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# Organic Polyvalent Iodine Compounds

Peter J. Stang*

*Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112*

Viktor V. Zhdankin*

*Department of Chemistry, University of Minnesota-Duluth, Duluth, Minnesota 55812*

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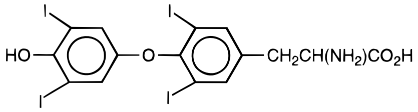
## *I. Introduction*

Iodine was first isolated from the ash of seaweed by the industrial chemist B. Courtois in 1811 and named by J. L. Gay Lussac in 1813. Its name derives from the Greek term “violet-colored” reflecting the characteristic lustrous, deep purple color of resublimed crystalline iodine.[1] By 1819 pure KI was used as a remedy for goiter, an enlargement of the thyroid gland. The thyroid gland is responsible for the production of thyroxine (**1**) a metabolism-regulating hormone. Hence, iodine is an essential trace element for humans and plays an important role in many biological organisms. Tincture of iodine is used as an antiseptic. Early sources of iodine came from the saltpeter deposits of Chile, whereas more modern sources include natural brines.[1]



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Organoiodine compounds have been used since the mid 1800s, notably in Hofmann’s alkylation of amines, the Williamson ether synthesis, and the Wurtz coupling reactions.[1] Iodine occurs most often in monovalent compounds, with an oxidation state of −1, and forms relatively weak bonds with first row elements, including carbon (the BDE of a typical C−I bond being about 55 kcal/mol). Because iodine is the largest, most polarizable, and least electronegative of the common halogens it is also able to form stable polycoordinate, multivalent compounds.

The first polyvalent organic iodine compound $PhICl_2$ was prepared by the German chemist Willgerodt[2] 110 years ago in 1886. This was rapidly followed by the preparation[3] of $PhI(OAc)_2$, $Ar_2I^+HSO_4^-$, the first iodonium salt,[4] and many others so that when Willgerodt published[5] his comprehensive treatise in 1914 on polyvalent organoiodine species nearly 500

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Peter J. Stang was born in 1941 in Nürnberg, Germany, raised in Hungary until 1956, and educated in the United States. He earned a B.S. in chemistry, magna cum laude, from DePaul University in Chicago in 1963 and a Ph.D. from U.C.—Berkeley in 1966. After NIH postdoctoral work at Princeton, he joined the faculty at Utah in 1969 where, since 1992, he holds the rank of Distinguished Professor of Chemistry, and served as Department Chair from 1989 to 1995. His research interests over the years involved reactive intermediates like vinyl cations and unsaturated carbenes, organometallic chemistry, strained ring systems, and, most recently, polyvalent iodine and alkynyl ester chemistry. His current efforts focus on using coordination and chelation to construct supramolecular species via self-assembly, especially molecular squares and related metallomacrocycles. He is the author or coauthor of over 290 scientific publications, including two dozen reviews and three monographs. From 1982 until the present he has been as Associate Editor of the *Journal of the American Chemical Society* and also serves on numerous Editorial Advisory Boards. Professor Stang has been the recipient of the A. von Humboldt Senior Scientist Award (1977); JSPS Fellow, Fukuoka Japan (1985); Lady Davis Fellow, Haifa, Israel (1986); Fulbright Hays Senior Scholar, Zagreb, Croatia (1988). In 1992 he was awarded honorary doctorates from the Russian Academy of Sciences and Lomonosov Moscow State University. Besides chemistry, he enjoys travel, classical music, gourmet food, and wines.

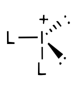
Viktor V. Zhdankin was born in 1956 in Sverdlovsk, Russia. His M.S. (1978), Ph.D. (1981), and Dr.Chem.Sci. (1986) degrees were earned at Moscow State University in the research laboratories of Professor N. S. Zefirov. In 1987 he was appointed as Senior Research Fellow—Head of Research Group at the Department 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 accepted a permanent faculty position at the University of Minnesota, Duluth. He has published more than 130 research papers as well as five 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.

such compounds were known. The most investigated species were diaryliodonium salts, which are used today in industry in lithography and as polymerization initiators. In the intervening century since Willgerodt's first report of $PhICl_2$ interest in polyvalent organic iodine compounds has ebbed and flowed. Since the early 1980s interest in these compounds has experienced a renaissance. This resurgence of interest in multivalent organic iodine compounds is due to several factors; the realization that the chemical properties and reactivity of iodine(III) species are similar to those of Hg(II), Tl(III), and Pb(IV) but without the toxic and environmental problems of these heavy metal congeners; the recognition of the similarities (reductive elimination, ligand exchange, etc.) between organic transition metal complexes and polyvalent main group compounds such as organoiodine species; the timely publication of a number of key reviews and surveys (vide infra) in the early 1980s, and finally the commercial availability of key precursors such as $PhI(OAc)_2$.

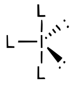
It is the purpose of this review to acquaint the reader with the unique properties and many uses of polyvalent organoiodine compounds in contemporary organic chemistry. Emphasis is placed on the post 1970s literature as many hundreds of references have appeared in just the last dozen years. Moreover, extensive coverage is given to the recent Russian literature as well as to the biological properties of polyvalent iodine compounds. The review is organized into six major parts: ***II***, general aspects; ***III***, derivatives of I(III) with one carbon ligand; ***IV***, derivatives of I(III) with two-carbon ligands; ***V***, iodine (III) species with three-carbon ligands; ***VI***, derivatives of iodine (V); ***VII***, biological properties of I(III) species. A number of previous reviews, some comprehensive, most dealing with specific aspects of selected polyvalent organoiodine species, have appeared.[6−25] Most notable is the comprehensive monograph by Varvoglis[19] titled, and devoted to the organic chemistry of polycoordinated iodine. Our own literature coverage is through the middle of 1995.

## II. General Aspects

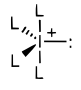
A broad variety of structural classes are known for iodine in oxidation states other than the common −1. These polyvalent iodine species differ in the number of valence electrons (N) surrounding the central atom, the number of ligands (L) and their chemical nature. In terms of the Martin−Arduengo N-X-L designation,[26] four structural types of polyvalent iodine species (**2**−**5**) are the most important for organic chemistry. The first two species, 8-I-2 (**2**) and 10-I-3 (**3**), also called iodanes, are conventionally considered as derivatives of trivalent iodine, and the last two, 10-I-4 (**4**) and 12-I-5 (**5**) periodanes, represent the most common structural types of pentavalent iodine.



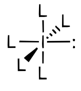
8-I-2
**2**



10-I-3
**3**



10-I-4
**4**



12-I-5
**5**

The most general, traditional classification of the polyvalent organic iodine compounds is based on the number of carbon ligands attached to the iodine atom in structures **2**−**5**.[8,11,19] According to this classification, three general classes are known for the organic compounds of trivalent iodine: (1) structural types **2** or **3** with one carbon ligand, (2) structural types **2** or **3** with two carbon ligands (iodonium salts), and (3) structural type **3** with three carbon ligands. Compounds of iodine(III) with one carbon ligand are represented by a great variety of organic iodosyl compounds (RIO) and their derivatives ($RIX_2$, where X is any non-carbon ligand). The second class includes various iodonium salts ($R_2I^+X^-$). The overwhelming majority of known, stable organic compounds of polyvalent iodine belong to these two classes. The third class, derivatives of iodine(III) with three carbon ligands ($R_3I$), in general are less investigated and less important for synthetic organic chemistry because of their low thermal stability. Organic derivatives of pentavalent iodine can also be classified on the basis of the number of carbon ligands. Only compounds of iodine(V) with one and two carbon ligands are known; the first class is represented by organic iodyl compounds ($RIO_2$) and various derivatives ($RIX_4$ or $RIX_2O$), and the second class includes iodyl salts ($R_2IO^+X^-$).

The structural aspects of polyvalent iodine compounds were thoroughly discussed previously in Koser's reviews[11] and the book by Varvoglis.[19] The most important structural features of the organic derivatives of iodine(III) available from numerous X-ray data may be summarized as follows:

(1) The 10-I-3 species (**3**) have an approximately T-shaped structure with a collinear arrangement of the most electronegative ligands. Including the nonbonding electron pairs, the geometry about iodine is a distorted trigonal bipyramid with the most electronegative groups occupying the axial positions, and the least electronegative group and both electron pairs residing in an equatorial position.

(2) The I−C bond lengths in both iodoso derivatives (**3**) and iodonium salts (**2**) are approximately equal to the sum of the covalent radii of iodine and carbon, ranging generally from 2.00 to 2.10 Å.

(3) For 10-I-3 species (**3**) with two heteroligands of the same electronegativity, both I−L bonds are longer than the sum of the appropriate covalent radii, but shorter, than purely ionic bonds. For example, the I−Cl bond lengths in $PhICl_2$ are 2.45 Å,[27] and the I−O bond lengths in $PhI(OAc)_2$ are 2.15−2.16 Å,[28] while the sum of the covalent radii of I and O is 1.99 Å.

(4) The 8-I-2 species (iodonium salts) (**2**) generally have a typical distance between iodine and the nearest anion of 2.6-2.8 Å and are considered as ionic compounds with pseudotetrahedral geometry about the central iodine atom. However, with consideration of the anionic part of the molecule, the overall experimentally determined geometry is T-shaped similar to the 10-I-3 species. For example, available X-ray data on alkynyliodonium triflate salts clearly indicate a T-shaped geometry.[20,25]

The structural features of the organic iodine(III) compounds are generally explained by the hypervalent bonding model, thoroughly discussed by Musher in 1969[29] and more recently employed by Martin[30] in his work on hypervalent halogen and sulfur compounds. In the hypervalent model, only nonhybridized 5p orbitals of iodine are involved in bonding. The least electronegative ligand is bound by a normal covalent bond to the singly occupied equatorial 5p orbital, while the other two ligands are attached, one to each lobe, of the axial doubly occupied 5p orbital of the iodine atom. As a result, a linear three-center, four-electron (3c-4e) bond is formed. Such bonds, termed “hypervalent”, are weaker and longer than covalent bonds.

Recently Reed and Schleyer provided a general theoretical description of chemical bonding in hypervalent molecules in terms of the dominance of ionic bonding and negative hyperconjugation over d-orbital participation.[31]

In contrast to iodine(III), only a few single-crystal X-ray analyses have been reported for the iodine(V) compounds.[32−40] Depending on the ligands and with the consideration of secondary bonding, the overall observed geometry for the structural types **4** and **5** can be square bipyramidal, pseudo-trigonal bipyramidal, and pseudooctahedral.

The bonding in iodine(V) compounds, $IL_5$, with a square-bipyramidal structure may be described in terms of a normal covalent bond between iodine and the ligand in an apical position, and two orthogonal, hypervalent 3c-4e bonds, accommodating four ligands. The carbon ligand and unshared electron pair in this case should occupy the apical positions with the most electronegative ligands residing at equatorial positions.

## III. Derivatives of Iodine(III) with One Carbon Ligand

In the traditional, conventional classification scheme, compounds of iodine(III) with one carbon ligand, $RIX_2$, are regarded as derivatives (salts or esters) of the parent iodosyl compounds, RIO, or nonisolable acids $RI(OH)_2$.[6,16,19] This classification is justified by the facile conversion of RIO into various $RIX_2$ by the action of the respective acids HX. The reverse reaction leading to RIO can be generally carried out by the hydrolysis of $RIX_2$ in the presence of a strong base.

The general reactivity pattern of iodosyl derivatives is determined by the hypervalent, loose nature of the I−X bonds and by a distinct positive charge on the iodine atom. These structural features are responsible for the enhanced electrophilic properties of $RIX_2$ and explain such typical pathways as ligand exchange and reductive ligand transfer in their reactions with organic compounds. Due to these properties, iodosyl derivatives have found broad application in organic synthesis as selective oxidants and electrophilic ligand transfer reagents. The ever-growing interest in the synthetic application of these compounds is also explained by their ready availability and absence of toxic properties and associated environmental concerns.

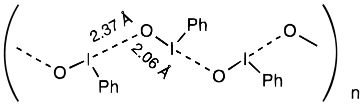
A broad variety of stable iodosyl derivatives have been reported in the literature. The overwhelming majority of these compounds have a benzene ring as a carbon ligand linked to the iodine atom. Derivatives of polyvalent iodine with an alkyl substituent at iodine are highly unstable and generally can exist only as short-lived reactive intermediates in the oxidations of alkyl iodides. However, introduction of an electron-withdrawing substituent in the alkyl moiety may lead to significant stabilization of the molecule. Typical examples of such stabilized compounds with I$-$C$_{sp^3}$-bonding are perfluoroalkyliodosyl derivatives.

The two heteroatom ligands X attached to iodine in $RIX_2$ are commonly represented by fluorine, chlorine, O and N substituents. In general, only derivatives bearing the most electronegative substituents X are sufficiently stable.

## A. Iodosylarenes

Iodosylbenzene, PhIO, is the most important and best investigated member of the family of iodosyl compounds. It is best prepared by hydrolysis of PhI(OAc)$_2$ with aqueous NaOH.[41] Iodosylbenzene is a yellowish amorphous powder, which cannot be recrystallized due to its polymeric nature. Heating or extended storage at room temperature results in disproportionation of iodosylbenzene to PhI and colorless, explosive iodylbenzene, $PhIO_2$. Drying of PhIO at elevated temperatures should be avoided because of the possibility of severe explosion.[42] However, handling of even large amounts of PhIO at room temperature is relatively safe.

Recent X-ray powder diffraction and EXAFS analyses of amorphous PhIO clearly indicated a linear polymeric, asymmetrically bridged structure in the solid state having the expected T-shaped geometry around the iodine centers (**6**).[43] The I$-$O bond lengths in this structure are distinctly different with a longer one of 2.37 Å and a shorter one of 2.06 Å. These data are consistent with the earlier structural information determined from IR-Raman[44] and Mössbauer spectroscopy[45] of PhIO.



**6**

Another important iodosyl derivative is 2-iodosylbenzoic acid. However, this compound is in fact bicyclic and is different from the other iodosylarenes by its structure and properties (see section III.E).

A comprehensive bibliography on the preparation and properties of a variety of other known iodosylarenes was published by Beringer and Gindler.[7] More recent examples include modified procedures for the preparation of a variety of *ortho-*, *meta-*, *para-*monosubstituted iodosylbenzenes from the respective iododiacetates,[46] and the preparation of *p*-bis(iodosyl)benzene by alkaline hydrolysis of the corresponding tetrachloride.[47]

Iodosylbenzene has found wide synthetic application as a starting material in the preparation of numerous iodine(III) compounds and as an effective oxidant.

### *1. Iodosylarenes as Precursors to Other Iodine(III) Compounds*

Iodosylbenzene can be easily transformed into various $PhIX_2$ derivatives **7** under mild, aprotic conditions by the action of the respective trimethylsilylated reagents (eq 1).[48,49]

$$\text{PhIO} + 2\text{Me}_3\text{SiX} \xrightarrow[-(\text{Me}_3\text{Si})_2\text{O}]{\text{CH}_2\text{Cl}_2} \underset{\mathbf{7}}{\text{PhIX}_2} \qquad (1)$$

X = Cl, OAc, $OCOCF_3$, OTs, OTf, $N_3$, CN, etc.

