliodonium tosylates **542** can be prepared by the treatment of diacetate **109** (see section II.C.1) with terminal alkynes in the



presence of *p*-toluenesulfonic acid (eq 224).[452] Polymers **542** are efficient alkynylating reagents toward sodium sulfinates and benzotriazole.

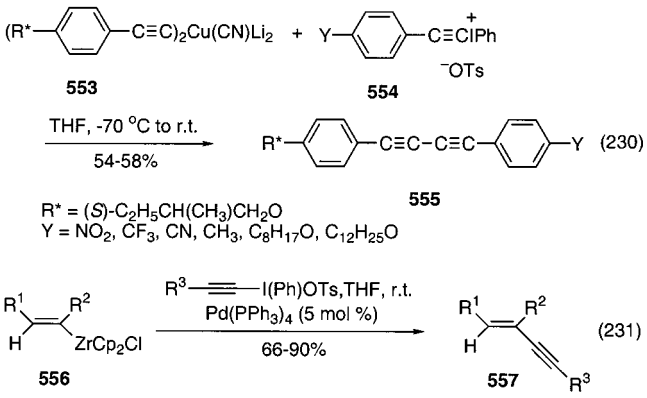




Reactions of alkynyliodonium salts with nucleophiles proceed via an addition−elimination mechanism involving alkylidene carbenes as a key intermediates. Depending on the structure of the alkynyliodonium salt, specific reaction conditions, and the nucleophile employed, this process can lead to a substituted alkyne due to the carbene rearrangement or to a cyclic product via intramolecular 1,5-carbene insertion.[16] Both of these reaction pathways have been widely utilized in organic synthesis.

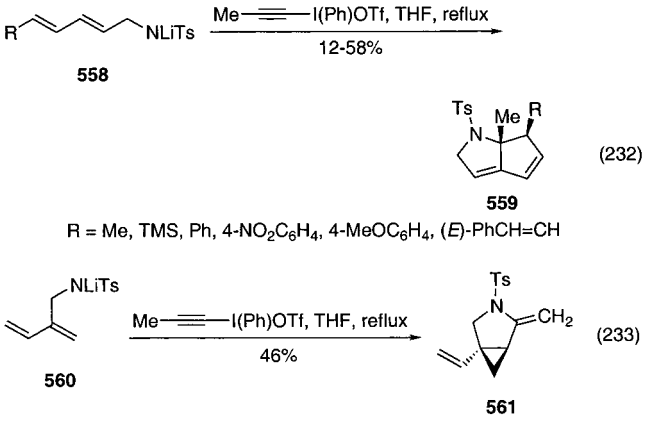
Alkynyl(phenyl)iodonium salts have found synthetic application for the preparation of various substituted alkynes. Recent examples include the synthesis of acetylenic selenides and tellurides **544** (eq 225),[453−455] alkynylphosphonates **546** (eq 226),[456] alkynylbenzotriazoles **548** (eq 227),[457,458] *N*-functionalized 1-alkynylamides **550** (eq 228),[459−461] and organometallic triene **552** (eq 229).[462]

Alkynyl(phenyl)iodonium salts can be efficiently coupled with organocopper (**553**)[463] and organozirconium (**556**)[464−467] complexes (eqs 230 and 231). The chiral diaryldiacetylenes **555** (eq 230) are potent ferroelectric liquid crystals.[463]

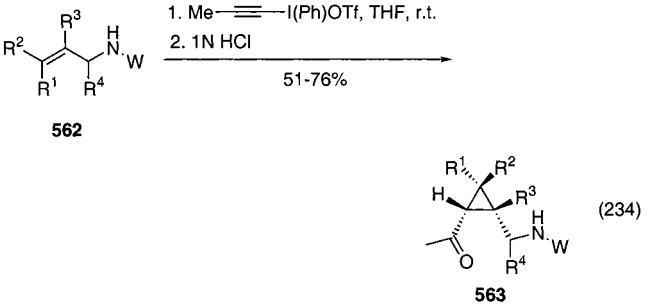


A variety of five-membered heterocycles can be prepared efficiently by inter- or intramolecular addition/cyclizations of appropriate nucleophiles with alkynyliodonium salts via alkylidene carbene intermediates. Feldman and Mareska recently utilized the intermolecular variant of this cyclization in the synthesis of highly substituted dihydropyrrole derivatives.[468−471] In a specific example, the addition of pentadienyltosylamide derivatives **558** to phenyl(propynyl)iodonium triflate initiates a sequence of transformations that furnishes the complex, highly functionalized cyclopentene-annelated dihydropyrrole products **559** in moderate yields with complete stereoselection (eq 232).[468−470] Under similar reaction conditions, the isomeric isoprene-derived tosylamide **560** reacts with propynyliodonium triflate to give azabicyclo[3.1.0]hexane **561** as the final product (eq 233).[470]

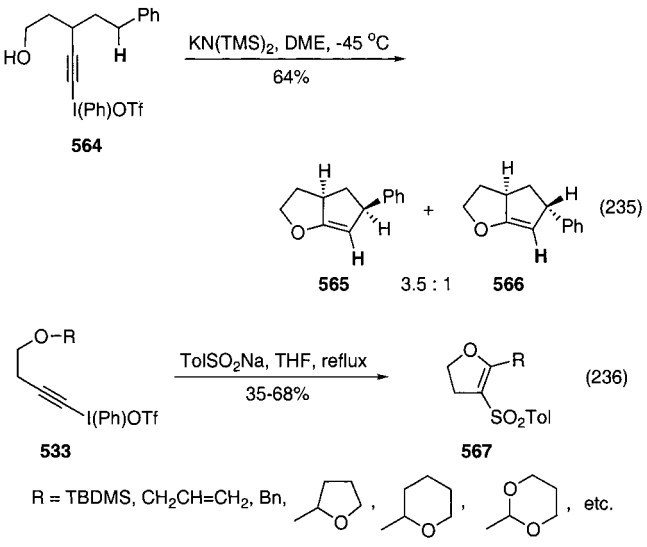
Lee and Lee recently reported a stereoselective synthesis of 1-acetyl-2-aminomethyl cyclopropanes **563** based on a similar reaction of anions of tosylallylamines **562** and phenyl(propynyl)iodonium



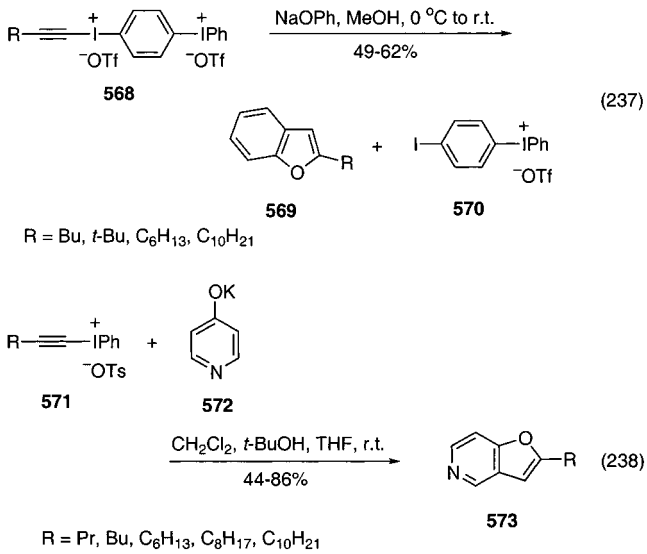
triflate followed by an acidic hydrolysis of the intermediately formed azabicyclo[3.1.0]hexane products (eq 234).[472]



The intramolecular variant of the alkylidene carbene cyclization is achieved by the treatment of functionalized alkynyliodonium salts with the appropriate nucleophile. Recently, Feldman and coworkers utilized the intramolecular variant of this cyclization in the synthesis of cyclopentannelated tetrahydrofurans **565** and **566** (eq 235)[447] and in the preparation of substituted dihydrofurans **567** (eq 236).[448] Alkynyliodonium salts **564** and **533**, the key precursors in these reactions, are conveniently prepared from the appropriate alkynylstannanes (see eqs 218 and 219) and can be used without additional purification.

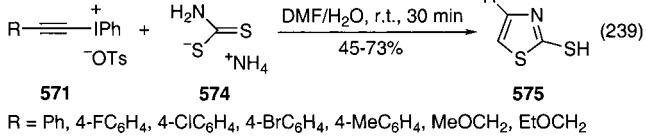


Kitamura and co-workers reported the preparation of 2-substituted benzofurans **569** (eq 237)[473] and furopyridine derivatives **573** (eq 238)[474] by the intramolecular aromatic C−H insertion of the alkylidenecarbenes generated by the reaction of alkynyliodonium salts **568** and **571** with the appropriate anions.



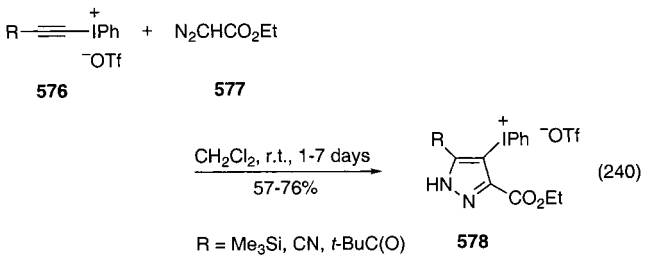
A similar reaction of trimethylsilylethynyl(phenyl)iodonium triflate with the potassium salts of some acidic phenols leading to 2-substituted benzofurans via the intramolecular alkylidenecarbenes C−H insertion was reported by Varvoglis, Rodios, and Nikas.[475]

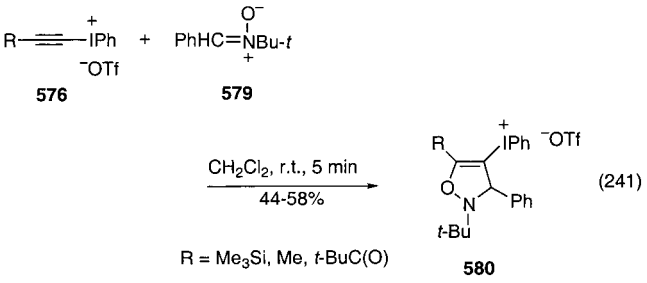
Chen and Zhang reported the synthesis of 2-mercaptothiazoles **575** by the cyclocondensation of alkynyl(phenyl)iodonium tosylates with ammonium dithiocarbamate **574** (eq 239).[476] A plausible mechanism of this reaction is analogous to the earlier reported[477] synthesis of thiazoles from alkynyl(phenyl)iodonium salts and thioamides and involves the intramolecular cyclization of the intermediate alkylidenecarbene.