This method represents the most general approach to iodosyl derivatives. It is especially convenient for the generation of unstable or moisture sensitive derivatives in situ. For example, the combination of iodosylbenzene and trimethylsilyl azide, PhIO/TMSN$_3$, is a well-known, efficient reagent for the introduction of the azido function into organic molecules.[50-56] Azidoiodanes, PhI(N$_3$)X or PhI(N$_3$)$_2$, were proposed as reactive intermediates in the azidonation reactions; however, attempts to isolate these species always resulted in fast decomposition at $-25$ to 0 °C with the formation of iodobenzene and dinitrogen.[48,50-53] Similarly, iodosylbenzene and trimethylsilyl triflate react with the formation of the unstable and hygroscopic PhI(OTf)$_2$,[48] which can be used in situ as a highly electrophilic, efficient reagent for the generation of iodonium salts and other useful transformations.[57,58]

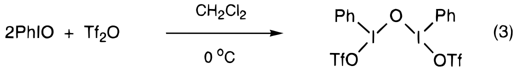
The analogous sequential reaction of PhIO with two different trimethylsilylated reagents, one of which is a trimethylsilanesulfonate, $TMSOSO_2R$, leads to mixed iodonium sulfonates **8** according to eq 2.[59]

$$\text{PhIO} + \text{Me}_3\text{SiOSO}_2\text{R} + \text{Me}_3\text{SiX} \xrightarrow[-30\text{ to }-5\ ^\circ\text{C}]{\text{CH}_2\text{Cl}_2} \underset{\mathbf{8}}{\text{PhI(OSO}_2\text{R)X}} \qquad (2)$$

X = OAc, NHAc, NCO, CN
R = *p*-Tol, $CF_3$, $C_4F_9$

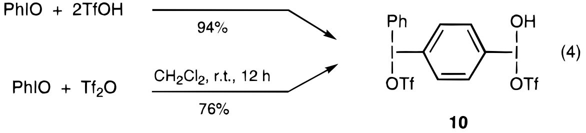
This reaction (eq 2) is especially useful for the preparation of cyano(phenyl)iodonium triflate (**8**, X $=$ CN, R $=$ $CF_3$), which is a highly efficient iodonium transfer reagent in the syntheses of various alkynyl and alkenyl(phenyl)iodonium salts.[60-68]

Acids or acid anhydrides also react with PhIO with the formation of $PhIX_2$ or similar derivatives. Addition of triflic anhydride to 2 equiv of PhIO at 0 °C gives a bright yellow precipitate of $\mu$-oxobis[(trifluoromethanesulfonyloxy)iodobenzene] **9** (Zefirov's reagent) (eq 3), a useful reagent for the preparation of iodonium salts.[69]



**9**

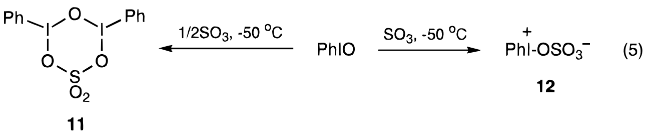
Similar reaction of PhIO with triflic acid or 1 equiv of triflic anhydride at room temperature yields bisiodonium triflate **10** as the principal product (eq 4).[70-72]



**10**

Sulfur trioxide forms two different adducts with PhIO depending on the ratio of reactants (eq 5).[73]

Both sulfates **11** and **12** are hygroscopic solids, highly reactive toward nucleophilic organic substrates.



Among other synthetically important transformations of PhIO are the reactions with HF or $SF_4$ leading to $PhIF_2$,[74] reaction with $HN_3$ generating $PhI(N_3)_2$ in situ,[75] and the formation of isolable, but hygroscopic $PhI(OMe)_2$ in methanol solution.[76]

Iodosylbenzene is also a useful precursor to a variety of iodonium salts via reactions with the corresponding nucleophilic organic substrates, such as carbonyl compounds, arenes, alkenes, alkynes, and their silicon or tin derivatives (see part IV of this review). In most cases, these reactions require activation of PhIO with $BF_3$−etherate, $HBF_4$, $H_2SO_4$, trifluoromethanesulfonic acid or its anhydride.

### *2. Oxidations with Iodosylarenes*

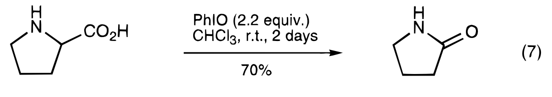
Iodosylbenzene is an effective oxidizing reagent; however, its insolubility due to its polymeric structure significantly restricts its practical usefulness. The overwhelming majority of the known reactions of PhIO require the presence of hydroxylic solvent (water or methanol) or a catalyst (Lewis acid or complexes of transition metals), which actually results in the generation of activated monomeric species, chemically different from the original reagent.

Only a few noncatalytic oxidations or dehydrogenations with PhIO in nonhydroxylic solvents have been reported in the literature. A typical example of such a noncatalytic reaction is a low yield oxidation of toluene or primary alcohols into aldehydes in refluxing dioxane.[77] Primary aliphatic amines can be dehydrogenated by PhIO to nitriles in dry dichloromethane at room temperature (eq 6).[78]

$$\text{R-CH}_2\text{NH}_2 + \text{PhIO} \xrightarrow[\text{48-57\%}]{\text{CH}_2\text{Cl}_2,\ \text{r.t., 3 days}} \text{R-C}\equiv\text{N} \qquad (6)$$

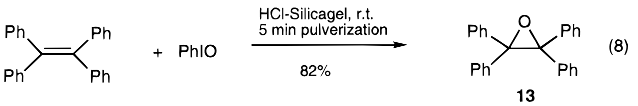
$\text{R} = \text{Ph},\ n\text{-C}_5\text{H}_{11}$

Cyclic amino acids are oxidatively decarboxylated with PhIO in chloroform or dichloromethane with the formation of lactams in moderate yield (eq 7).[79]



Similarly, α,*β*-unsaturated carboxylic acids can be oxidatively halo-decarboxylated with PhIO in acetonitrile in the presence of *N*-chloro-, *N*-bromo-, or *N*-iodosuccinimide.[80]

Recently, several oxidations with polymeric PhIO in the solid state were reported.[81,82] In this case, iodosobenzene is mechanochemically activated by pulverization with an acid-treated silica gel by a pestle in a mortar. 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. For example, the solid-state reaction of PhIO with tetraphenylethylene in an HCl-treated silica gel affords the respective epoxide **13** in 82% yield (eq 8).[81]



Under similar conditions, organic sulfides are oxidized to sulfonyl chlorides (eq 9) or sulfones.[82] Sulfides with benzylic substituents such as dibenzyl, alkyl benzyl, and benzyl phenyl sulfides are converted by this reaction (eq 9) into the corresponding sulfonyl chlorides in high yields of 89−98%. Other types of sulfides such as dialkyl and alkyl phenyl sulfides give sulfonyl chlorides only in moderate yield.

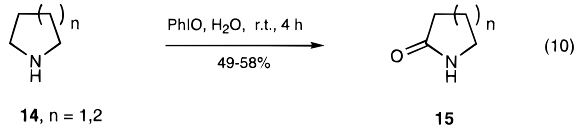
$$\text{R}-\text{S}-\text{R}' + \text{PhIO} \xrightarrow{\substack{\text{HCl-Silicagel, r.t.} \\ \text{5 min pulverization}}} \text{R-SO}_2\text{Cl} + \text{R}'\text{-SO}_2\text{Cl} \qquad (9)$$

$\text{R, R}' = \text{PhCH}_2,\ \text{PhCH}_2\text{CH}_2,\ \text{Ph},\ \text{CH}_3,\ \text{C}_4\text{H}_9,\ \text{C}_8\text{H}_{17}$, etc.

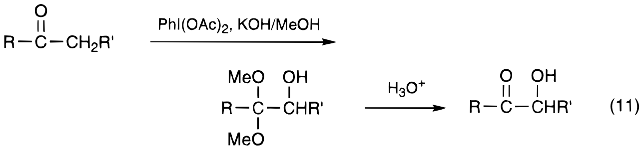
The authors[81,82] claim that the solid-state method utilizes polymeric PhIO without any depolymerization activation. However, the actual reactive intermediate in these reactions most likely is the in situ-generated $PhICl_2$.

Heterogeneous reactions of iodosylbenzene in dichloromethane can be effectively activated by ultrasonic irradiation. In recent work, the ultrasonic reaction of PhIO was used for a selective oxidation of triarylbismuthines or triarylstibines to the corresponding oxides.[83]

A variety of noncatalyzed oxidations with iodosylbenzene can be carried out in water or methanol as a solvent. Iodosylbenzene is slightly soluble in water due to the reversible formation of monomeric, hydrated species $PhI(OH)_2$, which can be involved in subsequent reaction with an organic substrate. PhIO in water is especially useful as a reagent for the oxidation of various amines.[78,79] Several different products can be obtained in these reactions, depending on the nature of the amine.[78,79] For example, treatment of cyclohexylamine or cycloheptylamine with equimolar amounts of PhIO in water results in the formation of cyclohexanone or cycloheptanone in 49−52% yield.[78] Oxidation of cyclic amines **14** under similar conditions lead to lactams **15** (eq 10).[78]



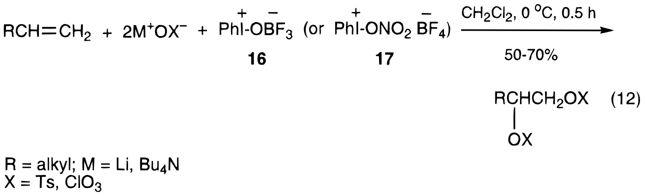
The solubility of PhIO in methanol is very high, >0.5 g/mL, which is due to depolymerization with the formation of $PhI(OMe)_2$.[76] This is why methanol is a solvent of choice for many synthetically useful oxidations with PhIO. In a typical example, iodosylbenzene in methanol oxidizes *o*- and *p*-hydroquinones to the corresponding benzoquinones in high yield.[84] Even more useful and convenient are oxidations with the commercially available (diacetoxyiodo)benzene in basic methanolic solution, where the same reactive ingredient, $PhI(OMe)_2$, is generated in situ. The reagent system $PhI(OAc)_2$/KOH/MeOH is especially efficient for hydroxylation of enolizable ketones via the initially formed α-hydroxydimethylacetal (eq 11).[15,85−88]



The synthetic potential of this reaction (eq 11) was thoroughly discussed in previous reviews.[15,19] Hydroxylation of some substituted acetophenones under these conditions is especially useful for the synthesis of various oxygen-containing heterocyclic compounds.[21−23]

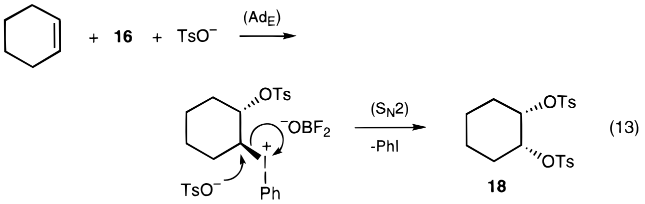
In most cases, the oxidative properties of PhIO are related to the electrophilic reactivity of the iodine(III) atom. Only a few examples of reactions due to the initial nucleophilic attack by the oxygen atom of PhIO at electron-deficient multiple bonds are known. For example, reaction of PhIO with tetracyanoethylene at room temperature affords tetracyanooxirane,[89] while dimethyl acetylenedicarboxylate under similar conditions undergoes oxidative cleavage with the formation of $PhI(O_2CCO_2Me)_2$.[90]

The relatively weak electrophilic reactivity of PhIO can be considerably increased in the presence of Lewis acids such as $BF_3{\cdot}Et_2O$, $NO_2BF_4$, $Et_3O^+{\cdot}BF_4^-$, $HBF_4{\cdot}Et_2O$, and salts of nonredox metals. This activation is usually explained by the formation of nonisolable, highly electrophilic complexes such as $PhI^+OBF_3^-$ (**16**), $PhI^+ONO_2{\cdot}BF_4^-$ (**17**), etc.[91] Reactions of these complexes with unsaturated organic substrates can afford various products depending on the reaction conditions and structure of the organic substrate. Alkenes react with reagents **16** or **17** in the presence of perchlorate or tosylate anions as external nucleophiles to give 1,2-diperchlorates or -ditosylates as major products (eq 12).[91]

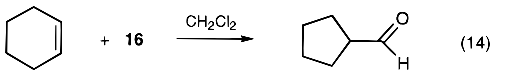

$$RCH{=}CH_2 + 2M^+OX^- + \underset{\mathbf{16}}{Ph\overset{+}{I}\text{-}O\overset{-}{B}F_3} \text{ (or } \underset{\mathbf{17}}{Ph\overset{+}{I}\text{-}ONO_2\,\overset{-}{B}F_4}) \xrightarrow[50\text{-}70\%]{CH_2Cl_2,\ 0\ ^\circ C,\ 0.5\ h} \underset{\displaystyle OX}{RCHCH_2OX} \quad (12)$$

R = alkyl; M = Li, $Bu_4N$
X = Ts, $ClO_3$

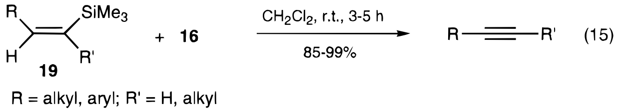
Cyclohexene in this reaction gives exclusively *cis*-ditosylate **18** as the result of an addition−substitution mechanism (eq 13).[91]



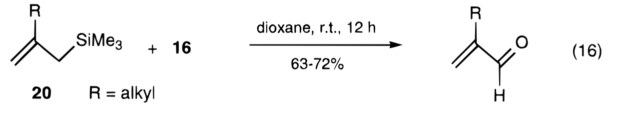
Under similar conditions, but in the absence of external nucleophiles, cyclohexene affords formylcyclopentane resulting from a carbocationic ring contraction (eq 14).[92]



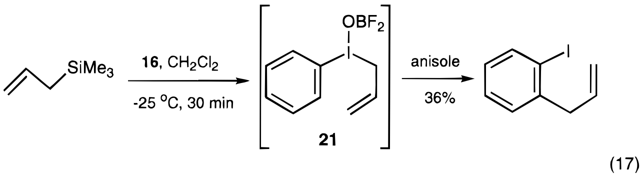
A variety of different products can be prepared by the reaction of complex **16** with unsaturated silylated substrates, such as silylalkenes, silylalkynes, and silyl enol ethers. (*E*)-Vinylsilanes react with **16** to give stable alkenyl(phenyl)iodonium tetrafluoroborates (see section IV.C), whereas (Z)-vinylsilanes **19** undergo dehydrosilylation and are cleanly converted into alkynes (eq 15).[93−95]



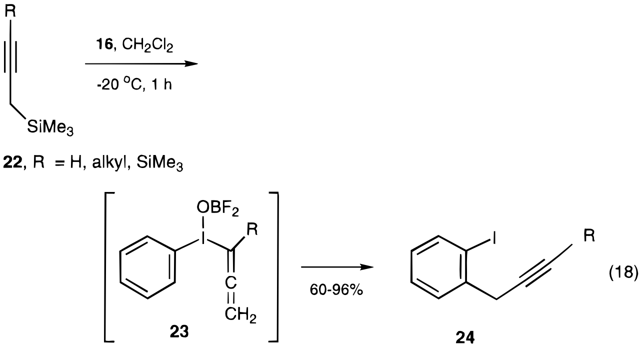
Allylsilanes **20** are oxidized with complex **16** to conjugated enals (eq 16).[96]



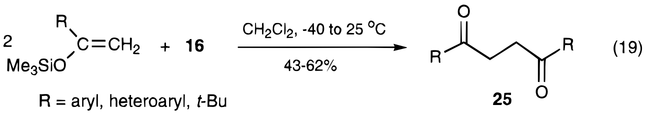
This reaction (eq 16) involves an intermediate generation of highly unstable allyl(phenyl)iodonium salts, which can be trapped with activated aromatics or alcohols to afford allylarenes or allyl ethers.[96−98] Under appropriate conditions, the intermediate allyl(phenyl)iodonium species **21** generated from **16** and allylsilane may undergo a reductive iodonio-Claisen rearrangement to form *o*-allyliodobenzene (eq 17).[98]



Reactions of 1-alkynylsilanes with iodosylbenzene in the presence of Lewis acids yield alkynyl(phenyl)iodonium salts (see section IV.B). Under similar conditions, propargylsilanes **22** react with complex **16** to afford *o*-propargyliodoarenes **24** as a result of a reductive iodonio-Claisen rearrangement of the intermediate, unstable allenyliodanes **23** (eq 18).[99,100]



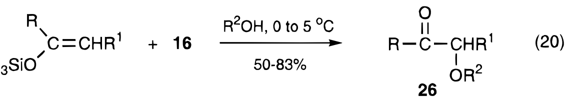
Reactions of reagent **16** with silyl enol ethers are widely used in organic synthesis for the formation of new C−C bonds,[18] preparation of α-substituted ketones, and synthesis of oxygen-containing heterocyclic compounds.[21−23] These reactions in nonnucleophilic solvents usually afford 1,4-butanediones **25** as major products (eq 19).[101]



(19)

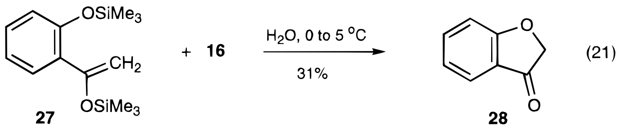
R = aryl, heteroaryl, *t*-Bu

In the presence of water or alcohols the same reagents give α-hydroxy- or α-alkoxyketones **26** (eq 20).[102] Similar intramolecular reaction of silyl enol ether **27** with **16** affords heterocycle **28** (eq 21).[103]



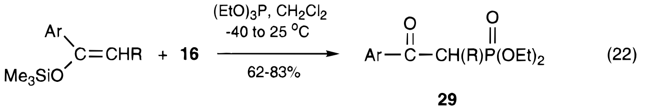
(20)

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



(21)

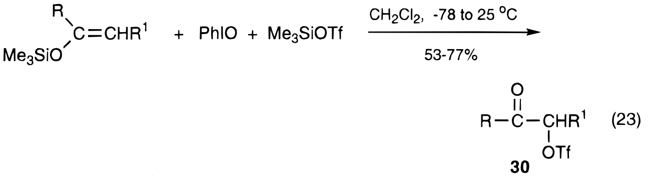
Reaction of **16** with silyl enol ethers in the presence of triethyl phosphite as an external nucleophile yields β-keto phosphonates **29** in good yield (eq 22).[104]



(22)

R = H, Me

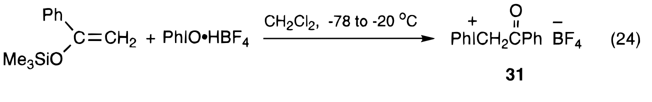
A variety of Lewis acids and strong Brønsted acids can be used instead of $BF_3 \cdot Et_2O$ to catalyze reactions of PhIO with unsaturated compounds. For example, the complex of PhIO with trimethylsilyl triflate reacts with silyl enol ethers to afford α-[(trifluoromethyl)-sulfonyl]oxy ketones **30** (eq 23).[105]



(23)

R = aryl, hetaryl; $R^1$ = H, alkyl;
or R + $R^1$ = cycloalkyl

β-Carbonylmethyl(phenyl)iodonium salts are plausible intermediates in all these reactions (eqs 19–23). Similar tetrafluoroborate salts **31** can be selectively generated at low temperature by the reaction of PhIO/$HBF_4$ with 1 equiv of silyl enol ether (eq 24).[106] β-Carbonylmethyl(phenyl)iodonium tetrafluoroborates **31** are stable in solution up to 0 °C and can be trapped with a variety of carbon nucleophiles, such as alkenes, allylsilanes, and silyl enol ethers to afford products with a new C–C bond (see section IV.E).[106,107]



(24)

The oxidation reactions of iodosylbenzene can be effectively catalyzed by metal salts and complexes. A significant interest in PhIO is due to its ability to serve as an oxygen atom donor in mechanistic studies of cytochrome P-450, a heme-containing monooxygenase enzyme, and its metalloporphyrin models.[108] 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.[108–114] It is generally agreed that iron(IV) oxo species participate as oxygen atom transfer agents in these reactions.[108,109,111] Similar catalytic effects on oxygenations with PhIO occur with complexes of some other transition metals, such as Mn(II), Co(II), Ni(II), Cu(I), Ru(III), etc.[115–120] In some cases, the intermediate high-valent oxo complexes responsible for oxygen transfer in these oxygenations can be isolated as relatively stable individual compounds. For example, the Ru(III)–diphenylglyoxime complex reacts with PhIO at room temperature in aqueous dioxane to afford an isolable, stable Ru(V) oxo complex in a 68% yield. This oxo complex was shown to be the actual intermediate in the Ru(III)-catalyzed epoxidation of cyclohexene with PhIO.[117] The alternative explanation for the catalytical activity of metal complexes in oxygenations of alkenes with PhIO involves the action of a metal ion as a Lewis acid thereby increasing the electrophilic reactivity of iodine(III) in a mechanistic scheme similar to the one shown in eq 13.[121] Such a mechanism provides the only reasonable explanation for the catalytic effect of salts of nonredox metals (such as aluminum and zinc salts or porphyrin complexes) on olefin epoxidation by iodosylbenzene.[122,123]

## B. Halides

Iodoaryl halides, $ArIX_2$, can generally be prepared either by the reaction of iodosylarenes, ArIO, with the respective acids HX, or by halogenation of aryl iodides. The overwhelming majority of known compounds of this structural type are chlorides and fluorides. Only two examples of a stable bromoiodane was reported in the literature.[124] A large variety of iodoaryl chlorides (>200 chloroiodanes[19]) and a number of fluorides are presently known, most of them already reported in older papers and reviews. In the last 5–10 years the research activity in this area was relatively low; however, both iodoaryl chlorides and fluorides are still widely used in organic synthesis as halogenating or oxidizing reagents. A study of the electronic structure and bonding in $PhICl_2$ and $PhIF_2$ by means of extended Hückel and CNDO/2 quantum chemical approaches was recently reported by Varvoglis and co-authors.[125] Likewise, an interesting structure determination via X-ray crystallography has been reported for a highly hindered $ArICl_2$ [Ar = 2,6-bis(3,5-dichloro-2,4,6-trimethylphenyl)benzene].[126]

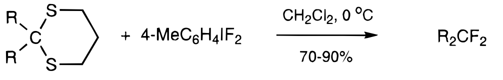
### 1. Fluorides

(Difluoroiodo)arenes, $ArIF_2$, are best prepared by reactions of iodosylarenes or their derivatives with hydrofluoric acid or sulfur tetrafluoride. The most common method involves the reaction of (dichloroiodo)arenes with 48% HF and yellow HgO.[127] However, methods based on the use of hydrofluoric acid have several disadvantages. First, (difluoroiodo)-arenes often are hygroscopic and highly hydrolizable, which make their separation from aqueous hydrofluoric acid and crystallization extremely difficult. Second, the high acidity of the reaction media complicates reactions of basic and acid sensitive substrates, such as heterocycles. Reaction of iodosylarenes with $SF_4$ usually gives better results.[74] In this method, $SF_4$ is bubbled at −20 °C through a suspension of the iodosyl compound in dichloromethane (eq 25). All the byproducts in this reaction are volatile, so evaporation of the solvent under anhydrous conditions affords (difluoroiodo)arenes of high purity.[74]

$$\mathrm{RIO} + \mathrm{SF_4} \xrightarrow[\text{82-100\%}]{\mathrm{CH_2Cl_2},\ -20\ \text{to}\ -10\ ^\circ\mathrm{C}} \mathrm{RIF_2} \qquad (25)$$

Fuchigami and Fujita recently reported a convenient procedure for the electrochemical preparation of (difluoroiodo)arenes.[128] In this method, the electrosynthesis of *para*-substituted $ArIF_2$ was accomplished by anodic oxidation of the respective iodoarenes with $Et_3N{\cdot}3HF$ in anhydrous acetonitrile. This procedure works especially well for the preparation of $p\text{-}NO_2C_6H_4IF_2$, which precipitates from the electrolytic solution in pure form during the electrolysis.

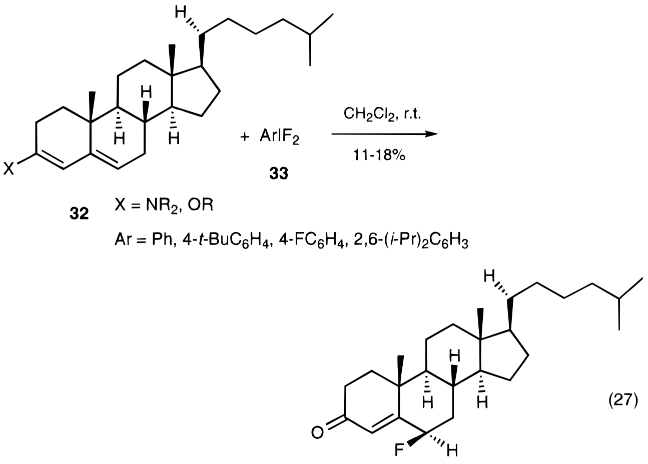
(Difluoroiodo)arenes have found some synthetic application as fluorinating regents.[129−135] 4-Methyl(difluoroiodo)benzene can convert some steroidal silyl enol ethers to the respective α-fluoro ketones in a moderate yield,[129] while $PhIF_2$ reacts with 1,1-diarylalkenes to afford rearranged, geminal difluorides.[130] A clean and selective preparation of *gem*-difluorides can be achieved by the reaction of 4-methyl(difluoroiodo)benzene with dithioketals (eq 26).[131]



(26)

R = aryl, alkyl

Steroidal dienes **32** react with (difluoroiodo)arenes **33** to afford fluorinated product **34** with a high degree of regioselectivity and stereoselectivity (eq 27).[132]



**32** X = $NR_2$, OR **33**

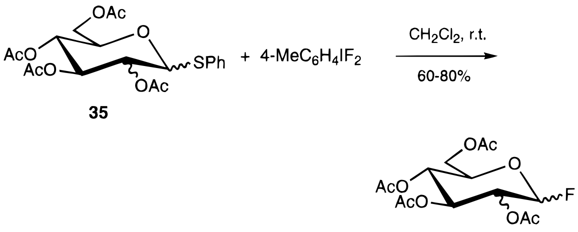
Ar = Ph, 4-*t*-$BuC_6H_4$, 4-$FC_6H_4$, 2,6-(*i*-Pr)$_2C_6H_3$

(27)

**34**

Fluorination of 1-(arylthio)glycosides **35** with 4-methyl(difluoroiodo)benzene provides a mild and general approach to various 1-fluoroglycosides **36** (eq 28).[133] Depending on the structure of glycoside **35**, the stereochemical outcome of this reaction may change from complete retention to inversion of configuration at C-1.

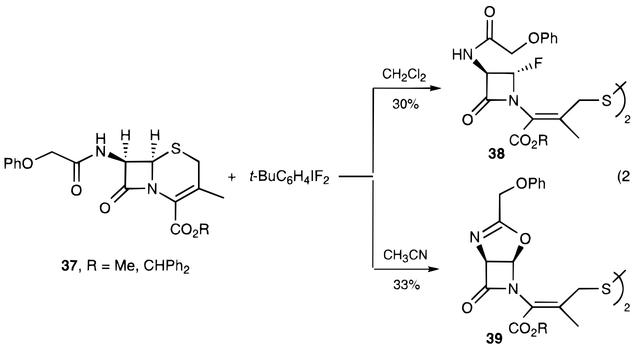
Reaction of 4-*tert*-butyl(difluoroiodo)benzene with esters of cephalosporin V (**37**) is solvent-dependent: the major product in dichloromethane is fluoroazetidine **38**, while the same reagents in acetonitrile afford oxazoline disulfide **39** (eq 29).[134]



**35**

(28)

**36**



**37**, R = Me, $CHPh_2$

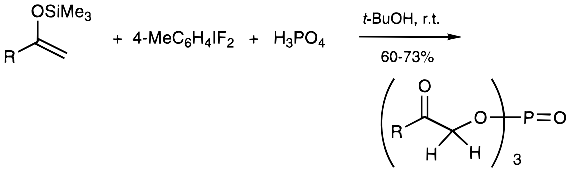
**38**

(29)

**39**

Comparison of the various (difluoroiodo)arenes in fluorination reactions (eqs 26−29) reveals that 4-alkyl(difluoroiodo)benzenes (methyl and *tert*-butyl derivatives) are the preferred reagents, due to their facile preparation and crystallization, relatively high stability, and solubility in organic solvents.[131−134]

In some reactions (difluoroiodo)arenes can be used as general oxidizing reagents. For example, Koser and co-workers applied a 4-methyl(difluoroiodo)benzene−phosphoric acid mixture as a reagent for direct conversion of silyl enol ethers to tris-ketol phosphates (eq 30).[136]

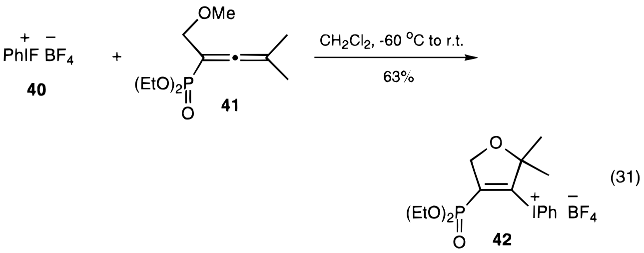


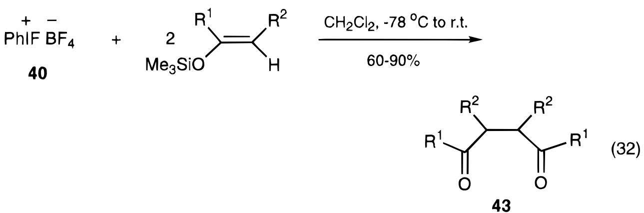
(30)

R = Me, *t*-Bu, Ph, 2-Pyridyl, 2-Furyl

Fluorination and oxidation reactions of $ArIF_2$ are usually rationalized by the initial electrophilic attack of the iodine atom on the nucleophilic organic substrate with subsequent transformation of the intermediate iodonium species. The electrophilic reactivity of (difluoroiodo)benzene can be further increased in the presence of a Lewis acid. $PhIF_2$ reacts with $BF_3$−etherate in dichloromethane at low temperature to form the highly electrophilic complex **40**.[137,138] Complex **40** is stable at 0 °C and can be used as a reagent for the preparation of iodonium salts by reactions with unsaturated organic substrates. For example, reaction of complex **40** with allene **41** affords vinyliodonium salt **42** in good yield (eq 31).[137]

Reaction of complex **40** with an excess of silyl enol ether cleanly affords 1,4-diketones **43** under very mild conditions (eq 32).[138]





$R^1$ = Ph, Me, cyclo-$C_3H_5$; $R^2$ = H
$R^1$ + $R^2$ = -$(CH_2)_4$-

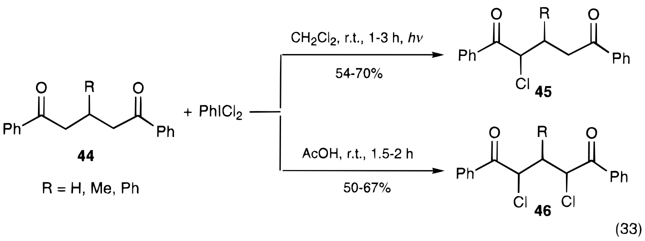
β-Carbonylmethyl(phenyl)iodonium salts are proposed as the intermediates in this reaction (eq 32).[138]

## 2. Chlorides

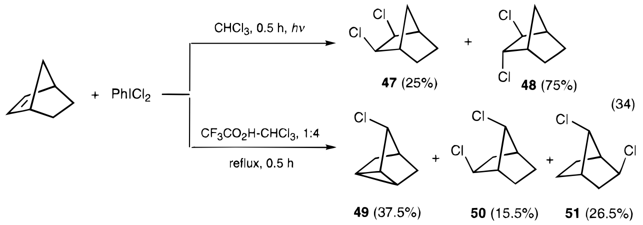
Historically, (dichloroiodo)benzene, $PhICl_2$, was the first reported organic compound of polyvalent iodine. It was prepared by Willgerodt in 1886 by the reaction of iodobenzene with $ICl_3$ or, preferably, with chlorine.[2] Reactions of aryliodides with chlorine in chloroform is still the most general approach to (dichloroiodo)arenes.[139] (Dichloroiodo)arenes are generally yellow solids, which are easy to handle and can be purified by recrystallization. Most of these compounds have relatively low thermal stability and can be stored only for short periods after preparation.