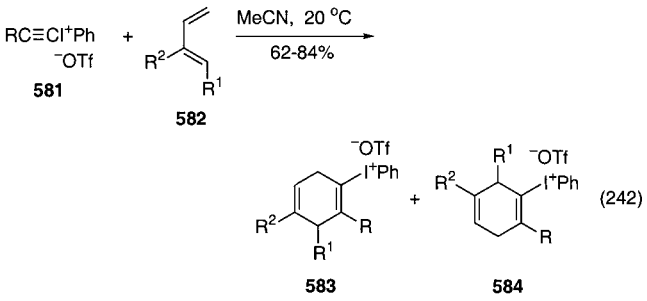
Alkynyliodonium salts represent highly activated, electron-deficient alkynes with a strongly polarized triple bond. Due to the dipolar structure, they can behave as good 1,3-dipolarophiles in various [3+2] cycloaddition reactions. In a recent example, the cycloaddition of various β-substituted ethynyliodonium triflates **576** with ethyl diazoacetate **577** (eq 240) or *N*-*tert*-butyl-α-phenyl nitrone **579** (eq 241) results in single regioisomeric pyrazoles **578** or dihydroisoxazoles **580**, respectively, in moderate yields.[477]

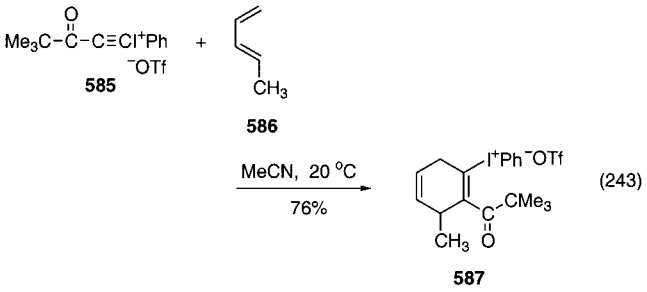
Alkynyliodonium salts functionalized with electron-withdrawing substituents in the β-position readily undergo [4+2] Diels−Alder cycloadditions with a wide range of dienes.[1,16]





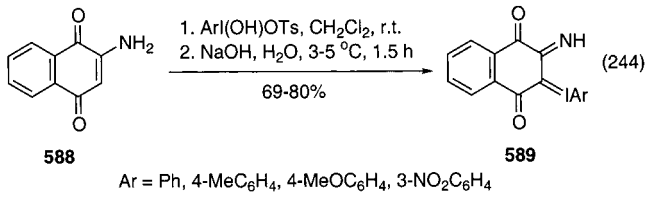
The reaction of alkynyliodonium salts **581** with unsymmetrically substituted dienes **582** results in a mixture of two regioisomeric cyclohexadienes **583** and **584** (eq 242).[478] In general, this cycloaddition (eq 242) shows low regioselectivity in the case of 2-substituted dienes and has a better degree of regioselectivity in the case of 1-substituted dienes. Moreover, the reaction of 1-methylbutadiene **586** with alkynyliodonium salt **585** selectively affords a single regioisomer **587**, whose structure was established by X-ray analysis (eq 243).[478]



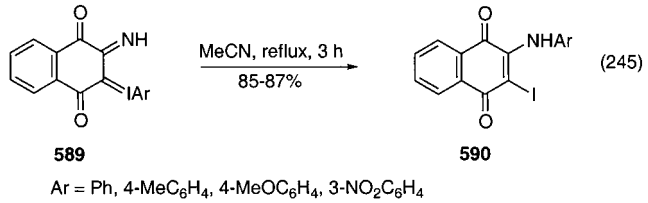


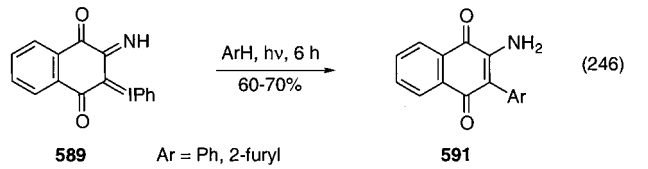
J. Iodonium Ylides

Several new, potentially important classes of iodonium ylides have been prepared and investigated in the last 5 years.[479−487] Spyroudis and Varvoglis reported the synthesis of a new class of stable zwitterionic aryliodonium compounds **589** from 2-amino-1,4-naphthoquinone **588** and [hydroxy(tosyloxy)iodo]arenes (eq 244).[479−481]

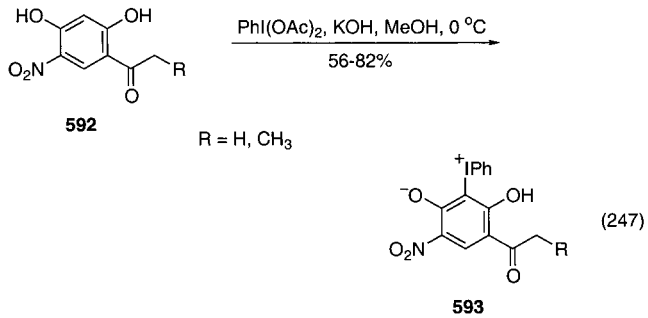


Ylides **589** show an interesting reactivity: upon heating, aryl migration from iodine to nitrogen is observed (eq 245), while the photochemical reaction with aromatic compounds and furan leads to substitution products **591** (eq 246). Nucleophilic attack of sodium alkoxide derivatives on these zwitterions resulted in opening of the quinone ring affording synthetically interesting multifunctional products.[480]





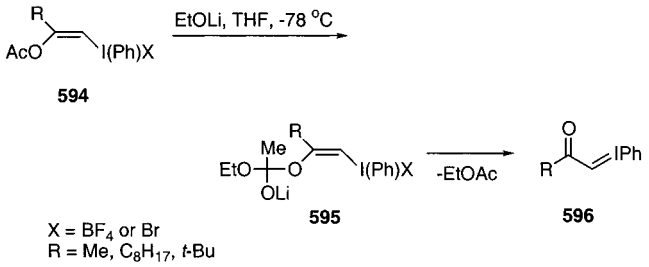
Prakash and co-workers reported the preparation of the stable zwitterionic aryliodonium compounds **593** by the reaction of 2,4-dihydroxyacetophenones **592** with (diacetoxyiodo)benzene (eq 247).[482] Heating of these compounds leads to aryl migration from iodine to oxygen with the formation of the appropriate *o*-iodophenoxy ethers.



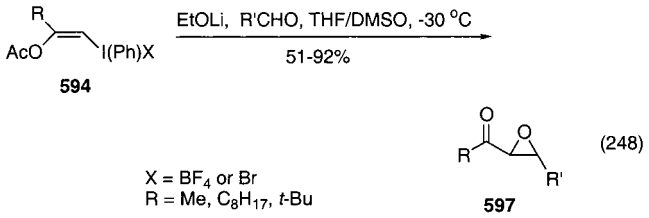
Ochiai and co-workers reported a quantitative generation of monocarbonyl iodonium ylides **596** from (*Z*)−(2-acetoxyvinyl)iodonium salts **594** via an ester exchange reaction with EtOLi in THF at −78 °C (Scheme 22).[483−485] ^{1}H NMR measurements indicate that ylide **596** is stable up to −30 °C.[483]

Ylide **596**, generated in situ from iodonium salts **594**, reacts with aldehydes in THF−DMSO at −30 °C to afford α,β-epoxy ketones **597** (eq 248) with the predominant formation of the trans isomers. A Hammett correlation with the σ constants of substituents afforded the reaction constant $\rho = 2.95$ ($r = 1.00$),

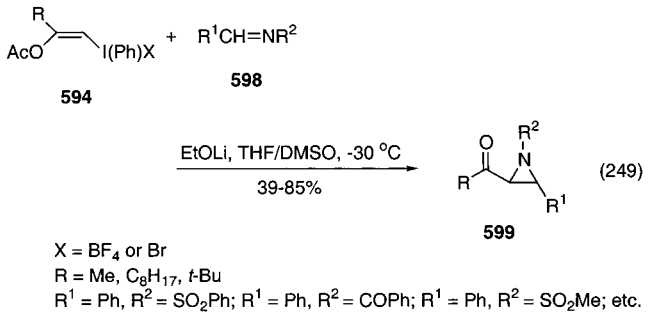
Scheme 22



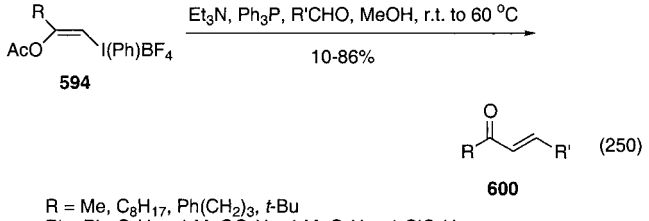
which indicates that the monocarbonyl iodonium ylide is moderately nucleophilic in nature.[483]



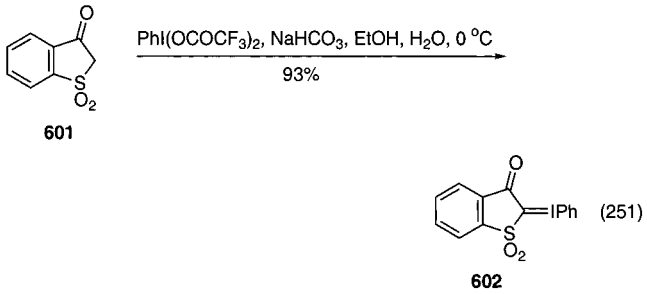
Monocarbonyl iodonium ylides, generated in situ from iodonium salts **594**, undergo alkylidene transfer reactions to activated imines **598** yielding 2-acylaziridines **599** in good yields (eq 249). The stereochemical outcome of this aziridination is dependent on both the activating groups of the imines and the reaction solvents; for example, the 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.[484,485]



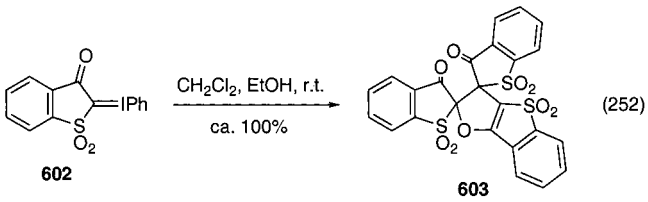
The treatment of iodonium salts **594** with triethylamine in methanol in the presence of triphenylphosphine and aldehydes results in Wittig olefination (eq 250), which involves the intermediacy of monocarbonyl iodonium ylides **596** and their subsequent conversion to the respective phosphonium ylides upon the in situ reaction with Ph_3P.[486]



Hadjiarapoglou and Schank prepared the stable iodonium ylide **602** from the reaction of the β-ketosulfone **601** with [bis(trifluoroacetoxy)iodo]benzene (eq 251).[487]