(Dichloroiodo)arenes have found broad synthetic application as reagents for chlorination and oxidation of various organic substrates. The most typical chlorinations of alkanes or alkenes with (dichloroiodo)benzene proceed via a radical mechanism and generally require photochemical conditions or the presence of radical initiators in solvents of low polarity, such as $CHCl_3$ or $CCl_4$. However, the alternative ionic pathways are also possible due to the electrophilic properties of the iodine atom in $PhICl_2$ or electrophilic addition of $Cl_2$ generated by the dissociation of the reagent. An alternative synchronous molecular addition mechanism in the reactions of $PhICl_2$ with alkenes has been discussed and recently was found to be theoretically feasible.[125] The general reactivity patterns of $ArICl_2$ were thoroughly discussed in earlier reviews.[13,16,19]

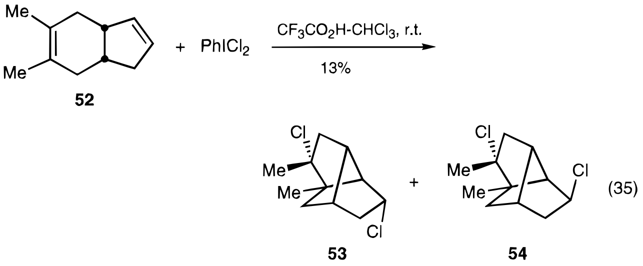
(Dichloroiodo)benzene was effectively applied for a substitutive chlorination at $sp^3$-carbon of various organic substrates, such as alkanes, ethers, esters, thioethers, ketones, sulfoxides, etc.[13,16,19,140−149] Ketones can be chlorinated in the α-position under both radical or ionic conditions. In a typical example, 1,5-diketones **44** react with $PhICl_2$ in dichloromethane under radical conditions with predominate formation of monochlorides **45**, while the same reagents in acetic acid in the dark (ionic conditions) selectively afford dichlorides **46** (eq 33).[140]



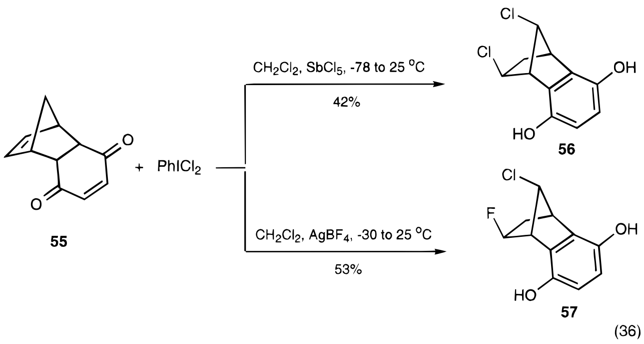
Similarly, depending on the conditions, reaction of $PhICl_2$ with alkenes may follow a radical or ionic mechanism. Under radical conditions, the reaction gives exclusively products of 1,2-addition of chlorine, often with high trans stereoselectivity; while under polar conditions chlorination is usually accompanied by skeletal rearrangements. For example, norbornene reacts with $PhICl_2$ in nonpolar solvents with the formation of 1,2-adducts **47** and **48** (eq 34) as the only detectable products.[142] The same reaction in the presence of trifluoroacetic acid affords exclusively products of skeletal rearrangement **49**−**51** (eq 34).[142]



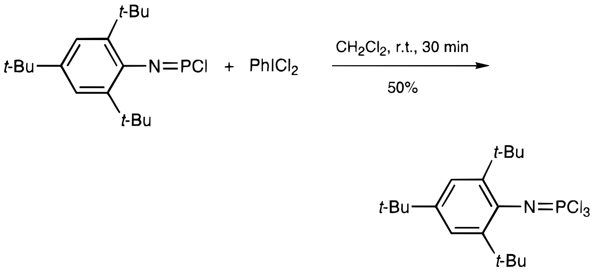
Bicyclic diene **52** reacts with $PhICl_2$ under similar polar conditions to afford tricyclic, rearranged products **53** and **54** in moderate yield (eq 35).[143]



The electrophilic reactivity of $PhICl_2$ can also be increased by addition of Lewis acids or $AgBF_4$. Reaction of $PhICl_2$ with diene **55** yields exclusively rearranged products **56** and **57** clearly resulting from an ionic mechanism of addition (eq 36).[144]



A variety of organic compounds containing heteroatoms can be effectively chlorinated by $PhICl_2$. Numerous examples of chlorinations at sulfur, phosphorus, selenium, arsenic, antimony, and some metals have been reported in older papers.[13,16,19] More recent examples include reactions of $PhICl_2$ with molybdenum[145] and iridium[146] complexes affording higher valent metal chlorides, as well as the preparation of trichlorophosphine imides **58** (eq 37).[147]



(37)

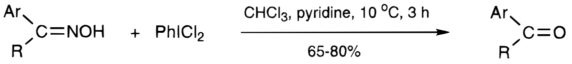
**58**

Under appropriate conditions, usually in the presence of amines, $PhICl_2$ can serve as an efficient oxidizing reagent. Oxidation of aldoximes **59** with $PhICl_2$ in the presence of pyridine generates unstable nitrile oxides **60** (eq 38) as principal products, which can be trapped in situ by olefinic compounds to afford the respective 1,3-cycloaddition products in good yields.[148]

$$\underset{\mathbf{59}}{\text{Ar–CH=NOH}} + PhICl_2 \xrightarrow[\text{reflux, 5-24 h}]{CHCl_3\text{, pyridine}} \underset{\mathbf{60}}{\text{Ar–C}\equiv\text{N}\rightarrow\text{O}} \qquad (38)$$

Ar = Ph, 4-$MeOC_6H_4$, 3,4,5-$(MeO)_3C_6H_2$, 4-$(CH_2{=}CHCH_2O)C_6H_4$

Ketoximes **61** react with $PhICl_2$ under similar conditions to afford the corresponding ketones **62** (eq 39) as a result of oxidative deoximation.[149]



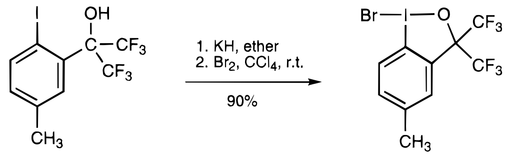
(39)

**61** **62**

Ar = Ph, 4-$NO_2C_6H_4$, 3-F-(4,6-$Cl_2$)$C_6H_2$, 4-$(Me_2CHCH_2)C_6H_4$
R = Ph, Me, Et

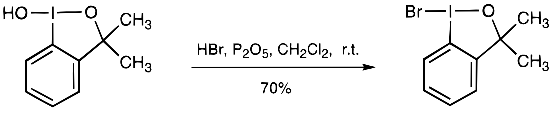
### 3. Bromides

(Dibromoiodo)arenes with general formula $ArIBr_2$ usually lack stability and cannot be isolated as individual compounds. However, two representatives of monobromoiodanes (**64** and **66**), stabilized due to the involvement of the iodine in a five-membered ring, were reported in the literature.[124] Bromide **64** can be prepared by addition of bromine to aryl iodide **63** (eq 40), while bromoiodane **66** is formed in the reaction of benziodoxole **65** with HBr under anhydrous conditions (eq 41).



(40)

**63** **64**



(41)

**65** **66**

Both bromoiodanes **64** and **66** are isolable, crystalline solids with melting points of 173 and 98 °C, respectively. Bromide **64** is substantially more stable than **66** due to the presence of the electron-withdrawing $CF_3$ substituents in the apical positions of the hypervalent iodine atom.[124] Bromoiodanes **64** and **66** may find some application in synthesis as highly selective free-radical brominating reagents. For example, under photochemical conditions these compounds react with toluene or cyclohexene to afford the respective benzylic or allylic bromides in almost quantitative yield.[124]

## C. Carboxylates

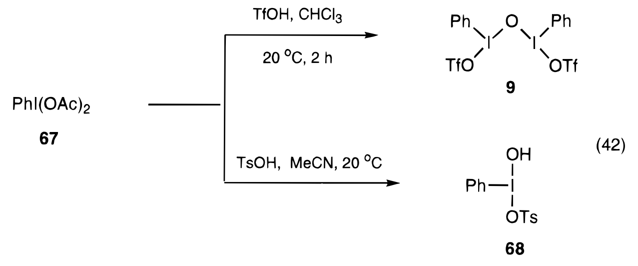
[Bis(acyloxy)iodo]arenes, $ArI(O_2CR)_2$, are the most important, well investigated, and practically useful organic derivatives of iodine(III). Two of them, (diacetoxyiodo)benzene (DIB) and [bis(trifluoroacetoxy)iodo]benzene (BTI), are commercially available or can be easily prepared by oxidation of iodobenzene with the respective peracid.[150] A similar peroxide oxidation of substituted iodobenzenes can be used for the preparation of other [bis(acyloxy)iodo]arenes.[151−155] For example, various mono- and di[bis(trifluoroacetoxy)iodo]-substituted arenes were synthesized in 70−85% yield from the respective iodoarenes and peroxytrifluoroacetic acid.[151−153] [Bis(acetoxy)iodo]arenes can be prepared in excellent yields by oxidation of iodoarenes with sodium perborate in acetic acid.[154−156] A broad variety of other carboxylates are easily accessible by the ligand exchange reaction of acetates with the appropriate carboxylic acid.[16] Of particular interest is the employment of the last method for the preparation of [(acyloxy)iodo]benzenes with chiral ligands by the reaction of DIB with dibenzoyl-L-tartaric acid.

[Bis(acyloxy)iodo]arenes are generally colorless, stable microcrystalline solids which can be easily recrystallized and stored for extended periods of time without significant decomposition. Single-crystal X-ray structural data for $ArI(O_2CR)_2$ indicate the expected T-shaped geometry around the iodine centers with almost collinear acyloxy groups. The I−O bond distances in $ArI(O_2CR)_2$ are considerably longer than the sum of their covalent radii (1.99 Å) and may vary in a broad range between 2.14 and 2.98 Å.[19,28,90,155,158,159]

[Bis(acyloxy)iodo]arenes and, especially, DIB and BTI have found wide synthetic application as starting materials in the preparation of numerous iodine(III) compounds, effective oxidizers, and radical initiators.

### 1. [Bis(acyloxy)iodo]arenes as Precursors to Other Iodine(III) Compounds

[Bis(acyloxy)iodo]arenes are widely used as readily available precursors to a variety of other iodosyl derivatives, $ArIX_2$, or iodonium salts, $Ar_2I^+X^-$. Iodosyl derivatives are usually obtained by ligand exchange of [(diacetoxy)iodo]arenes with the respective acids or acid derivatives. For example, the highly electrophilic, synthetically useful tosylate **68**[159,160] and triflate **9**[161] are conveniently prepared from DIB (**67**) and *p*-toluenesulfonic or triflic acids (eq 42). A similar reaction of DIB with aqueous fluoroboric, fluoroantimonic, and fluorophosphoric acids affords the corresponding iodosylbenzene derivatives **69** (eq 43).[162,163]



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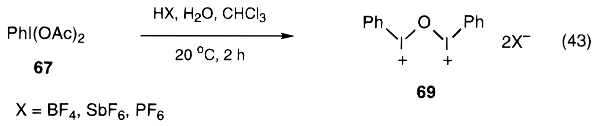
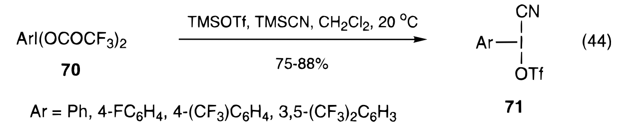


(43)

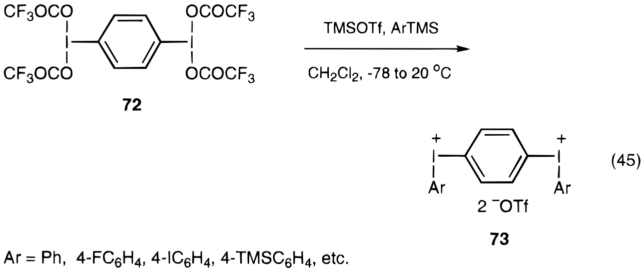
Reactions of [bis(trifluoroacetoxy)iodo]arenes (**70**) with trimethylsilyl triflate and cyanotrimethylsilane cleanly produce (cyano)aryliodonium triflates (**71**, eq 44), which are important iodonium transfer reagents.[151]



(44)

Similarly, the unstable azidoiodanes, $PhI(N_3)_2$ and $PhI(OAc)N_3$, can be generated at low temperature in situ from DIB and azidotrimethylsilane (see section III.F.3).

A broad variety of iodonium salts can be synthesized from [bis(acyloxy)iodo]arenes and the appropriate nucleophilic organic substrates. A convenient general method for the preparation of diaryliodonium salts involves the reaction of DIB with arenes in the presence of triflic acid.[164] Likewise, bis(iodonium) triflate salts **73** can be prepared from *p*-bis[bis(trifluoroacetoxy)iodo]benzene **72** and the respective arylsilanes (eq 45).[153] The analogous reaction was also applied in the synthesis of macrocyclic tetraaryltetraiodonium cationic molecular squares (see Section IV.D.1).[152]

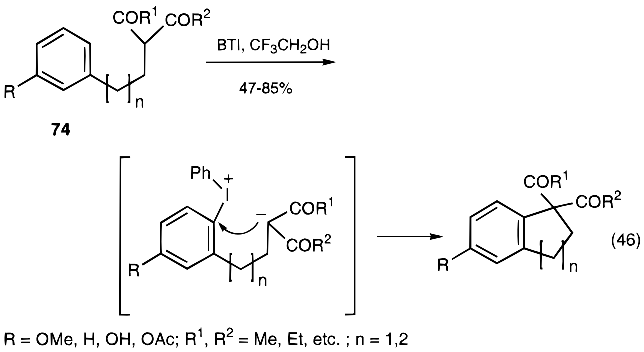


(45)

In many cases, [bis(acyloxy)iodo]arenes are used for the generation of unstable iodonium salts, which serve as reactive intermediates in the consequent transformations. In a typical example, Kita and coworkers applied BTI to induce cyclization of α-(aryl)-alkyl *β*-dicarbonyl derivatives **74** (eq 46).[165]

In general, oxidations of nucleophilic organic substrates with [bis(acyloxy)iodo]arenes usually involve unstable iodonium salts as principal intermediates.

Reaction of DIB with 1,3-dicarbonyl compounds under basic conditions represent the most general approach to iodonium ylides (see Section IV.F).

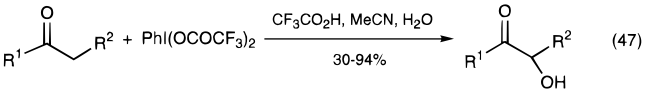


(46)

## 2. Oxidations with [Bis(acyloxy)iodo]arenes

In the last 10−15 years [bis(acyloxy)iodo]arenes have seen widespread application as general, universal oxidizing reagents. The oxidative properties of DIB and BTI are similar to those of Tl(III), Hg(II), and Pb(IV) derivatives, but without the toxic and concomitant environmental problems of these heavy-metal analogues.

A particularly useful reaction is hydroxylation of enolizable ketones by DIB under basic conditions (see Section III.A.2).[15,21−23] Similar hydroxylation can also be performed with BTI under acidic conditions (eq 47).[166]

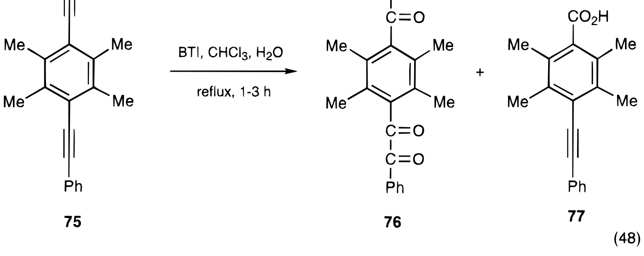


(47)

A plausible mechanism for this hydroxylation involves initial electrophilic addition of BTI to the enolized ketone and subsequent nucleophilic substitution of the iodonium intermediate. In the presence of appropriate external nucleophiles this reaction may afford the respective α-substituted ketone.[15,19]

The analogous reaction of alkenes with DIB or BTI in the presence of external nucleophiles affords the respective derivatives of 1,2-diols. For example, 1-hexene reacts with BTI in the presence of $LiClO_4$ or LiOTf to produce diperchlorate or -triflate esters of 1,2-hexanediol.[167]

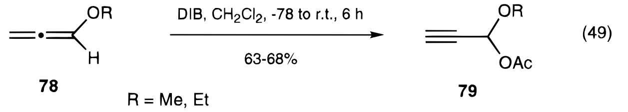
Merkushev and co-workers have found that alkynes can be oxidized with BTI to afford the respective 1,2-diones in excellent yields.[168−170] In some cases, this reaction is accompanied by a complete triple-bond cleavage with the formation of carboxylic acids. For example, the oxidation of phenylethynyl durene **75** by BTI yields two principal products—1,2-dione **76** and acid **77** (eq 48).[169]



(48)

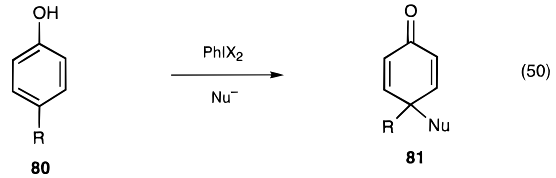
A similar oxidative cleavage of alkynes to carboxylic acids with 2 equiv of [bis(trifluoroacetoxy)iodo]pentafluorobenzene was reported by Moriarty and coauthors.[171]

Alkoxyallenes **78** are oxidized with DIB under mild conditions to yield 3-acetoxy-3-alkoxypropynes (**79**, eq 49).[172]



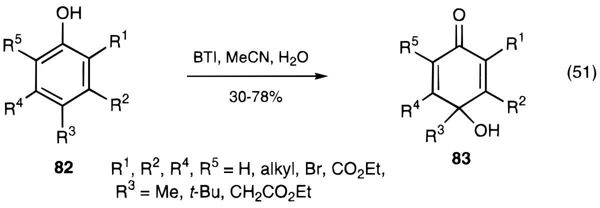
Alkynyl- or alkenyliodonium salts have been proposed to be the key intermediates in these oxidations (eqs 48 and 49).

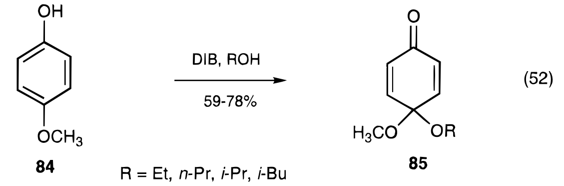
During the last few years DIB and BTI have been widely used for the oxidation of phenols. DIB is the reagent of choice for the oxidation of various substituted *o*- and *p*-hydroquinones to the corresponding benzoquinones. The oxidation generally proceeds in methanol solution at room temperature, and the yield of benzoquinones is almost quantitative.[173] Especially interesting and synthetically useful is the oxidation of 4-substituted phenols **80** in the presence of an appropriate nucleophile (Nu) leading to the respective 4,4-disubstituted cyclohexadienones **81** according to general eq 50. No definitive mechanisms have been established for these reactions, however, it is widely assumed that they proceed by an ionic process via some electrophilic reactive intermediate.[173,174]



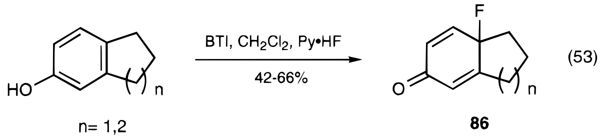
Various nucleophiles, such as water, alcohols, fluoride ion, carboxylic acids, amides, oximes, and electron-rich aromatic rings, have been used successfully in this reaction (eq 50) in either an inter- or intramolecular mode.[173−187]

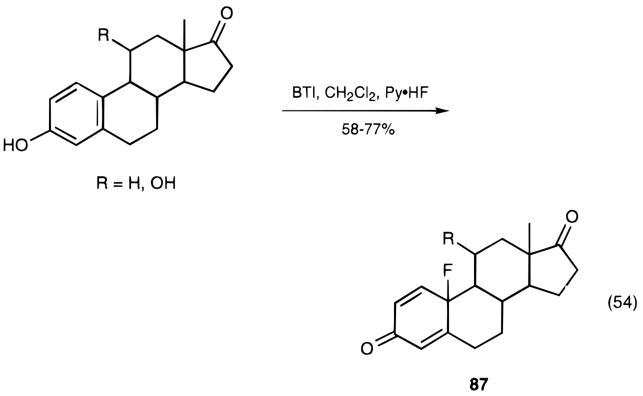
McKillop and co-workers have found that the oxidation of substituted phenols **82** with BTI in aqueous acetonitrile affords *p*-quinols **83** in moderate to good yields (eq 51).[174] Even higher yields of *p*-quinols **83** are obtained when tripropylsilyl ethers of phenols are used as starting material. A similar oxidation of *p*-alkoxyphenols **84** with DIB in the presence of alcohols affords the respective quinone monoketals **85** (eq 52).[173,175,177]



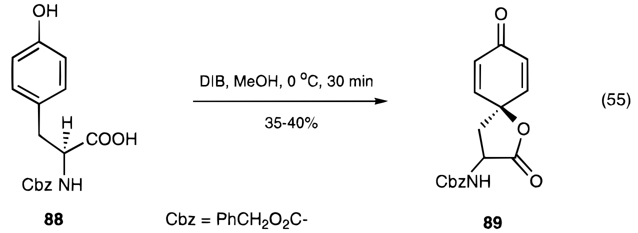


The oxidation of 4-alkylphenols with BTI in the presence of pyridinium polyhydrogen fluoride as the source of fluoride anion results in nucleophilic *ipso*-fluorination.[178] This reaction can be used for the preparation of polycyclic 4-fluorocyclohexa-2,5-dienones **86** and **87** (eqs 53 and 54).

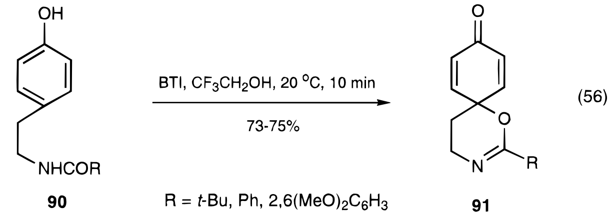


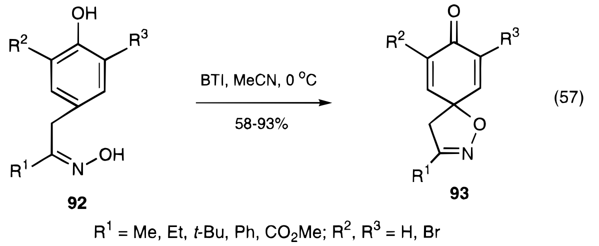


Intramolecular oxidative cyclization of the appropriate 4-substituted phenols with DIB or BTI provides a powerful synthetic tool for the creation of an important spirocyclohexa-2,5-dienone structural fragment. Wipf and co-workers used the oxidatively induced cyclization in *N*-protected tyrosine **88** as an approach to the spirocyclic core **89** (eq 55) in the total synthesis of the antitumor antibiotic Aranorosin.[179]

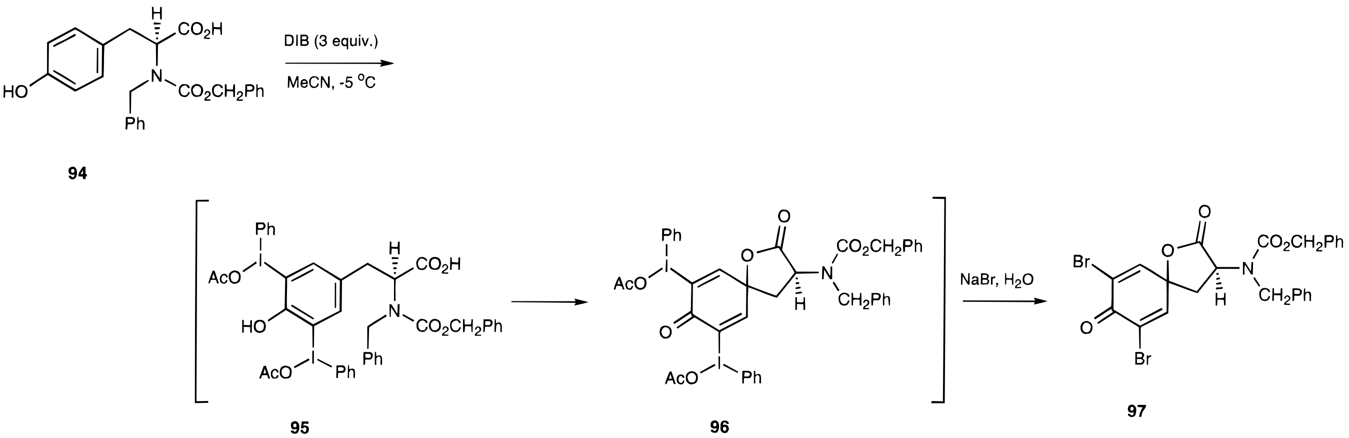


The analogous cyclizations of amides **90** and ketoximes **92** by the action of BTI in nonnucleophilic solvents afford the respective spirohexadienones **91** and **93** in good yield (eqs 56 and 57).[180−182]



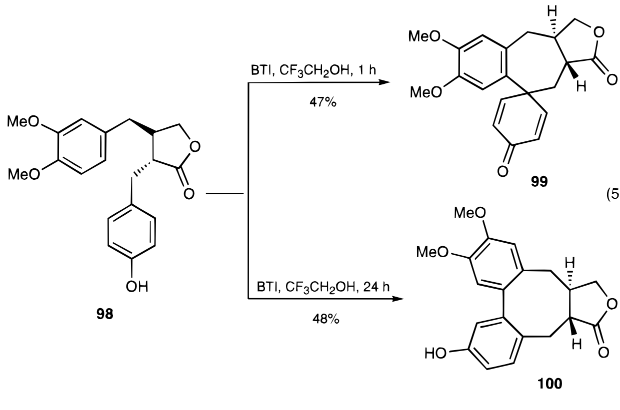


**Scheme 1**



Oxidation of tyrosine derivative **94** with an excess of DIB in cold acetonitrile followed by quenching with aqueous sodium bromide results in the formation of brominated spirolactone **97** in 80% yield. A plausible mechanism for this reaction involves iodonium intermediates **95** and **96** as the intermediates and subsequent substitution of the phenyliodonium group with bromide anion (Scheme 1).[183]

Of particular interest are oxidatively induced cyclizations of phenolic precursors in which carbon–carbon bond formation is achieved. Pelter and coworkers have reported oxidative cyclizations of dibenzylbutyrolactone **98** by treatment with BTI in trifluoroethanol.[184] The major product of the cyclization is either the spirodienone **99** or the dibenzocyclooctadiene **100**, depending upon the time allowed for this reaction (eq 58). The second pathway of this cyclization leading to the dibenzocyclooctadiene **100** was used recently in the synthesis of isostegane derivatives.[185]

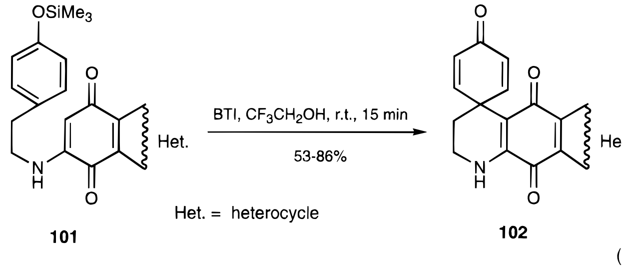


(58)

A BTI-induced spiro cyclization of silylated phenol derivatives **101** provides a convenient general approach to aza spirodienones **102** (eq 59). Using this method, Kita and co-workers accomplished the first total synthesis of the alkaloid discorhabdin C.[186]

Oxidation of *p*-methoxy-substituted phenols **103** by BTI in the presence of electron-rich styrenes **104** affords in good yield dihydrobenzofurans **105** resulting from a formal 1,3-oxidative cycloaddition of the phenol to the styrene derivative (eq 60).[187]

DIB and BTI have found wide application for the oxidation of organic derivatives of such elements as nitrogen, sulfur, selenium, tellurium, and others. The use of [bis(acyloxy)iodo]arenes for the oxidation of various organonitrogen compounds was thoroughly discussed in earlier reviews by Varvoglis.[9,13,19] More recent examples include the application of DIB for the preparation of N-oxides from nitroisoquinoline derivatives,[188] oxidations of hydrazones and similar carbonyl derivatives leading to regeneration of the carbonyl function,[189−194] Hofmann-type oxidation of carboxamides to carbamates,[195] oxidative amination of indoles with aromatic amines,[196] oxidation of papaverine,[197] and oxidatively assisted preparation of nitrogen heterocycles.[198,199]



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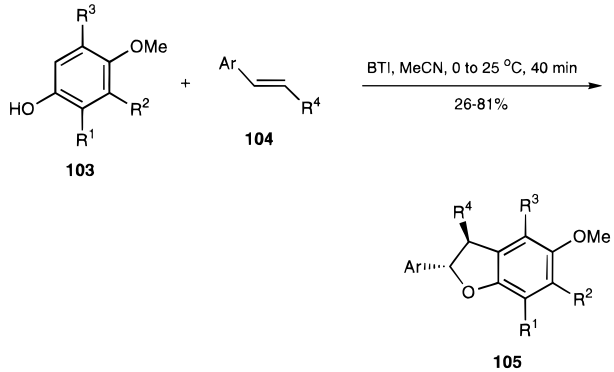
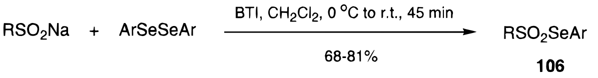


(60)

$R^1$ - $R^3$ = H, Me, MeO, Cl, allyl; $R^4$ = H, Me; Ar = 4-$MeOC_6H_4$ or 1,2-$(MeO)_2C_6H_3$

Thioacetals and thioketals are efficiently cleaved to carbonyl compounds with BTI under mild conditions. This reaction is especially useful for the selective deprotection of either thioacetals or thioketals and is compatible with a variety of other functional groups, such as PhS, HO, TsO, $R_2N$, double bond, etc.[200] Recently this method was used in the deprotection steps in the synthesis of the roflamycoin system[201] and in the asymmetric synthesis of α-sulfenyl aldehydes.[202]

BTI can oxidatively cleave the Se−Se bond in diaryl diselenides to form arylselenyl trifluoroacetates.[203] On the basis of this reaction, Chen and Chen recently developed a convenient one-pot synthesis of selenosulfonates **106** from diaryl diselenides and sodium sulfinates (eq 61).[203] A similar oxidation was recently reported for diaryl ditellurides.[204]

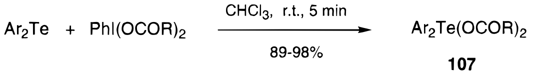


$$RSO_2Na + ArSeSeAr \xrightarrow[68\text{-}81\%]{BTI,\ CH_2Cl_2,\ 0\ ^\circ C\ to\ r.t.,\ 45\ min} RSO_2SeAr \quad (61)$$

**106**

R, Ar = Ph, 4-$MeC_6H_4$, 4-$ClC_6H_4$

Diaryltellurides react with [bis(acyloxy)iodo]benzenes under mild conditions to afford diaryltellurium dicarboxylates **107** in high yield (eq 62).[205]



$$Ar_2Te + PhI(OCOR)_2 \xrightarrow[89\text{-}98\%]{CHCl_3,\ r.t.,\ 5\ min} Ar_2Te(OCOR)_2 \quad (62)$$

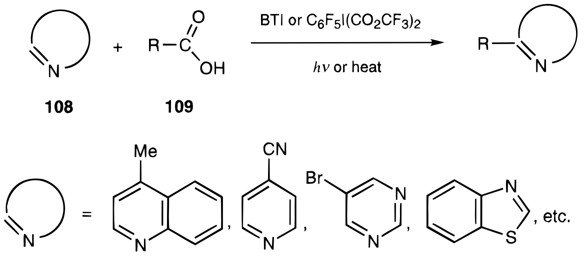
**107**

Ar = 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 4-$ClC_6H_4$; R = Me, $CH_3$, Ph

A mixture of BTI with iodine is used as an efficient electrophilic iodinating reagent toward heterocycles and other nucleophilic organic substrates.[206-208] Trifluoroacetyl hypoiodite, $CF_3COOI$, is a plausible reactive intermediate in these oxidative iodinations.