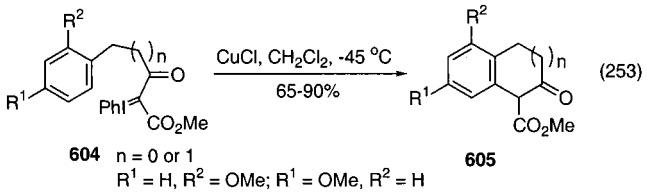


Ylide **602** readily decomposes in a solution of dichloromethane/ethanol with the quantitative formation of trimer **603**. Similar to other stable iodonium ylides, compound **602** readily participates in various carbenoid reactions in the presence of copper(II) catalysts.[487]

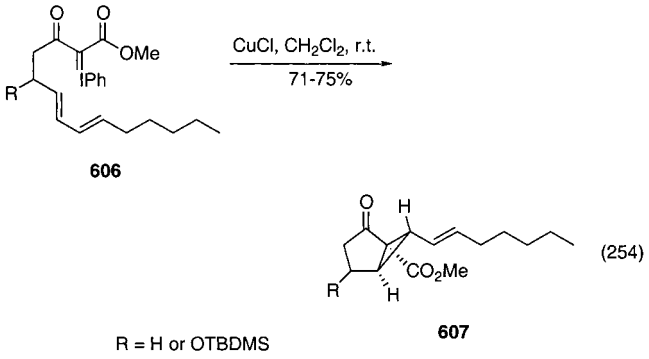


Iodonium ylides can serve as convenient precursors to the respective carbene intermediates under thermal, photochemical, or catalytic conditions. DeLuca and co-workers reported a computational and experimental study on the carbene generation from iodonium ylides.[488] According to computational results, the thermal decomposition of iodonium ylides leading to carbenes should be facile, requiring an enthalpy change of no more than of 15 kcal/mol. The experiment demonstrated that ylide $PhI{=}C(CO_2Et)_2$ readily decomposes in cyclohexane at 100 °C affording the C−H insertion product together with iodobenzene as the major products. The thermal reaction of this ylide with *trans*- and *cis*-3-heptenes results in a stereospecific cyclopropanation. Under photochemical conditions, this cyclopropanation is not stereoselective. These results indicate that the thermal decomposition of the iodonium ylides under mild conditions is an efficient source of a singlet carbene intermediate, uncontaminated with excited states of the precursor that would attend the photolysis.[488]

There has been substantial recent interest in the transition-metal-catalyzed reactions of iodonium ylides.[489−501] Moriarty and co-workers found that copper(I)-catalyzed decomposition of phenyliodonium ylides **604** affords the corresponding substituted tetralones **605** in good preparative yields (eq 253).[489]

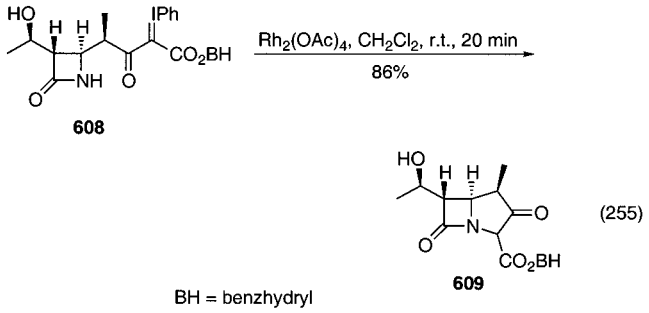


Under similar conditions, iodonium ylides **606** undergo regio- and stereoselective intramolecular cyclopropanation to form the key bicyclo[3.1.0] intermediates **607** (eq 254) for prostaglandin synthesis.[490]



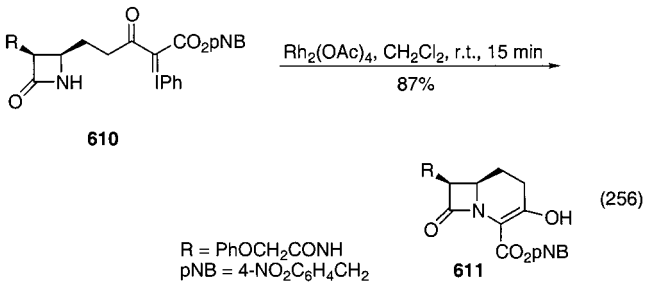
(254)

Kume and co-workers reported an efficient and practical method for the synthesis of the antibiotic 1β-methylcarbapenem based on the iodonium ylide **608** cyclization to the bicyclic β-keto ester **609** in the presence of either a rhodium(II) catalyst or an acid (eq 255).[491]



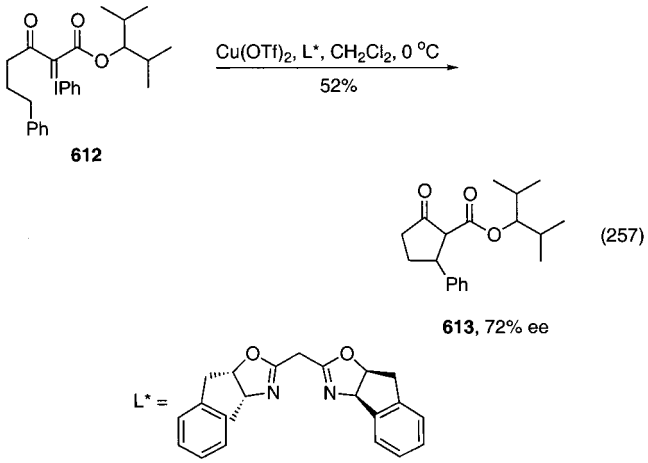
(255)

Likewise, compound **611**, a key intermediate in the synthesis of carbacephalosporin antibiotics, was prepared utilizing either a rhodium(II)- or an acid-catalyzed cyclization of iodonium ylide **610** (eq 256).[492]



(256)

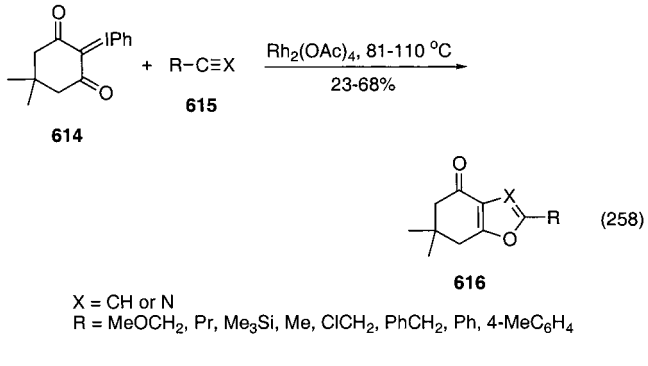
The scope and mechanism of the metal-catalyzed carbenoid decomposition of iodonium ylides with regard to their application in asymmetric carbenoid reactions were investigated by Müller and co-workers.[493−496] In a specific example, the copper(II)-catalyzed intramolecular C−H insertion of phenyliodonium ylide **612** has been investigated in the presence of several chiral ligands (eq 257).[495] Enantioselectivities in this reaction vary in the range of 38−72% for different chiral ligands and are higher than those resulting from a similar reaction of the diazo compounds. These results are consistent with a carbenoid mechanism for the copper(II)-catalyzed decomposition of phenyliodonium ylides.



(257)

Doyle and co-workers investigated enantiocontrol in the reactions of the iodonium ylides generated from the allyl iodide/ethyl diazoacetate system in the presence of chiral dirhodium(II) catalysts.[497] Examination of the stereochemistry of this reaction shows that the metal-associated ylides are the primary product-forming intermediates in [2,3]-sigmatropic rearrangements. Asymmetric induction in ylide-derived processes can be achieved using chiral catalyst methodologies.

The cyclic β-dicarbonyl iodonium ylides undergo [3+2] cycloaddition reactions with various substrates under catalytic or photochemical conditions, presumably via a stepwise mechanism.[498−501] In a recent example, iodonium ylide **614**, derived from dimedone, undergoes dirhodium(II)-catalyzed thermal [3+2]-cycloaddition with acetylenes and nitriles **615** to form the corresponding furans and oxazoles **616**, respectively (eq 258). Under photochemical conditions, ylide **614** reacts with various alkenes to form dihydrofuran derivatives **618** (eq 259).[501]



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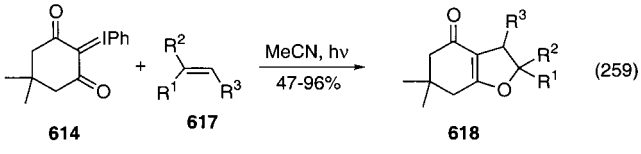


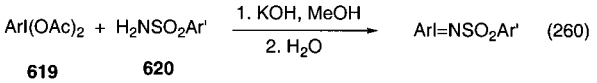
(259)

K. Iodonium Imides

1. Preparation and Structure

Iodonium imides, ArI=NSO$_2$R, have attracted a significant recent interest due to their application as

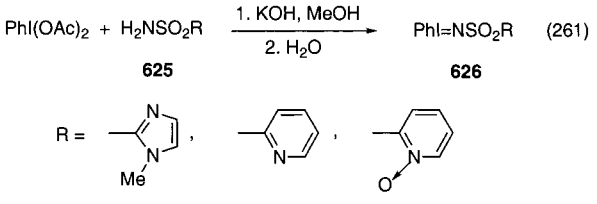
nitrene precursors in the transition-metal-catalyzed aziridination of olefins and various amidation and imidation reactions. The best known and widely used iodonium imide is *N*-tosyliminophenyliodinane, PhI=NTs, the structural features of which were discussed in our previous review.[1] Recently, Protasiewicz and co-workers prepared and crystallographically characterized a series of iodonium imides **621**−**624** (eq 260).[502] A comparison of these compounds to the previously structurally characterized imides (PhINTs, *o*-TolylINTs, MesINTs) demonstrates that apparently minor perturbations of the aromatic rings have substantial consequences on the supramolecular assemblies of these materials. The structures range from zigzag polymers (PhINTs, MesINTs), linear polymers (*o*-TolylINTs), layered structures (**621**), two-dimensional ladders (**622**, **623**, *o*-TolylINTs), to even three-dimensional stepladders (**624**). These structural shapes appear to optimize secondary bonding contacts between the charged $INSO_2$ arrays.