### 3. [Bis(acyloxy)iodo]arenes as Radical Initiators

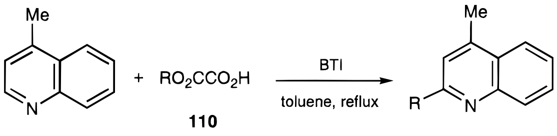
During the last five years DIB and BTI have attracted significant interest and research activity as efficient initiators of radical processes. Under photochemical conditions, both reagents were found to be efficient initiators for the homopolymerizations of 2-[2-((dimethylamino)ethyl)methacrylate (DMAEM) and methyl methacrylate (MMA) and also the copolymerizations of DMAEM with MMA or styrene.[209] Togo and co-workers have found that upon irradiation or heating [bis(acyloxy)iodo]arenes undergo decarboxylative decomposition, generating alkyl radicals which can be effectively trapped with various heteroaromatic bases or electron-deficient alkenes.[210-215] On the basis of this observation, the authors have developed a general, convenient experimental procedure for the radical alkylation of nitrogen heterocycles **108** with a broad variety of carboxylic acids **109** in the presence of BTI or [bis(trifluoroacetoxy)iodo]pentafluorobenzene (eq 63).[210,212] This reaction is especially useful for the preparation of *C*-nucleosides and their analogues.[213]



**108** **109** (63)

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

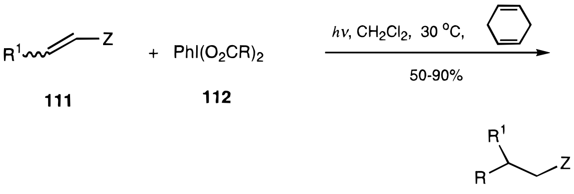
Further modification of this procedure allows the use of alcohols as the source of alkyl radicals. In this case, alcohols are first converted into the oxalic acid monoalkyl esters **110**, which are used as reagents in the radical alkylation of heteroaromatic bases (eq 64).[211-213]



**110** (64)

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

Similar experimental procedures can be used for the radical alkylation of electron-deficient alkenes **111** (eq 65). In this process, a mixture of alkene **111** and [bis(acyloxy)iodo]arenes **112** (prepared from DIB and the respective carboxylic acid or monoalkyl esters of oxalic acid) is irradiated with a high-pressure mercury lamp in dichloromethane in the presence of 1,4-cyclohexadiene to give a reductive addition product **113**.[214,215]

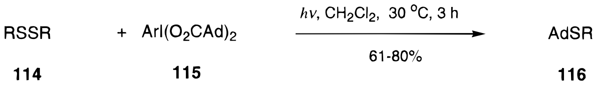


**111** **112** **113** (65)

Z = $SO_2Ph$, SOPh, $CO_2Me$, $P(O)(OEt)_2$; $R^1$ = H, Me

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

Recently the same researchers[216] reported an efficient procedure for the preparation of adamantyl sulfides **116** by radical decarboxylation of [bis(1-adamantylcarboxy)iodo]benzene **115** (Ar = Ph) in the presence of disulfides **114** (eq 66). A special study of the reactivity of various [bis(1-adamantylcarboxy)iodo]arenes in this reaction revealed that the introduction of strong electron-withdrawing groups, such as nitro and perfluoro, into the aromatic ring of the reagent **115** significantly reduced the yield of the product **116**. The authors explained the low reactivity of *p*-nitro and perfluorophenyl derivatives **115** in radical reactions by the increased I—O bond strength in these compounds.[216]



$$RSSR + ArI(O_2CAd)_2 \xrightarrow[61\text{-}80\%]{h\nu,\ CH_2Cl_2,\ 30\ ^\circ C,\ 3\ h} AdSR \quad (66)$$

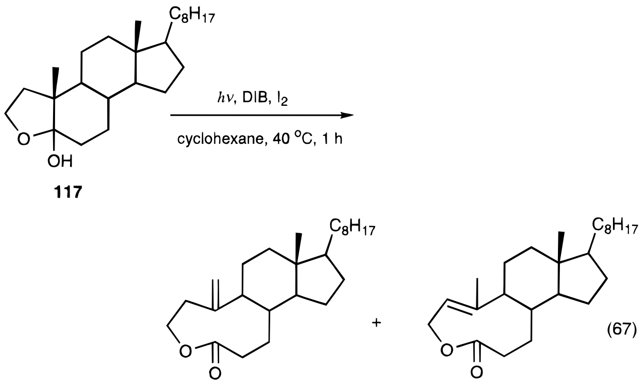
**114** **115** **116**

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

Ar = 4-$MeOC_6H_4$, 4-$MeC_6H_4$, Ph, 4-$ClC_6H_4$, 4-$NO_2C_6H_4$, $C_6F_5$

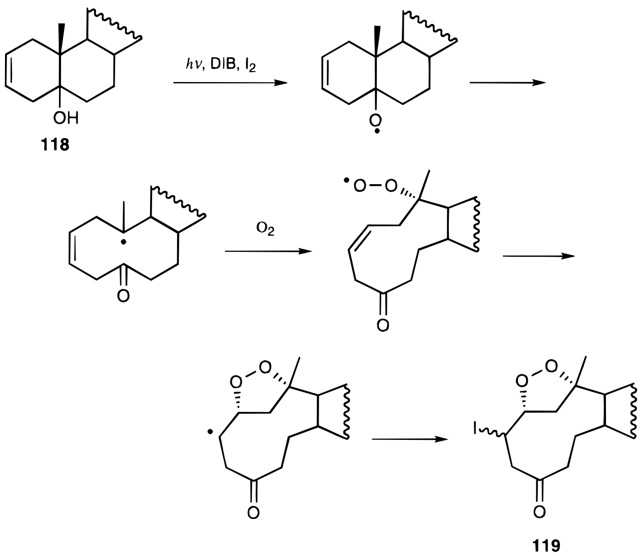
Photolysis of DIB with cyclic alcohols in the presence of iodine leads to the generation of the respective alkoxy radical which can sequentially undergo fragmentation, rearrangement, or cyclization. Recently this methodology was effectively used in a number of syntheses. Suàrez and co-workers applied a sequential alkoxy radical fragmentation for the preparation of highly functionalized macrocycles and some steroidal derivatives.[217-222] For example, photolysis of steroidal hemiacetals, such as **117** (eq 67), with stoichiometric amounts of DIB and iodine in the absence of oxygen affords medium-sized lactones in good yield as a result of alkoxy radical fragmentation.[217]

When the reaction of cyclic alcohols **118** is conducted under an oxygen atmosphere the initially produced C-radical traps a molecule of $O_2$ yielding



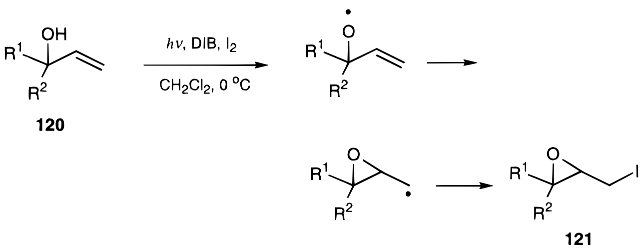
peroxide **119** according to general Scheme 2.[218,219] This and similar sequential alkoxy radical fragmentations can be applied to the preparation of various synthetically interesting medium-sized ketones and lactones.[219−222]

**Scheme 2**



Photolysis of DIB with tertiary allylic alcohols **120** in the presence of iodine leads to the formation of α-iodo epoxides **121** (50−72% yield) as a result of alkoxy radical rearrangement (Scheme 3).[223]

**Scheme 3**

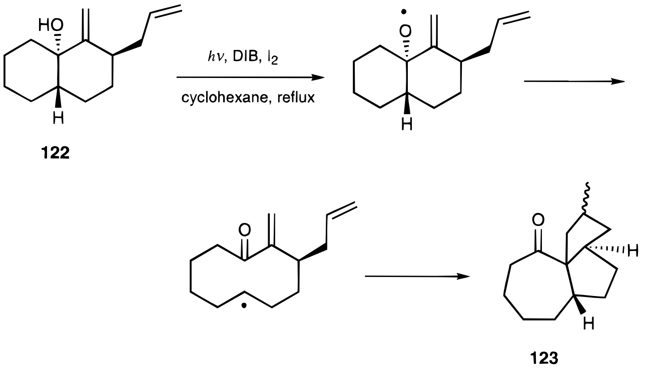


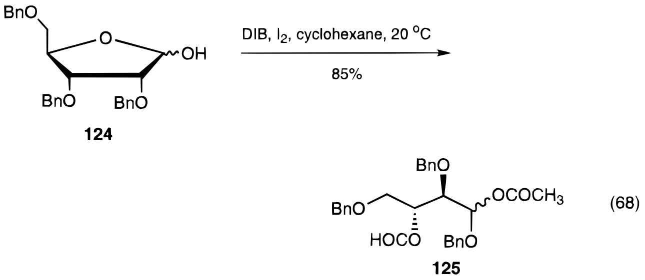
$R^1 = C_2H_5, C_5H_{11}$; $R^2 = CH_3, C_2H_5$; or $R^1 + R^2 = (CH_2)_n$, n = 4, 5, 6, 7

Treatment of bicyclic dienol **122** with DIB-$I_2$ in degassed cyclohexane under irradiation and reflux results in a cascade radical fragmentation−transannulation−cyclization sequence leading to ketone **123** in 81% yield (Scheme 4).[224]

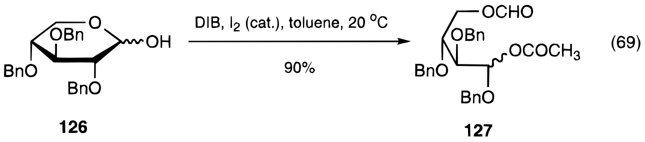
Fragmentation of anomeric alkoxy radicals, generated from appropriate carbohydrates by a similar method, provides a convenient entry into useful chiral synthetic intermediates.[225,226] Suàrez and co-workers reported the DIB-initiated radical fragmentation of protected furanoses **124** leading to four-carbon chiral building blocks of the erythrose type (**125**) in good yield (eq 68).[225]

**Scheme 4**

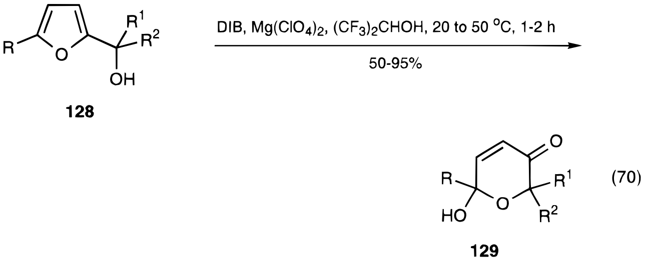




Inanaga and co-workers have found a similar fragmentation of pyranose derivatives **126** (eq 69). Interestingly, these reactions (eqs 68, 69) proceed smoothly at room temperature and do not require irradiation.[226]



Recently, the binary reagent DIB-Mg($ClO_4$)$_2$ was found to be very efficient for the conversion of 2-furyl-1-alcohols **128** into pyranones **129** (eq 70).[227]



R = H, Me; $R^1$ = H, Ph; $R^2$ = H, Me, Et, $C_4H_9$, $C_{10}H_{21}$ or $R^1 + R^2$ = cyclohexyl

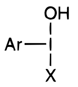
This reaction (eq 70) also does not require irradiation and is rationalized by a single-electron transfer process with the generation of a cation radical as the key intermediate.[227]

## D. Derivatives of Strong Acids

In contrast to aryl iodosyl dihalides and dicarboxylates, the analogous disubstituted derivatives of strong acids, $ArIX_2$ (X = $RSO_3$, $ClO_4$, $NO_3$, etc.), are generally unstable and extremely moisture sensitive.

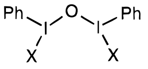
The existence of several such derivatives was assumed in the literature; however, none of them was isolated as an individual, stable compound. For example, Koser and Wettach reported some evidence for the intermediate formation of the ditosylate $PhI(OTs)_2$ in the reaction of $PhICl_2$ with silver tosylate, but an attempt to isolate this compound failed.[228] Similarly, triflate $PhI(OTf)_2$,[48] sulfate $PhISO_4$,[73] and nitrate $PhI(ONO_2)_2$[229] lack stability and typically can only be generated in situ, at low temperature, under absolutely dry conditions.

The most likely, stable structural types of the iodosyl derivatives of strong acids are represented by hydroxy-substituted (**130**) and $\mu$-oxo-bridged (**131**) iodanes which are products of partial hydrolysis of the initial $ArIX_2$.



**130**

X = $OSO_2R$, $OP(O)(OR)_2$; Ar = Ph, $4\text{-}FC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}IC_6H_4$, $4\text{-}MeC_6H_4$, $4\text{-}NO_2C_6H_4$, $4\text{-}PhC_6H_4$, $2\text{-}PhCH_2C_6H_4$, $2\text{-}(MeNHCO)C_6H_4$, $2\text{-}(PhCH_2NHCO)C_6H_4$, $2\text{-}MeC_6H_4$, 2-naphthyl, $3\text{-}MeC_6H_4$, $2\text{-}FC_6H_4$, $3\text{-}FC_6H_4$, $C_6F_5$



**131**

X = $OSO_2OH$, OTf, $OClO_3$, $ONO_2$, $O_2CCF_3$, $BF_4$, $SbF_6$, $PF_6$

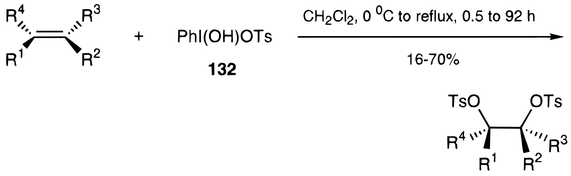
Both types of compounds (**130** and **131**) generally can be prepared by the reaction of iodosyl arenes or dicarboxylates with the appropriate aqueous acid. Hydroxy derivatives **130** are colorless, stable microcrystalline solids which can be recrystallized and stored for extended periods of time without significant decomposition. The most important representative of **130**, [hydroxy(tosyloxy)iodo]benzene, PhI(OH)OTs, is commercially available. Single-crystal X-ray structural data for PhI(OH)OTs indicates the expected T-shaped geometry around the iodine center with almost collinear O-ligands and two different I–O bonds of 2.47 Å (I–OTs) and 1.94 Å (I–OH) consistent with the ionic character of this compound.[160] $\mu$-Oxo-bridged iodanes **131** are the most typical iodosyl derivatives of strong inorganic acids, such as sulfuric, nitric, perchloric, trifluoromethanesulfonic, etc.; however, compounds of this type are also known for carboxylic acids. A distinctive feature of all $\mu$-oxo-bridged iodanes **131** is the bright yellow color due to the $^{+}I{-}O{-}I^{+}$ bridging fragment.[230] The available X-ray structural data for **131** (X = $ONO_2$,[231] and OCOR[28,232]) is also consistent with the ionic character of the I–X bonds.

In the last dozen years iodosyl derivatives of strong acids and, especially, iodosyl sulfonates, have found wide synthetic application as starting materials in the preparation of numerous iodine(III) compounds and effective oxidizers. It should be emphasized that the reactivity pattern of sulfonates is generally different from halides and carboxylates. In particular, radical reactions are not typical for sulfonates, while their electrophilic reactivity toward nucleophilic organic substrates under polar conditions is significantly enhanced. The application of iodosyl sulfonates in organic synthesis was recently reviewed by Moriarty, Vaid, and Koser.[17]

### *1. [Hydroxy[(organosulfonyl)oxy]iodo]arenes*

The first preparation of [hydroxy(tosyloxy)iodo]benzene (HTIB, **132**) from (diacetoxyiodo)benzene and *p*-toluenesulfonic acid monohydrate was reported in 1970 by Neiland and Karele.[159] A few years later, Koser and co-workers discovered that HTIB is an efficient reagent for the synthesis of various iodonium salts and oxytosylations,[233−237] so in the present literature HTIB is often referred for as "Koser's reagent".

HTIB is highly reactive toward nucleophilic organic substrates, such as alkenes, alkynes, ketones, enol ethers, and aromatic compounds. Reactions of HTIB with alkenes afford *vic*-ditosyloxyalkanes in moderate yield (eq 71).[235−237]

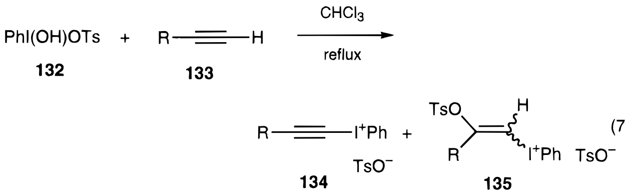


(71)

$R^1 - R^4$ = H, Me, Et, *n*-Pr, Ph, or $R^1 + R^4$ = $(CH_2)_3$, $(CH_2)_4$

In the case of cyclohexene and internal acyclic alkenes, this reaction proceeds as a stereospecific *syn*-addition, whereas phenyl-substituted alkenes and norbornene give products of skeletal rearrangements.[235−238] These results can be rationalized by a polar addition–substitution mechanism similar to the one shown in eq 13 (see Section III.A.1). The first step in this mechanism involves electrophilic *anti*-addition of the reagent to the double bond, and the second step is nucleophilic substitution of the iodonium fragment by tosylate anion with inversion of configuration. Such a polar mechanism also explains the skeletal rearrangements in the reactions of HTIB with polycyclic alkenes,[238] participation of external nucleophiles,[167] and the intramolecular participation of a nucleophilic functional group with the formation of lactones and other cyclic products.[239−241] Analogous reactivity pattern is also typical of [hydroxy[(methylsulfonyl)oxy]iodo]benzene.[242]

Reaction of HTIB (**132**) with alkynes **133** generally affords two products: alkynyl- and alkenyl(phenyl)iodonium tosylates **134** and **135**, respectively (eq 72).[243−247] Alkynyliodonium salts **134** are major products in the reactions of terminal alkynes bearing bulky substituents (R = *tert*-butyl, *sec*-butyl, cyclohexyl, aryl, etc.), while alkenyliodonium tosylates **135** are formed from nonsterically hindered terminal alkynes or from internal alkynes.



(72)

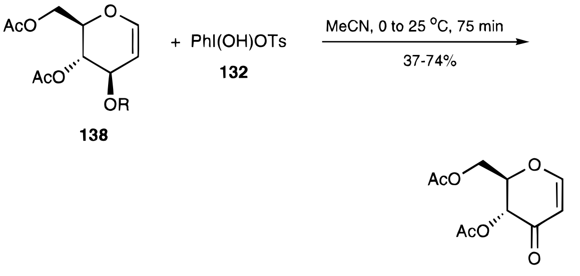
HTIB is an important reagent for the preparation of aryl- and heteroaryliodonium salts by reactions with the respective arenes or trimethylsilylarenes (see Section IV.D).[234,248,249]

Especially useful are reactions of HTIB with ketones or silyl enol ethers leading to α-tosyloxy ketones.[237,250,251] This reaction followed by treatment with the appropriate nucleophile in situ offers a convenient entry into a variety of other α-substituted ketones. In a typical example, treatment of acetophenones **136** with HTIB and potassium thiocyanate affords α-thiocyanotoacetophenones **137** in good yield (eq 73).[252]

$$\underset{\mathbf{136}}{ArCOCH_3} + \underset{\mathbf{132}}{PhI(OH)OTs} + KSCN \xrightarrow[52\text{-}78\%]{MeCN,\ reflux} \underset{\mathbf{137}}{ArCOCH_2SCN} \qquad (73)$$

The application of reactions of HTIB as an oxidant in the synthesis of various heterocycles was recently reviewed by Prakash and coauthors.[21-23] For the most recent examples of similar reactions see ref 253.

HTIB is also widely used as an efficient oxidizing reagent, generally more reactive than [bis(acyloxy)-iodo]arenes. Kirschning and co-workers have found that HTIB is a superior reagent for the regioselective oxidation of protected glycals **138** to dihydropyranones **139** (eq 74).[254,255] Interestingly, other polyvalent iodine reagents like DIB, BTI, and PhI(OMe)OTs are ineffective oxidants in this reaction.[255]



**138** **132** **139**

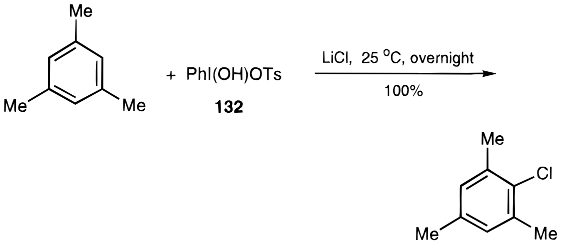
R = Ac, $PhCO_2$, $MeOCH_2$, $Me_3Si$, $t$-$BuMe_2Si$

(74)

Organic iodides of various types can be effectively oxidized by HTIB. When HTIB is mixed with aryl iodides, ligand transfer occurs to furnish iodobenzene and the corresponding [hydroxy(tosyloxy)iodo]arene.[233] Oxidation of alkyl iodides by HTIB leads to the formation of alkyl tosylates as products of oxidatively assisted nucleophilic substitution of iodine.[256,257] The latter reaction can be used to prepare cubyl sulfonates from iodocubane derivatives.[258]

HTIB can serve as an excellent oxidant in Hofmann-type degradation of aliphatic carboxamides to alkylamines.[259,260] The mechanism of this reaction involves initial formation of unstable *N*-phenyliodonio carboxamide salts (see Section III.F.1), which rearrange with loss of iodobenzene to give isocyanates.[259,261] Moriarty and co-workers used this reaction for the preparation of cubyl and adamantyl ammonium salts from the respective carboxamide derivatives.[262]

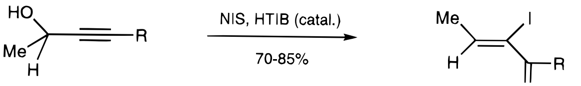
Polyalkylbenzenes react with HTIB in the presence of ionic halides or *N*-halosuccinimide to afford products of ring halogenation in good yield.[263-265] For example, reaction of mesitylene with HTIB in the presence of LiCl selectively gives monochlorinated product **140** in quantitative yield (eq 75).[265] In general, these oxidatively assisted ring halogenations can be carried out under mild conditions and are highly selective.



**132** **140**

(75)

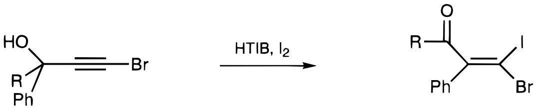
In a series of communications, McNelis and coworkers have reported the scope of reactions of the reagent combination HTIB/halogen or HTIB/*N*-halosuccinimide with alkynols resulting in the formation of various haloenones.[266-273] All these oxidative rearrangements involve iodonium intermediates and are highly regio- and stereoselective. For example, secondary alkynols **141** are cleanly converted to (*Z*)-α-iodoenones **142** upon treatment with *N*-iodosuccinimide in the presence of catalytic amounts of HTIB (eq 76).[266]



**141** R = Me, Et; NIS = *N*-iodosuccinimide **142**

(76)

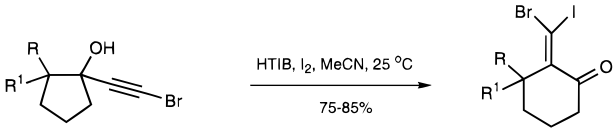
Bromoethynyl alcohols **143** can be similarly converted to *β*,*β*-dihaloenones **144** by the reaction with HTIB/$I_2$ system (eq 77).[268,269]



**143** R = Me, H **144**

(77)

Reactions of this type (eq 77) are especially useful for the preparation of cyclic *β*,*β*-dihaloenones by ring expansions of alkynyl cyclopentanols or alkynyl cyclohexanols. 1-(1-Bromoethynyl)cyclopentanols **145** react with equimolar amounts of iodine and HTIB under mild conditions to produce cyclohexanone derivatives **146** with a high degree of stereoselectivity (eq 78).[270]

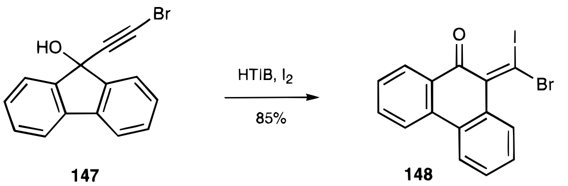


**145** R, R$^1$ = H, Me **146**

(78)

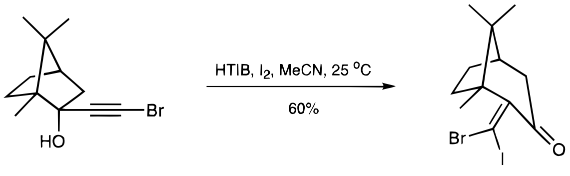
A similar reaction was used in the synthesis of phenanthrenone **148** from the readily available fluorenone derivative **147** (eq 79).[271]

Ring expansion of camphor and adamantanone derivatives (**149** and **150**, respectively) under the same conditions afforded the respective (*Z*)-bromo-

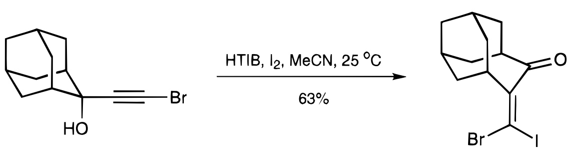


**147** **148** (79)

iodoenones **150** and **152** in good yield and in high stereoselectivity (eqs 80 and 81).[272,273]

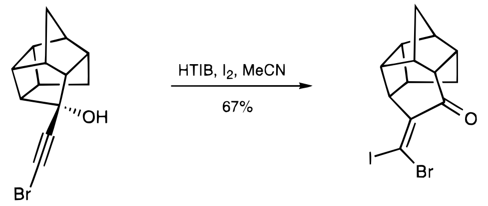


**149** **150** (80)



**151** **152** (81)

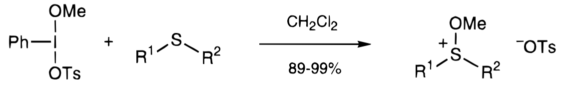
Interestingly, the analogous ring expansion of pentacycloundecane derivative **153** furnished (*E*)-bromoiodoenone **154**, but not the expected (*Z*)-isomer (eq 82).[274]



**153** **154** (82)

A variety of other sulfonate iodosyl derivatives of type **130** have been reported in the literature. [Hydroxy[(methylsulfonyl)oxy]iodo]benzene (**130**, Ar = Ph, X = $OSO_2Me$) can be prepared from (diacetoxyiodo)benzene and methanesulfonic acid and is very similar to HTIB in its chemical reactivity.[242,247,275] In particular, this reagent converts enolizable ketones or silyl enol ethers to α-mesyloxy ketones,[242,250,275] and reacts with alkenes analogously to HTIB affording the respective mesylates.[242] A chiral analogue of this reagent, [hydroxy[((+)-10-camphorylsulfonyl)oxy]iodo]benzene, has been recently reported by Varvoglis and co-workers.[276]

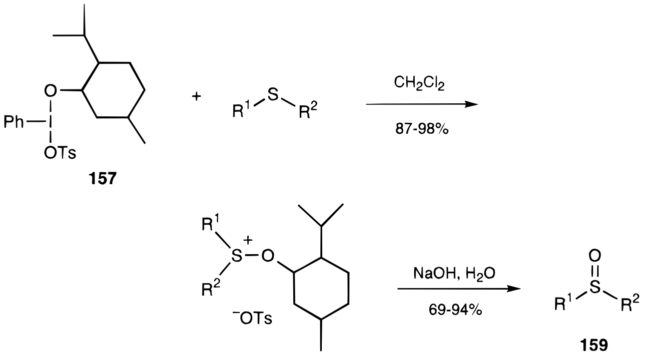
[Methoxy(tosyloxy)iodo]benzene (**155**) can be prepared by treatment of HTIB with trimethyl orthoformate.[277] This compound is a useful reagent for the oxidative degradation of aliphatic carboxamides to alkylamines,[261] and for the oxidation of sulfides to methoxysulfonium tosylates **156** (eq 83).[278,279]



**155** $R^1,R^2$ = Me, Pr, $PhCH_2$, 4-$BrC_6H_4$ **156** (83)

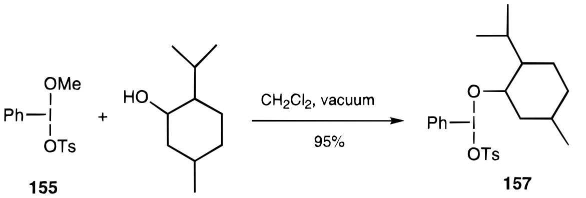
The methoxy ligand in **155** can be substituted with a chiral menthyloxy group by treatment with menthol (eq 84).[280] The product of this reaction, chiral [(menthyloxy)(tosyloxy)iodo]benzene **157**, is useful for the preparation of optically active menthyloxysulfonium tosylates **158** and sulfoxides **159** (Scheme 5).[280]

**Scheme 5**



**157** **158** **159**

$R^1,R^2$ = Me, *t*-Bu, $PhCH_2$, 4-$MeC_6H_4$

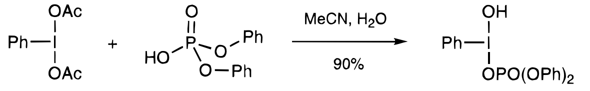


**155** **157** (84)

Several sulfonates **130** with the aryl substituent other than phenyl have been reported in the literature.[233,234,244,248,249,281] For example, [hydroxy(tosyloxy)iodo]pentafluorobenzene and the analogous mesylate derivative were prepared by treatment of [bis(trifluoroacetoxy)iodo]pentafluorobenzene in acetonitrile with *p*-toluenesulfonic or methanesulfonic acid, respectively.[281] [Hydroxy(tosyloxy)iodo]pentafluorobenzene was found to react with anisole and dimedone to give the corresponding iodonium salts.[281]

### 2. [Hydroxy(phosphoryloxy)iodo]arenes

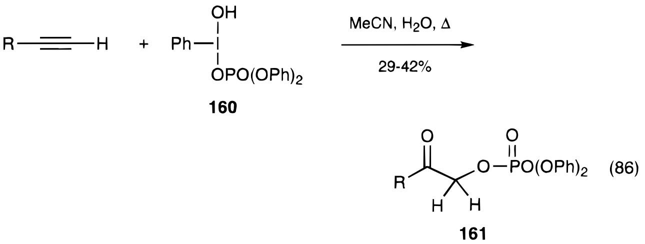
[Hydroxy[[(bis(phenyloxy)phosphoryl]oxy]iodo]benzene **160** can be prepared as a stable, crystalline solid by the reaction of (diacetoxyiodo)benzene with diphenyl phosphate in aqueous acetonitrile (eq 85).[282]