Ar = *m*-Tolyl, Ar' = *p*-$NO_2C_6H_4$: **621**
Ar = *m*-Tolyl, Ar' = *p*-Tolyl: **622**
Ar = *m*-Tolyl, Ar' = Ph: **623**
Ar = *p*-Tolyl, Ar' = *p*-Tolyl: **624**

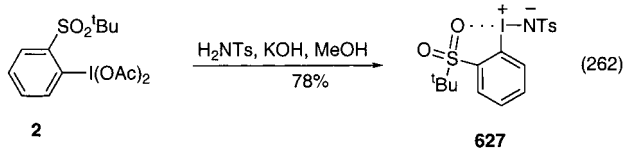
Andersson and co-workers described the preparation of several iodonium imides PhI=NSO_2Ar (Ar = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$, 2-$NO_2C_6H_4$, 4-FC_6H_4, 4-BrC_6H_4, 4-IC_6H_4) from (diacetoxyiodo)benzene and the appropriate amides under basic conditions (KOH, MeOH at 0 °C).[503] All these imides were evaluated for their utility as nitrene precursors for the copper-catalyzed aziridination of different olefins. The best results were obtained with 4-$NO_2C_6H_4$NIPh and 4-$MeOC_6H_4$NIPh, both of which were found to be superior to PhINTs, which previously has been the reagent of choice for this type of reaction.[503,504]

Several novel iodonium imides **626** bearing *N*-heterocyclic rings have been prepared from (diacetoxyiodo)benzene and the respective amides **625** (eq 261).[505] Imides **626** can be used as sources of the corresponding heterocycle-containing nitrenes in the copper-catalyzed aziridination and sulfimidization reactions.



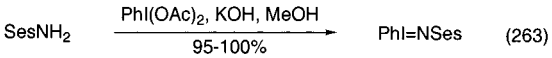
Protasiewicz and co-workers reported the preparation and X-ray structure of the novel, highly soluble, nitrene precursor **627** (eq 262), in which the intramolecular secondary I···O bond replaces intermolecular interactions that are typical of iodonium imides.[28]

Imide **627** is readily soluble in organic solvents (up to 0.14 M in chloroform, which is a 50-fold increase



over PhINTs) and can be analyzed by NMR in solution.[28] Single-crystal X-ray analysis of **627** showed a structure of loosely associated centrosymmetric dimers with a long-range intramolecular I···N and I···O distance of more than 3.0 Å, quite unlike the infinite polymeric chains adopted in the solid state for PhINTs. One of the sulfonyl oxygen atoms forms a short intramolecular I···O secondary bond to the iodine atom with a bond length of 2.667 Å. Because of the excellent solubility in common organic solvents, compound **627** has high activity in the copper-catalyzed aziridination and sulfimidization reactions.[28] Solubilization of various amides ArINTs in organic media can also be achieved by the addition of organic *N*-oxides, such as Me_3NO.[506]

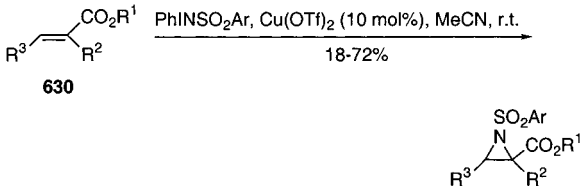
Dodd and co-workers reported the preparation of the new iminoiodinane **629** (PhINSes) by the reaction of amide **628** with (diacetoxyiodo)benzene (eq 263).[507] This reagent is useful for the copper-catalyzed aziridination of olefins leading to the synthetically versatile Ses-protected aziridines.



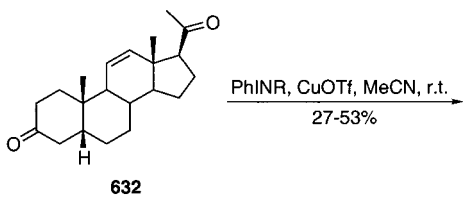
Ses = $Me_3SiCH_2CH_2SO_2$

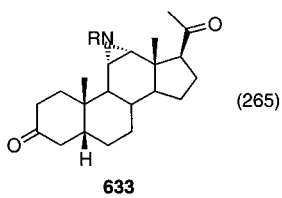
2. Transition-Metal-Catalyzed Aziridination of Olefins

A significant current interest in the transition-metal-catalyzed reactions of iodonium imides was initiated by the pioneering work of Evans[508−510] and Jacobsen[511,512] on the asymmetric aziridination of olefins using copper catalysts (2−10 mol %) with chiral dinitrogen ligands and PhINTs as the nitrene



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

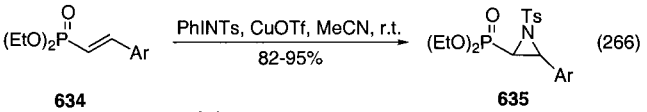




R = Ts, Ns, Ses

precursor. In the last 5−6 years the research activity in this area has surged. The copper-catalyzed aziridination of olefins has been utilized in numerous syntheses.[513−525] Dodd and co-workers applied the Evans aziridination procedure to 2-substituted acrylates and cinnamates **630** (eq 264)[513,514] and to steroids **632** (eq 265).[515,516]

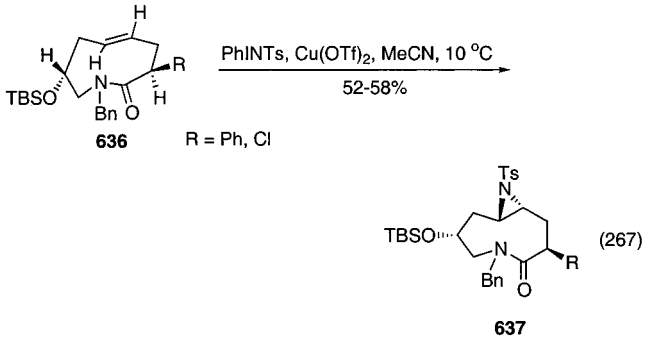
The copper-catalyzed aziridination of the appropriate alkenes was recently employed in the preparation of various 2-acylaziridines[517−519] and aziridinylphosphonates **635** (eq 266).[520]



634 **635**

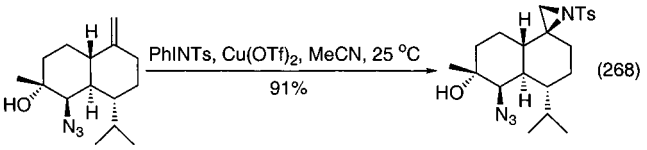
Ar = Ph, 4-ClC$_6$H$_4$, 1-naphthyl, 2-naphthyl

The copper-catalyzed aziridination was also applied toward the functionalization of the optically active azoninones **636** (eq 267),[521] in studies toward the total synthesis of kalihinane diterpenoids (eq 268),[522] in the synthesis of α-methylserinal derivatives (eq 269),[523] in the preparation of 2,4-disubstituted *N*-tosylpyrrolidines,[524] and in the synthesis of nosylaziridines.[525]

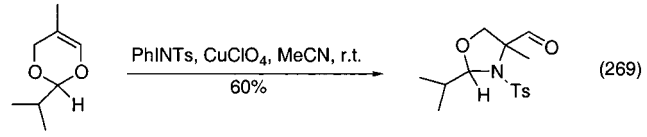


636 R = Ph, Cl

637



638 **639**



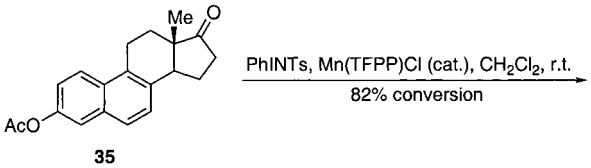
640 **641**

There has been a significant interest in the transition-metal-catalyzed asymmetric aziridination reactions with PhINTs.[526−538] A variety of new chiral ligands or counteranions 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,[526] chiral C_2-symmetric bisferrocenyldiamines,[527] chiral borate counteranion,[528] a phosphoramidite derived from (−)-(a*R*)-[1,1′-binaphthalene]-8,8′-diol,[529] bis(oxazolines) on zeolite Y,[530,531] chiral tartrate-derived bis-oxazoline ligands,[532] and C_2-symmetric bis(aziridine) ligands.[533] Highly enantioselective catalytic aziridination of styrenes was realized by using (salen)manganese(III) complexes,[534] manganese and iron tetramethylchiroporphyrins,[535] and the chiral rhodium(II) complexes.[536−538] 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,[539,540] poly(pyrazolyl)borate−copper complexes,[541] the copper(II) complexes of 1,4,7-triisopropyl-1,4,7-triazacyclononane,[542] a Cu(I) complex of ferrocenyldiimine,[543] bis(tosyl)imidoruthenium(VI) porphyrin complexes,[544] and methyltrioxorhenium.[545]

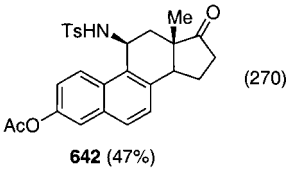
The mechanism of the copper-catalyzed aziridination was discussed in several recent papers.[546−548] Specifically, the kinetic studies indicate that copper nitrene species are the key intermediates for this reaction.

3. Transition-Metal-Catalyzed C–H Amidation

The transition-metal-catalyzed amidation of saturated C−H bonds using iodonium imides has recently been utilized in several syntheses.[66,67,549−551] Breslow and co-workers reported the regioselective amidation of steroidal derivatives catalyzed by metalloporphyrins.[66,67] Specifically, the aromatic steroid equilenin acetate **35** undergoes regioselective and stereoselective amidation catalyzed by a manganese porphyrin using PhINTs as the nitrene donor (eq 270).[66]



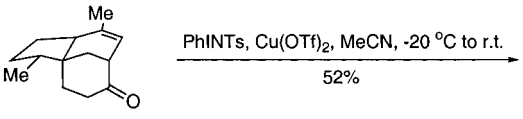
35



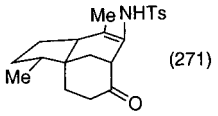
642 (47%)

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

Overman and Tomasi applied the copper-catalyzed amidation of compound **643** (eq 271) in the key step of the enantioselective total synthesis of the natural tetracyclic spermidine alkaloid (−)-hispidospermidin.[549]



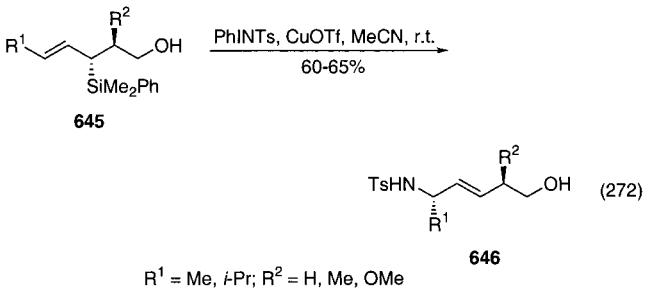
643



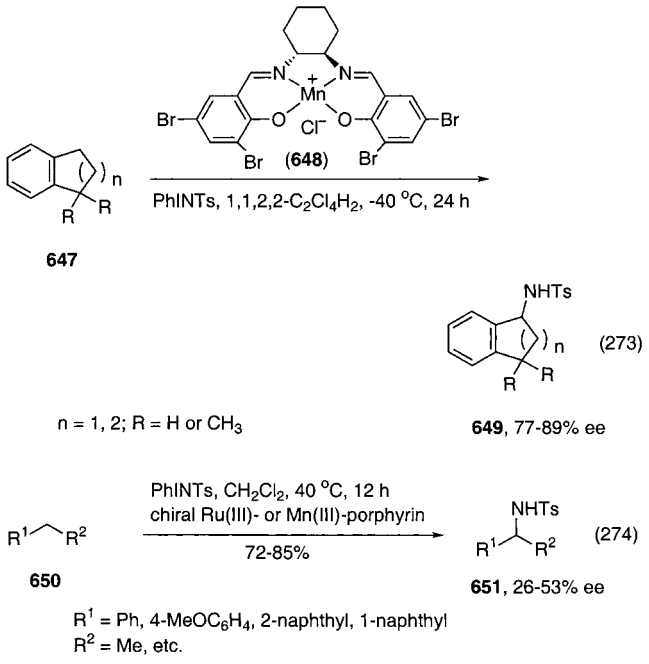
644

Allylic silanes can be converted into allylic tosylamides by the reaction with PhINTs in the presence of copper salts.[550,551] The copper(I)-catalyzed enantio-

selective amidation of the chiral (*E*)-crotylsilanes **645** (eq 272) was used in the asymmetric synthesis of (*E*)-olefin dipeptide isosteres.[551]



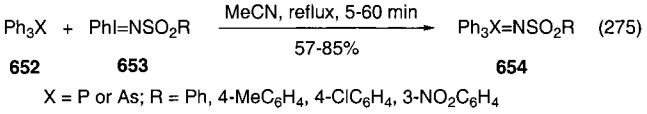
The amidation of saturated C−H bonds can be effectively catalyzed by ruthenium or manganese complexes.[552−555] Unfunctionalized hydrocarbons, such as adamantane, cyclohexene, ethylbenzene, cumene, indan, tetralin, diphenylmethane, and others, are selectively amidated with PhINTs in the presence of ruthenium or manganese porphirins or the ruthenium cyclic amine complexes to afford *N*-substituted sulfonamides in 80−93% yields with high selectivity.[552,553] The enantioselective amidation of a C−H bond can be achieved in the presence of the chiral (salen)manganese(III) complexes (eq 273)[554] or in the presence of chiral ruthenium(II) and manganese(III) porphyrins (eq 274).[555]



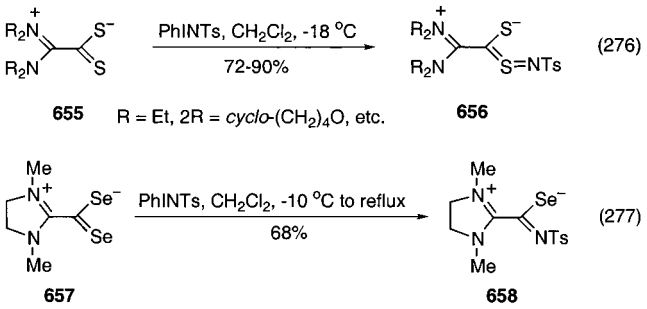
Du Boise and co-workers recently described a novel rhodium-catalyzed intramolecular amidation of saturated C−H bonds in sulfamate esters in the presence of (diacetoxyiodo)benzene and magnesium oxide.[556] The mechanism of this synthetially useful reaction most likely involves the intermediate formation of iodonium imides from sulfamate esters, $PhI(OAc)_2$, and MgO.

4. Imidations at Non-Carbon Atoms

Iodonium imides can be used for the transfer of the imido group to other elements under either noncatalytic or catalytic conditions. *N*-Sulfonyltriphenylphosphinimides and arsinimides **654** are formed in the reaction of iodonium imides **653** with triphenylphosphine or triphenylarsine **652** (eq 275).[557]

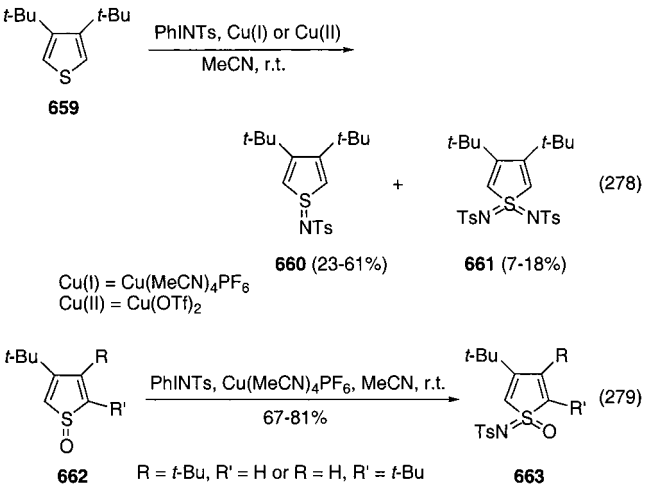


2,2-Diamino-2-ethylium-1-dithiocarboxylates **655** can be imidated at sulfur by PhINTs to afford the novel inner salts **656** (eq 276).[558] The analogous selenium substrate **657** reacts with PhINTs affording imide **658** (eq 277), formation of which is explained by the deselenation of the initial product of the imidation at the selenium atom of **657**.[559]



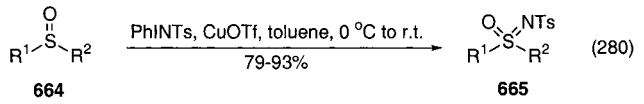
The reaction of PhINTs with complexes of ruthenium(II),[544] osmium(II),[560,561] and cobalt(III)[562] results in the imidation at the metal center with the formation of the respective tosylimidometal complexes. X-ray structures were determined for several bis(tosylimido)ruthenium(VI) and bis(tosylimido)osmium(VI) porphyrin complexes.

The imidation at sulfur and selenium atoms can be effectively catalyzed by complexes of transition metals. The reaction of 3,4-di-*tert*-butylthiophene **659** with PhINTs in the presence of copper(I) or copper(II) catalysts affords a mixture of imide **660** and diimide **661** as principal products (eq 278).[563−565] Likewise, the imidation of thiophene 1-oxides **662** under similar conditions gives imides **663** in good yield (eq 279).[566]



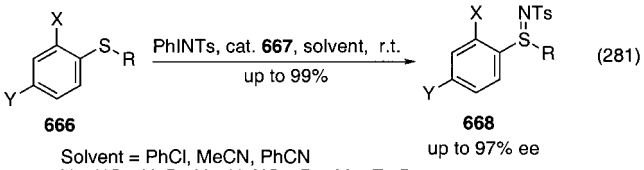
The reaction of PhINTs with sulfoxides **664** in the presence of catalytic amounts of copper(I) triflate affords the corresponding *N*-tosylsulfoximides **665** in

high yield (eq 280).[567] The use of enantiomerically pure sulfoxides **664** allows stereoselective access to *N*-tosylsulfoximides **665** with complete retention of configuration at sulfur. A similar imidation procedure was used for the preparation of the chiral ferrocenylsulfoximides.[568,569]

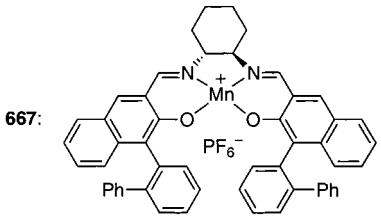


R^1 = Ph, 4-MeC_6H_4; R^2 = Me, Et, *i*-Pr, vinyl, allyl, $PhCH_2$

Enantioselective imidation of alkyl aryl sulfides **666** can be achieved by using the chiral manganese(salen) complex **667** as a catalyst (eq 281).[570,571]



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



Likewise, 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.[572,573] Under similar conditions, various 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.[574,575]

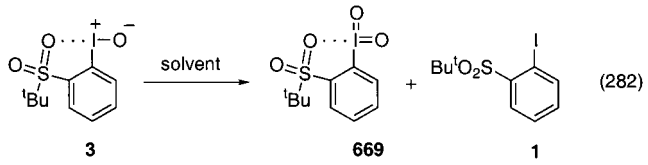
III. Iodine(V) Compounds

The chemistry of iodine(V) compounds, or λ^5-iodanes according to the IUPAC nomenclature, is substantially less developed in comparison with the chemistry of trivalent iodine. Only several examples of noncyclic λ^5-iodanes with one or more carbon ligands on the iodine atom are known.[1,23] In contrast, there has been very significant recent interest in the cyclic λ^5-iodanes, mainly iodoxybenzoic acid (IBX) and Dess−Martin periodinane (DMP), which have found broad practical application as mild and selective reagents for the oxidation of alcohols. This section of the present review will summarize recent research on λ^5-iodanes with emphasis on their application in organic synthesis.

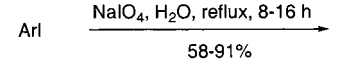
A. Organic Iodyl Compounds

Only several representatives of organic iodyl or iodoxy compounds, RIO_2, have been reported in the literature. With a few exceptions, only aryl-substituted iodoxy derivatives, $ArIO_2$, can form stable compounds. Clark and co-workers reported the matrix isolation and FTIR spectra of the unstable iodyl derivatives, RIO_2, generated by the co-deposition and photolysis of ozone with iodoethane, 2-iodopropane, pentafluoroiodoethane, 1,1,1-trifluoroiodoethane, 1,1,2,2-tetrafluoroiodoethane, 1,1,1,2-tetrafluoroiodoethane, or iodine cyanide in an argon matrix at 14−16 K.[576−578]

The preparation of several new, stable iodylarenes was recently reported.[29,579] Protasiewicz and co-workers reported the preparation of iodylarene **669** by the disproportionation of iodosylarene **3** (eq 282).[29] The X-ray structure of product **669** shows a pseudo-octahedral geometry with the I−O bond lengths in the iodyl group of 1.796 and 1.822 Å and an intramolecular distance of 2.693 Å between one of the sulfone oxygen atoms and the hypervalent iodine center.[29]



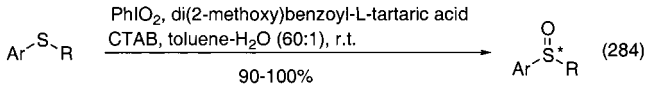
Skulski and co-workers developed a new method for the preparation of various iodylarenes **671** from the corresponding iodoarenes **670** using sodium periodate as the oxidant (eq 283).[579] To obtain 2- and 4-iodylbenzoic acids, the respective sodium salts of 2- and 4-iodobenzoic acids should be used as the starting substrates to improve the yield and the purity of the products.



Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 4-BrC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 3-$HO_2CC_6H_4$, 4-$NaO_2CC_6H_4$, 2-$NaO_2CC_6H_4$

Iodylarenes have found some practical application as oxidizing reagents. In recent results, iodoxybenzene was applied to the oxidation of various phosphorus, phosphorothiono, and phosphoroseleno compounds into the corresponding phosphonium oxides.[580] This oxidation proceeds with complete retention of configuration at the phosphorus atom.

Kita and co-workers developed a new catalytic asymmetric oxidation using iodoxybenzene in a cationic reversed micellar system in the presence of chiral tartaric acid derivatives. Under these conditions, sulfides **672** are oxidized to sulfoxides **673** in

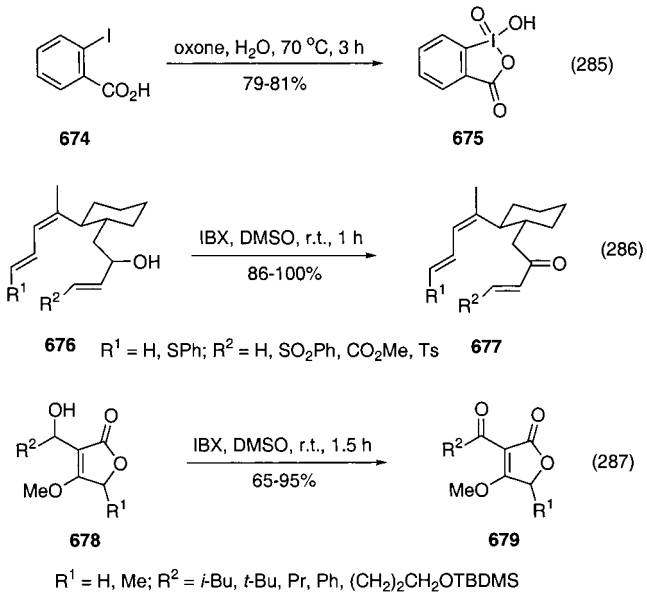


R = Me or Et
Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 4-CNC_6H_4, 4-BrC_6H_4, 3-$NO_2C_6H_4$, 2-naphthyl, etc.

high chemical yield with moderate to good enantioselectivity (eq 284).[581]

B. Benziodoxole Oxides

The most important representative of benziodoxole oxides is 2-iodoxybenzoic acid (IBX, **675**), or 1-hydroxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one according to the IUPAC nomenclature. The synthetic applications of IBX were recently summarized in an excellent overview by Wirth.[582] Most commonly IBX is prepared by the oxidation of 2-iodobenzoic acid with potassium bromate in an aqueous solution of sulfuric acid.[583] A new, convenient procedure for the preparation of IBX (**675**) by the oxidation of 2-iodobenzoic acid with oxone (eq 285) was recently reported by Santagostino and co-workers.[584]



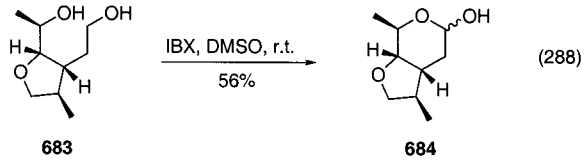
IBX samples, prepared by the oxidation of 2-iodobenzoic acid with potassium bromate, usually contain a mixture of the powder and the macrocrystalline forms. A detailed X-ray diffraction study of both forms of IBX was recently published by Stevenson and co-workers.[585] It was also noticed that the powder form of IBX is more reactive in the reaction with acetic anhydride than the macrocrystalline form and thus is more useful as the Dess−Martin periodinane precursor. Treatment of the macrocrystalline IBX with aqueous sodium hydroxide and then with HCl can be used to convert it to the more reactive powder form.[585]

IBX and its analogues have attracted increasing interest as mild and selective oxidizing reagents.[586−607] Solutions of IBX in DMSO are useful for the clean oxidation of alcohols to carbonyl compounds even in the presence of other functional groups. Several representative, recent examples of such oxidations are shown in eqs 286−291 and Scheme 23. Specifically, the allylic alcohols **676** are selectively oxidized by IBX to ketones **677** in high yield (eq 286).[586]

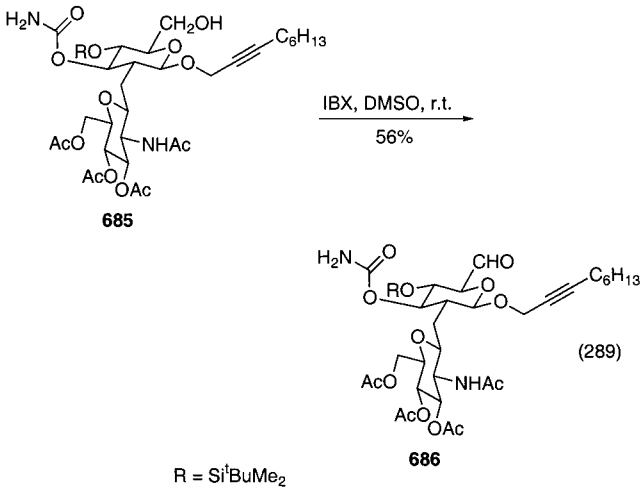
The oxidation of alcohols **678** under the same conditions selectively affords 5-monosubstituted 3-acyl-4-*O*-methyl tetronates **679** (eq 287), which are structurally similar to the tetrodecamycin antibiotics.[587]

The IBX oxidation of diol **680** was applied in the synthesis of the functionalized hexahydroanthracene dione **682** (Scheme 23), a model for the D ring of taxoids.[588]

Likewise, the oxidation of diol **683** affords hemiacetal **684** (eq 288), a key precursor to the antifungal agent GM222712.[589]



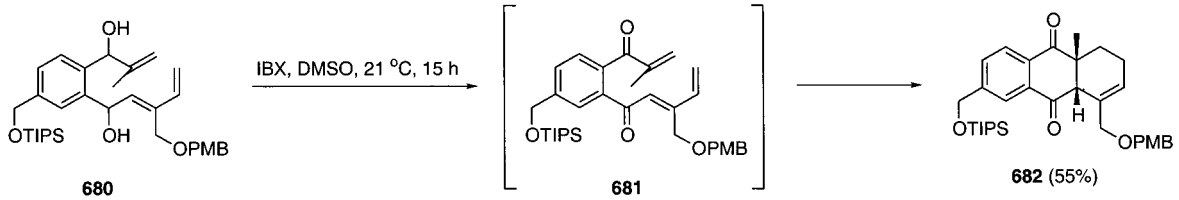
The IBX oxidation of carbohydrate **685** was used in the synthetic studies of moenomycin A disaccharide analogues (eq 289).[590]



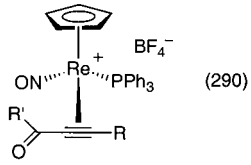
The chiral rhenium complexes of allylic and propargylic alcohols **687** are selectively oxidized by IBX to the respective carbonyl derivatives **688** in good yields under mild conditions (eq 290).[591]

Benzylic, allylic, and propargylic alcohols, as well as diols, can be oxidized with IBX in the presence of the stabilized Wittig ylide **690** to generate α,β-unsaturated esters **691** in one pot (eq 291).[592] This

Scheme 23



687

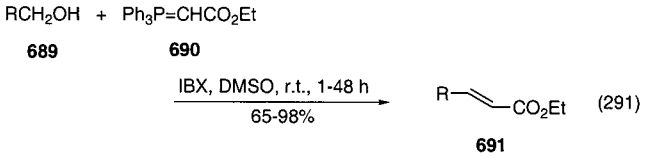


(290)

688

R = H, R' = Me; R = Me, R' = H

is a useful procedure when the intermediate aldehydes are unstable and difficult to isolate.



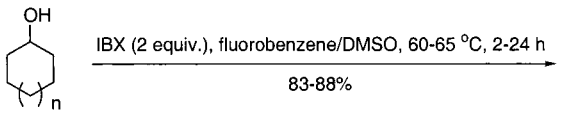
689 690 691 (291)

R = Ph, PhCH=CH, Me_2C=CHCH$_2$CH$_2$(Me)C=CH, HC≡C, C_5H_{11}C≡C, etc.

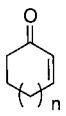
The oxidation of alcohols with IBX was also used in the development of a new silyl ether linker for solid-phase organic synthesis[593] and in the kinetic study of organic reactions on polystyrene-grafted microtubes.[594]

IBX is especially useful for the oxidation of glycols. In contrast to the Dess−Martin periodinane, which generally cleaves the glycol C−C bond, IBX oxidizes them to α-ketols[595,596] or α-diketones.[597,598] The mechanism of the alcohol and 1,2-diol oxidation by IBX and DMP has been examined by ^{1}H NMR spectroscopy.[598]

The practical value of IBX as a reagent was recently extended to a variety of other synthetically useful oxidative transformations.[599−607] In a series of papers, Nicolaou and co-workers demonstrated the utility of IBX for the one-step synthesis of α,β-unsaturated carbonyl systems from saturated alcohols and carbonyl compounds,[599,600] for the selective oxidation of the benzylic carbon,[601] for the oxidative cyclization of anilides and related compounds,[602,603] and for the synthesis of amino sugars and libraries thereof.[604] Specifically, alcohols, ketones, and aldehydes are oxidized to the corresponding α,β-unsaturated species in one pot using IBX under mild conditions.[599] For example, cycloalkanols **692** react with 2 equiv of IBX in a 2:1 mixture of either fluorobenzene or toluene and DMSO at gentle heating to afford the corresponding α,β-unsaturated ketones **693** in good yields (eq 292).



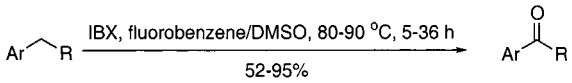
692 n = 1, 2, 6



(292)

693

IBX is an efficient and a selective reagent for the oxidation of benzylic and other similarly activated positions (eq 293).[601] This reaction is quite general and is not affected by the presence of water, *ortho*-substituents, or halogen substituents. Overoxidation to the corresponding carboxylic acids is not observed even in the presence of electron-rich substituents.

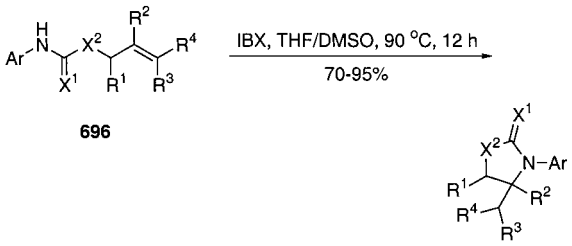


(293)

694 695

Ar = Ph, 4-*t*-BuC_6H_4, 2-MeC_6H_4, 3-IC_6H_4, 4-BrC_6H_4, 3,4-(MeO)$_2C_6H_3$, 2-PhC_6H_4, 4-(4-pyridyl)C_6H_4, etc.
R = H, C_3H_7, etc.

A variety of new heterocycles **697** can be synthesized by the treatment of unsaturated aryl amides, carbamates, thiocarbamates, and ureas with IBX (eq 294).[602] The mechanism of this reaction has been investigated in detail.[603a] 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 to a THF−IBX complex followed by deprotonation, radical cyclization, and concluding termination by hydrogen abstraction from THF.



696 (294) 697

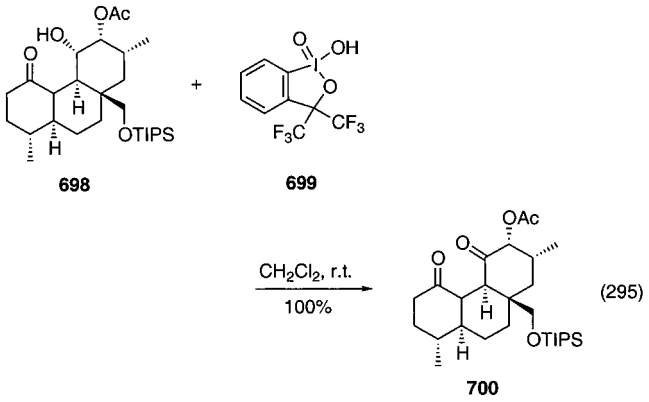
X^1 = O, S; X^2 = CH_2, O, N
Ar = Ph, 3-EtC_6H_4, 3-BrC_6H_4, 3-FC_6H_4, 4-EtC_6H_4, etc.
R^1 - R^4 = H, alkyl, cycloalkyl, etc.

A similar IBX-mediated cyclization was applied in the synthetic protocol for the stereoselective preparation of amino sugars.[603b]

IBX can be used as an efficient and selective reagent for the oxidative cleavage of oximes and tosylhydrazones to yield the corresponding carbonyl compounds under mild conditions in high yields.[604] IBX can oxidize thiols selectively to the corresponding disulfides.[605] As it was shown recently in the hydrolysis of phosphonofluoridates and nontoxic stimulants, IBX can be used as a catalyst with oxone being a stoichiometric oxidant.[606] Phenols can be regioselectively oxidized by IBX to *o*-quinones in excellent yields under mild conditions.[607]

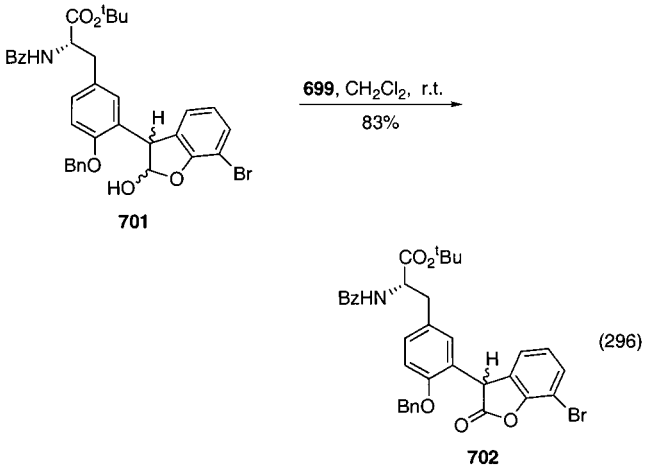
Several analogues of IBX have been reported in the literature.[608−613] Thottumkara and Vinod reported the preparation of the water-soluble analogue of IBX, *m*-iodoxyphthalic acid (mIBX), which is useful for the oxidation of alcohols to the corresponding carbonyl compounds in aqueous solutions.[608] Grieco and coworkers applied bis(trifluoromethyl)benziodoxole oxide **699** in the total syntheses of des-D-chaparrinone and bruceoside C.[609] Specifically, the oxidation of the

alcohol **698** with reagent **699** under mild conditions quantitatively afforded ketone **700** (eq 295), an important intermediate product in the synthesis of des-D-chaparrinone.[609a]



(295)

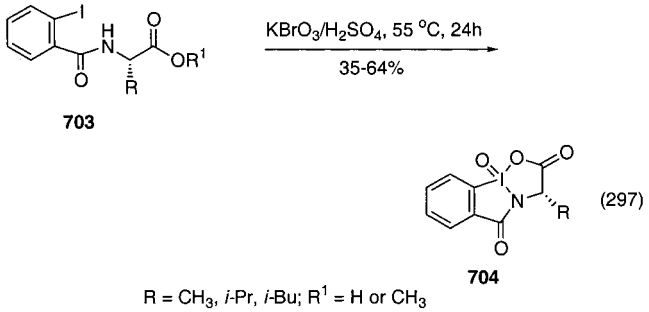
Moody and Lack used reagent **699** under similar conditions in the synthesis of benzofuranone derivative **702** (eq 296), a potential intermediate for the synthesis of the marine natural product diazonamide A.[610]



(296)

Parlow and co-workers performed the oxidation of various primary and secondary alcohols with reagent **699** and developed a simple and efficient methodology for sequestering byproducts and excess starting reagent from the solution phase using a novel thiosulfate resin.[611]

The new cyclic derivatives of pentavalent iodine, benziodazole oxides **704**, were prepared by the oxidation of the readily available 2-iodobenzamides **703** with potassium bromate (eq 297).[612]

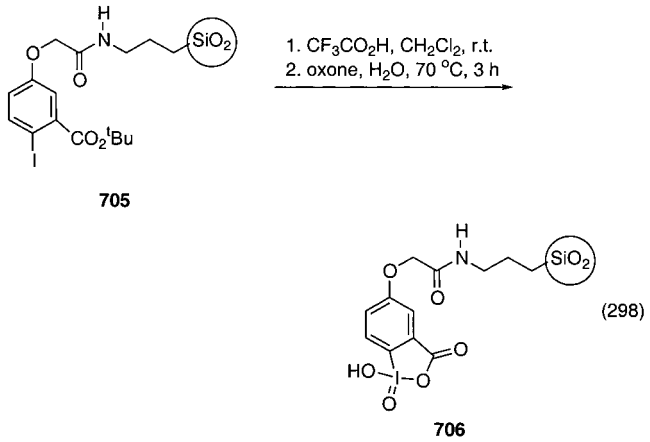


(297)

R = CH_3, *i*-Pr, *i*-Bu; R^1 = H or CH_3

Benziodazole oxides **704** can find practical application as selective, chiral oxidizing reagents in organic synthesis. Preliminary results indicate that reagents **704** can selectively oxidize primary alcohols to aldehydes in chloroform at 50 °C. Under similar conditions, reagents **704** oxidize organic sulfides to sulfoxides in almost quantitative yield. The oxidation of nonsymmetric sulfides affords chiral sulfoxides with moderate enantioselectivity (11−16% ee).[612]

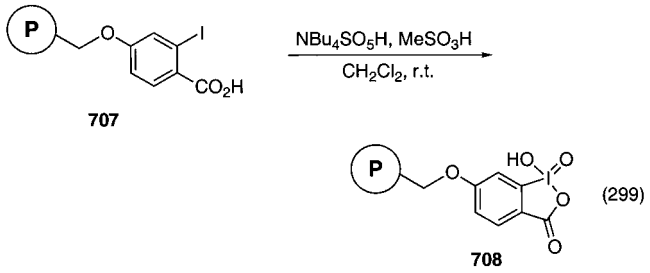
Very recently, two different groups reported the synthesis and oxidative reactions of the polymer-supported analogues of IBX.[613,614] Giannis and Mülbaier prepared the aminopropylsilica gel-based reagent **706** by the oxone oxidation of the polymeric precursor **705** (eq 298).[613]



(298)

Various primary and secondary alcohols can be oxidized by reagent **706** to the respective carbonyl compounds in excellent yields at room temperature in THF under heterogeneous conditions. The products of oxidation can be easily purified by filtration, and the reagent can be regenerated by oxidation with oxone without any loss of activity.[613]

Rademann and co-workers prepared the polystyrene-based polymeric analogue of IBX **708** by the oxidation of resin **707** by an equimolar mixture of tetrabutylammonium oxone and methanesulfonic acid (eq 299).[614] Polymer **708** was characterized by IR spectroscopy, elemental analysis, and MAS NMR spectroscopy.

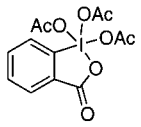


(299)

Reagent **708** oxidizes various primary, secondary, benzylic, allylic, terpene alcohols, and the carbamate-protected amino alcohols to afford the respective aldehydes or ketones in excellent yields and purities. Resin **708** can be recycled by repeated oxidation after extensive washings.[614]

C. Dess–Martin Periodinane

In recent years, Dess−Martin periodinane [DMP; 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3-(1*H*)-one, **709**] has emerged as the reagent of choice for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. The mild reaction conditions (room temperature and neutral pH), high chemoselectivity, and convenience of use have made this reagent especially suitable for the oxidation of substrates containing sensitive functional groups. Moreover, DMP is currently commercially available from Sigma-Aldrich[615] and other chemical companies. The synthetic applications of DMP were recently highlighted in two overviews.[616,617]

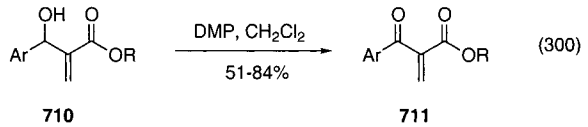


709, DMP

Due to the unique oxidizing properties and convenience of use, DMP is widely used in the synthesis of biologically important natural products. Recently, DMP was used in the key oxidation steps in the total syntheses of cyclotheonamide B,[618] (±)-deoxypreussomerin A,[619] racemic brevioxime,[620] erythromycin B,[621] (+)-discodermolide,[622] (+)-cephalostatin 7,[623] (+)-cephalostatin 12,[623] (+)-ritterazine K,[623] 3-*O*-galloyl-(2*R*,3*R*)-epicatechin-4β,8-[3-*O*-galloyl-(2*R*,3*R*)-epicatechin],[624] fredericamycin A,[625] indolizidine alkaloids (−)-205A, (−)-207A, and (−)-235B,[626] 1,19-aza-1,19-desoxy-avermectin B_{1a},[627] angucytcline antibiotics,[628] tricyclic β-lactam antibiotics,[629] and the platelet aggregation-inhibiting γ-lactam PI-091.[630] It was emphasized in many cases that DMP was the only reagent applicable in these oxidations, while other common oxidation methods, including Swern oxidation, Jones oxidation, and other chromium-based procedures, failed.[628,629]

In the numerous synthetic studies it has been demonstrated that DMP can be used for the selective oxidation of alcohols containing sensitive functional groups, such as unsaturated alcohols,[198,631−638] carbohydrates, polyhydroxy derivatives and polyethers,[639−645] silyl ethers,[646,647] amines and amides,[648−655] various nucleoside derivatives,[656−660] selenides,[661,662] tellurides,[663] phosphine oxides,[664,665] homoallylic and homopropargylic alcohols,[666] and fluoro alcohols.[667−671] Several representative examples of these oxidations are shown in eqs 300−303 and Scheme 24. Specifically, the functionalized allylic alcohols **710,** the Baylis−Hillman adducts of aryl aldehydes and alkyl acrylates, are efficiently oxidized with DMP to the corresponding α-methylene-β-keto esters **711** (eq 300).[636] The attempted Swern oxidation of the same adducts (**710**) resulted in S_N2'-type substitution of the allylic hydroxyl group by chloride.

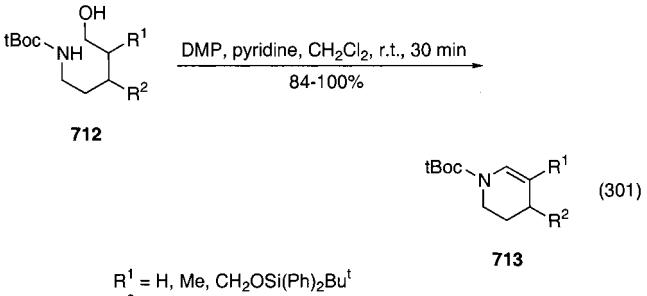
Cyclic enecarbamates **713** were prepared in excellent yields by the oxidation of ω-hydroxycarbamates **712** with DMP followed by cyclocondensation−



710 **711**

Ar = Ph, 2-ClC_6H_4, 4-MeC_6H_4, 3,4-$F_2C_6H_3$, 4-FC_6H_4, 4-$(CF_3)C_6H_4$
R = Me, Et

dehydration of the intermediate aminoaldehydes (eq 301).[655]

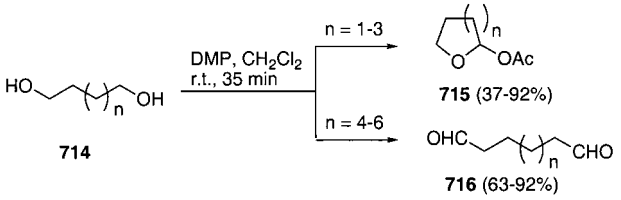


712 **713**

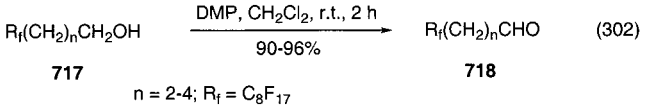
R^1 = H, Me, $CH_2OSi(Ph)_2Bu^t$
R^2 = H, OCH_2OCH_3, $OCH_2OCH_2CH_2SiMe_3$

Depending on the length of the carbon tether, α,ω-diols **714** either afford cyclic acetoxy acetals **715** or dialdehydes **716** upon treatment with DMP (Scheme 24).[642] In contrast, the treatment of 1,2-diols with DMP leads to the oxidative cleavage of the glycol bond.[598,642,672]

Scheme 24



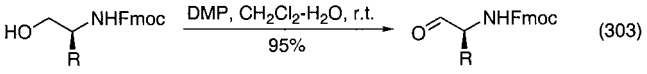
Polyfluorinated alcohols **717** can be selectively oxidized by DMP to the respective aldehydes **718** (eq 302) without the formation of dehydrofluorinated byproducts.[670,671]



717 **718**

n = 2-4; $R_f = C_8F_{17}$

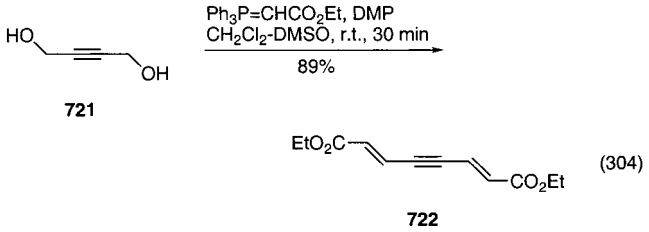
DMP is especially useful for the oxidation of the optically active, epimerization-sensitive substrates without loss of enantiomeric excess.[648,668,669,673] In a typical example, DMP was found to be a superior oxidant for the efficient, epimerization-free synthesis of optically active *N*-protected α-amino aldehydes **720** from the corresponding *N*-protected β-amino alcohols **719** (eq 303).[648] In contrast, the Swern oxidation of amino alcohols **719** afforded products **720** of only 50−68% ee.



719, 99% ee **720**, 99% ee

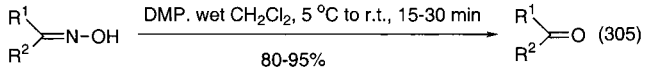
R = Me, Ph
Fmoc = fluorenylmethoxycarbonyl

Primary alcohols can be oxidized with DMP in the presence of stabilized Wittig ylides to afford the respective α,β-unsaturated esters in one pot.[662,674,675] This is a useful procedure 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 **721** with DMP and trapped by Wittig ylide in situ to provide the adduct **722** as a 4:1 mixture of *trans*−*trans* and *trans*−*cis* isomers (eq 304).[674]



721 **722** (304)

The practical value of DMP as a reagent was recently extended to a variety of other synthetically useful oxidative transformation.[676−686] DMP can be used as an efficient and selective reagent for the oxidative cleavage of oximes[676−679] and tosylhydrazones[679] to yield the corresponding carbonyl compounds under mild conditions in high yields. In a specific example, DMP oxidatively deoximates aldoximes as well as ketoximes **723** in very high yields, smoothly in short time, and under mild conditions (eq 305).[677] Deoximation occurs selectively in the presence of primary, secondary, and benzylic alcohols, *O*-methyl oximes, and acid-sensitive groups.



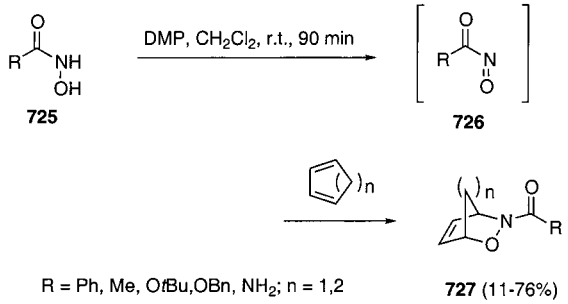
723 **724** (305)

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

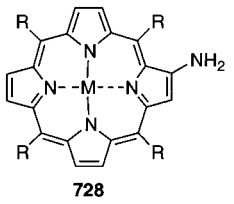
The oxidation of *N*-acyl hydroxylamines **725** with DMP generates the highly reactive acyl nitroso compounds **726**, which can be trapped by conjugated dienes to produce the corresponding cycloadducts **727** (Scheme 25).[680]

2-Hydroxyporphyrins and 2-aminoporphyrins **728**, as well as 2,3-aminoporphyrins, are oxidized by DMP to porphyrin-α-diones **729** (eq 306).[681−683] This reaction has been applied to the preparation of meso-functionalized porphyrin-α-diones, which are the basic building blocks for bis-porphyrin arrays.[682]

Scheme 25



725 **726** **727** (11-76%)



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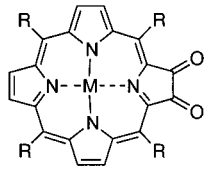
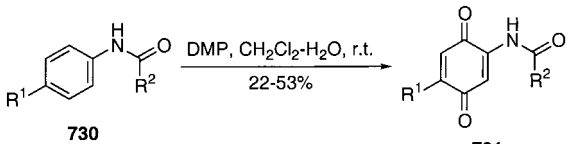


(306)

729

R = 3,5-(t-Bu)$_2C_6H_3$; M = 2H, Cu, Zn

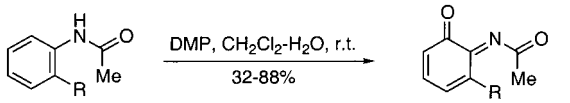
In a series of recent papers, Nicolaou and co-workers demonstrated the utility of DMP for the selective oxidation of 4-substituted anilides **730** to *p*-quinones **731** (eq 307) and 2-substituted anilides **732** to *o*-azaquinones **733** (eq 308).[684,685] The first process (eq 307) was applied to the short and efficient total synthesis of epoxyquinomycin B,[684] while the second type of oxidation (eq 308) allowed rapid access to complex analogues of pseudopterosin and elisabethin natural products.[685]



(307)

730 **731**

R^1 = H, Et, t-Bu, Ph, OMe, F, Cl, Br, I
R^2 = Me,Ph, t-Bu, i-Pr



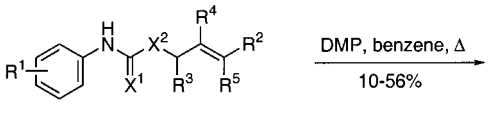
(308)

732 R = Et, t-Bu, Ph, OMe, Cl, Br, I **733**

Anilides with pendant double bonds **734** undergo stereoselective oxidative cyclization in the presence of DMP to give complex and diverse natural product-like polycycles **735** (eq 309).[686,687] A specific example of the oxidation of carbamates **736** leading to the benzomorpholine derivatives **737** is shown in eq 310.

This oxidative cyclization (eq 309) is proposed to occur by the initial *ortho*-directed oxidation of the anilide **734** to give an *ortho*-hydroxylated benzene ring, which is further oxidized to the quinone imine; the intramolecular Diels−Alder cyclization of the quinone imine with the pendant alkene gives the final product **735**.[686]

The unique oxidizing properties of DMP can be best illustrated by its wide application in the total synthesis of the CP-molecules recently published by Nicolaou and co-workers.[688−690]



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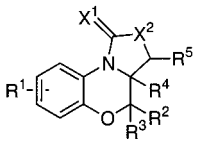
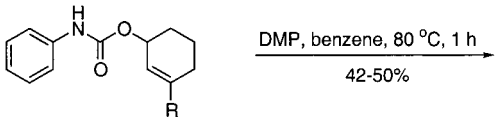


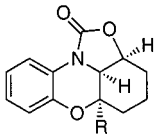
(309)

735

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



736 R = H, Me



(310)

737

IV. Conclusions

The preceding survey of the recent developments in the chemistry of polyvalent iodine compounds reflects an active current interest in this highly versatile class of valuable reagents. Just in the last 5 years a wide variety of new reagents have been introduced, and polyvalent iodine chemistry is employed increasingly in organic synthesis. This surging interest in iodine compounds is mainly due to the very useful oxidizing properties of polyvalent organic iodine reagents, combined with their benign environmental character and commercial availability. There has been a major surge of activity in several areas of organic polyvalent iodine chemistry. These areas include the synthetic applications of the Dess−Martin periodinane and similar oxidizing reagents based on iodine(V), catalytic oxygenations with iodosylbenzene and catalytic imidations with iodonium imides, azidations with azidoiodanes, the chemistry of benziodoxoles and benziodazoles, and synthetic and mechanistic studies of alkynyl and alkenyl iodonium salts. It can be anticipated that these areas of research will continue to attract significant research activity in the future. The use of the polymer-supported polyvalent iodine reagents and the transition-metal-catalyzed coupling reactions of iodonium salts may add a new dimension to the field of polyvalent iodine chemistry.

We hope and anticipate that this review will provide added stimulus for the further development of the chemistry of polyvalent iodine compounds.

V. Acknowledgment

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