**160** (85)

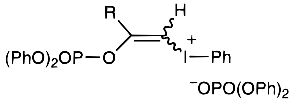
This compound (**160**) generally has a reactivity pattern similar to HTIB. It reacts with enolizable ketones or with pentenoic acids to afford the respective products of α-phosphoryloxylation or phosphoryloxy lactonization.[282] Reaction of reagent **160** with ketones is not regioselective, for example, the treatment of 2-hexanone with **160** gives a 1.3:1.0 mixture of the 1- and 3-diphenyl phosphate derivatives.[283] The regioselective preparation of ketol phosphates **161** can be achieved by the reaction of reagent **160** with terminal alkynes in aqueous acetonitrile (eq 86).[283]

The intermediates in this reaction (eq 86) are relatively stable iodonium salts **162** and **163**, which can be isolated pure and converted to phosphate

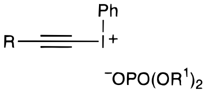


R = *i*-Pr, *t*-Bu, $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$, *cyclo*-$C_5H_9$, Ph

esters **161** by treatment with water in hot acetonitrile.[283]

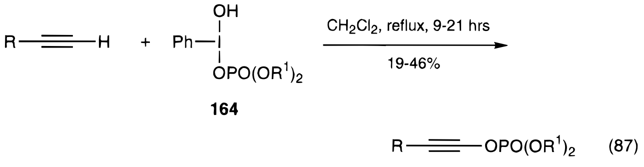


**162**



**163**, $R^1$ = Ph, Me, Et

Ethyl and methyl analogues of compound **160**, [hydroxy[[bis(alkyloxy)phosphoryl]oxy]iodo]benzenes (**164**), can be prepared in 99% yield by treatment of HTIB with the appropriate sodium dialkylphosphate in methanol.[284] These reagents (**164**) react with terminal alkynes under anhydrous conditions to afford alkynyl phosphates **165** (eq 87) via the intermediate formation of the respective alkynyl iodonium phosphates **163** ($R^1$ = Me, Et).[284]



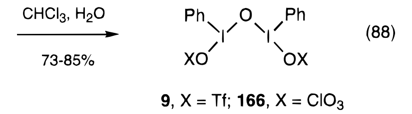
R = *t*-Bu, *s*-Bu, Bu; $R^1$ = Me, Et **165**

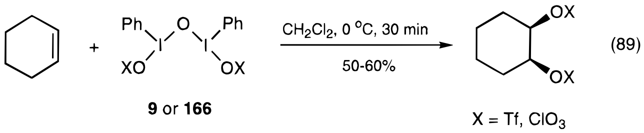
### 3. $\mu$-Oxo-bridged Iodanes

The structure of $\mu$-oxo-bridged iodanes, **131**, is typical for nitrates, sulfates, perchlorates, triflates, tetrafluoroborates, hexafluoroantimonates, and hexafluorophosphates. In older reports, some of these compounds, particularly, the nitrate and perchlorate, were incorrectly claimed to have the $PhIX_2$ structure.[5] However, more recent spectroscopic and X-ray studies revealed the $\mu$-oxo-bridged structure for all stable derivatives of strong inorganic acids.[230,231,285] These compounds are generally prepared by the reaction of $PhI(OAc)_2$ or PhIO with the respective acids or anhydrides.

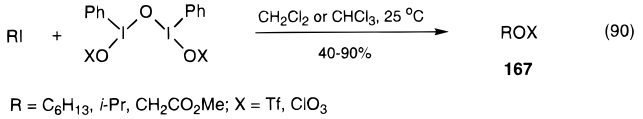
Triflate **9** and perchlorate **166** are prepared from (diacetoxyiodo)benzene and aqueous perchloric or trifluoromethanesulfonic acid (eq 88).[286] In a more convenient procedure triflate **9** can be generated in situ from PhIO and triflic anhydride (eq 3, see Section III.A.1).[69] Both triflate **9** and perchlorate **166** react with alkenes to afford *vic*-diperchlorates or ditriflates; in the case of cyclohexene this reaction proceeds as a stereospecific *syn*-addition (eq 89).[69,91,123,161]

Triflate **9**, generated in situ from PhIO and triflic anhydride, is a useful reagent for the preparation of various iodonium salts by reaction with the respective silylated or stannylated organic precursors (see Section IV). Propargylsilanes and -stannanes react with reagent **9** to afford *o*-propargyliodoarenes (**24**, eq 18) as a result of a reductive iodonio-Claisen rearrangement of the intermediate, unstable allenyliodanes similar to the one shown in eq 18 (see Section III.A.2). Mechanistic details of this reaction were investigated by Norton and co-workers.[57]



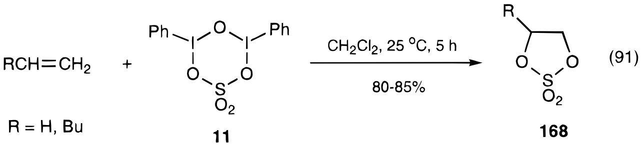


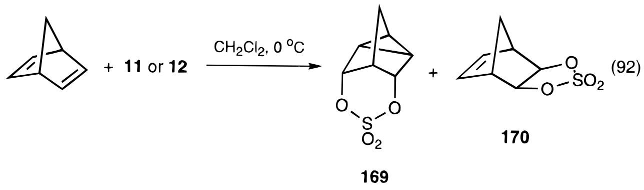
Iodoalkanes react with triflate **9** and perchlorate **166** to give the respective products of oxidative substitution of iodine **167** in good yield (eq 90).[286]

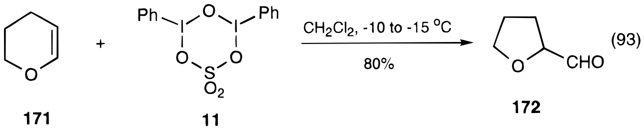


R = $C_6H_{13}$, *i*-Pr, $CH_2CO_2Me$; X = Tf, $ClO_3$

Sulfur trioxide can form two different adducts with PhIO (**11** and **12**) depending on the ratio of reactants (eq 5, see Section III.A.1).[73,91] Both sulfates **11** and **12** react with alkenes under mild conditions to give the respective cyclic sulfate esters, such as **168**–**170** (eqs 91 and 92).[73,91,287] Under similar conditions, reaction of dihydropyran **171** with reagent **11** results in a ring contraction to afford tetrahydrofurfural **172** (eq 93).[92]



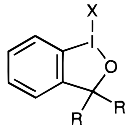




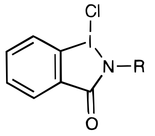
The newest representatives of $\mu$-oxo-bridged iodanes—derivatives of fluoroboric, fluoroantimonic, fluorophosphoric acids **69** (eq 43, see Section III.C.1)—can be prepared as yellow, microcrystalline solids by the treatment of $PhI(OAc)_2$ with aqueous solutions of the respective acids.[162,163] Small-scale operations with these reagents proved to be safe; however, large-scale preparation of the tetrafluoroborate resulted in a powerful explosion.[288] Reaction of reagents **69** with alkenes in the presence of external nucleophiles (methanol, acetic acid, lithium perchlorate) afford products of vicinal addition, while silyl enol ethers give 1,4-diketones due to oxidative coupling similar to eq 19 (see Section III.A.2).[162,163]

## E. Five-Membered Iodine(III) Heterocycles

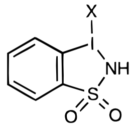
The overwhelming majority of known heterocyclic iodanes are derivatives of benziodoxole (**173**), with iodine and oxygen incorporated in the five-membered ring. A few examples of heterocyclic iodanes with other elements in five- or six-membered rings are represented by benziodazoles **174**,[289] benziodathiazoles **175**,[290] benziodoxathioles **176**,[291] cyclic phosphonate **177**,[292] and phosphate **178**.[293]



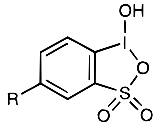
**173**



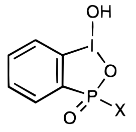
**174**, R = Cl, $CH_2CO_2Me$



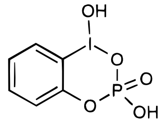
**175**, X = Cl, OH, OAc



**176**, R = H, Me



**177**, X = Me, OH

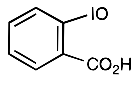


**178**

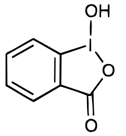
X-ray molecular structures were reported for a number of benziodoxole derivatives **173**,[294−298] as well as for benziodazoles **174**,[289] benziodoxathioles **176**,[291] and cyclic phosphonate **177** (X = Me).[292] The structural features of heterocyclic iodanes were thoroughly discussed in Koser's review[11] and the book by Varvoglis.[19] In general, the five-membered ring in heterocyclic iodanes is highly distorted with almost linear alignment of the two electronegative ligands. The I−O bond length in benziodoxoles **173** varies in a wide range from 2.11 Å in carboxylates (**173**, X = $m$-$ClC_6H_4CO_2$) to 2.48 Å in the phenyl derivative (**173**, X = Ph), which indicates considerable changes in the ionic character of this bond. The endocyclic C−I−O bond angle is typically around 80°, which is a significant deviation from the expected angle of 90° for the normal T-shaped geometry of hypervalent iodine.[294−298]

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[124] and also by better overlap of the lone pairs of electrons on the iodine atom with the $\pi$-orbitals of the benzene ring in **173**.[11,295] The greater stability of heterocyclic iodanes enables the isolation of otherwise unstable iodine(III) derivatives with I−Br, I−$N_3$, I−CN, I−OOR, and other bonds.

The most important and best investigated heterocyclic iodane is 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (**180**)—the cyclic tautomer of 2-iodosylbenzoic acid (**179**). The tautomeric form **180** gives the best representation for the actual structure of this compound, as indicated by its unusually low acidity (p$K_a$ 7.25 against 2.85 for the hypothetical 2-iodosylbenzoic acid (**179**)) and confirmed by X-ray analysis of **180** in the crystalline state.[294a] The I−O bond distance of 2.3 Å in the five-membered ring of **180** is significantly longer than the computed covalent I−O bond length of 1.99 Å, which indicates the highly ionic nature of this bond.

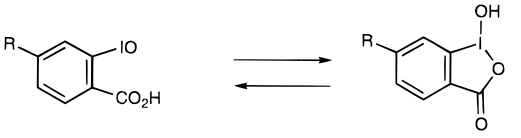


**179**



**180**

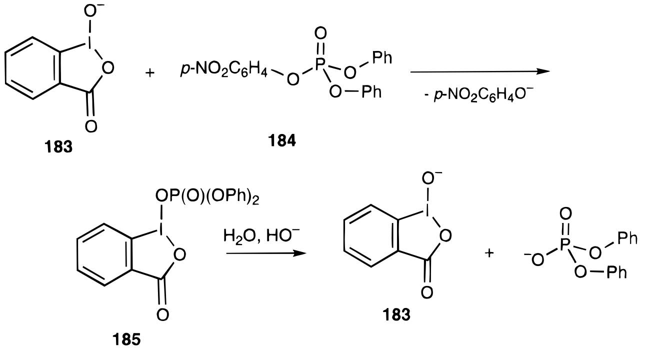
In the case of 4-alkyl-2-iodosylbenzoic acids both structural forms **181** and **182** (eq 94) can be isolated as individual compounds.[299]



**181** R = $C_3H_7$, $C_5H_{11}$ **182** (94)

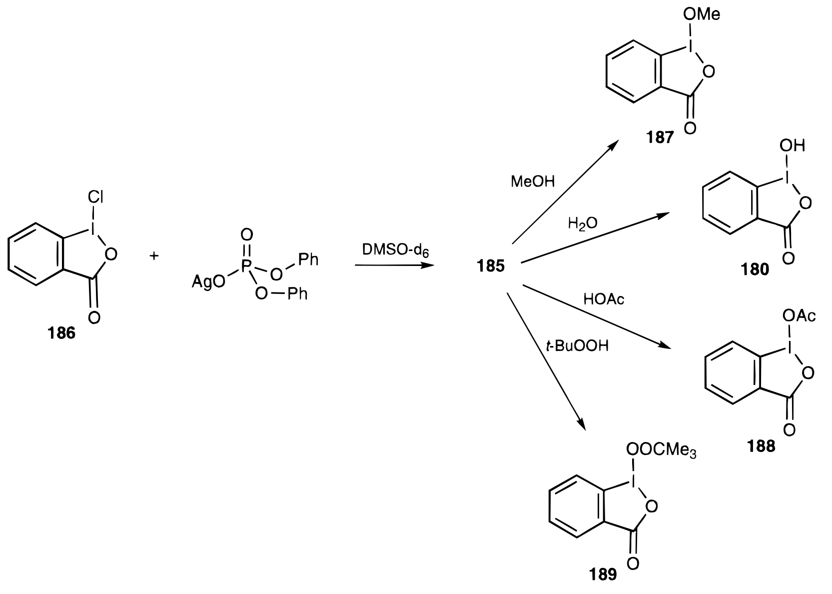
1-Hydroxy-1,2-benziodoxol-3(1*H*)-one (**180**) is commercially available or can be easily prepared by direct oxidation of 2-iodobenzoic acid or by basic hydrolysis of the respective iododichloride.[299,300] In the last 10 years benziodoxole **180** and its derivatives have attracted considerable research interest due to their excellent catalytic activity in the cleavage of toxic phosphates and reactive esters.[299,301−303] This activity is explained by a pronounced *O*-nucleophilicity of the benziodoxole anion **183** due to the α-effect. Spectral and kinetic mechanistic studies indicate that the highly unstable iodoxole derivatives, such as phosphate **185**, are the reactive intermediates in the catalytic cleavage of phosphates, as shown for the catalytic hydrolysis of a typical substrate **184** (Scheme 6).[302,303]

**Scheme 6**



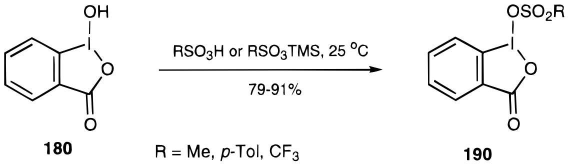
To prove this mechanism, Moss and co-workers have generated **185** in a DMSO-$d_6$ solution from chloride **186** and silver diphenyl phosphate, and investigated its NMR spectra and chemical reactions in situ (Scheme 7).[303] In particular, phosphate **185** in a DMSO solution is extremely sensitive to water, and instantaneously reacts with methanol, acetic

**Scheme 7**



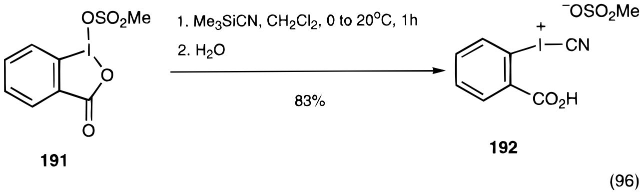
acid, or *tert*-butyl peroxide to afford the appropriate products of nucleophilic substitution (**187**−**189**).

Attempts to isolate phosphate **185** as a stable compound were unsuccessful; however, some other derivatives of strong acids, such as sulfonates **190**, are sufficiently stable and can be isolated as crystalline, moderately hygroscopic compounds (eq 95).[304]

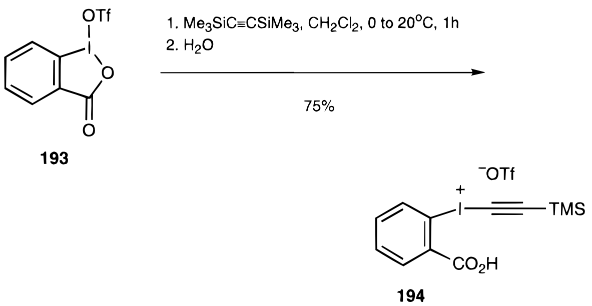


(95)

Like the other iodine(III) derivatives of strong acids (see Section III.D), sulfonates **190** are highly reactive toward unsaturated organic substrates and other carbon nucleophiles. As a representative example, mesylate **191** reacts with cyanotrimethylsilane with the formation of the cyanoiodonium salt **192** (eq 96), while the analogous reaction of triflate **193** with bis(trimethylsilyl)acetylene affords alkynyliodonium salt **194** (eq 97).[304]

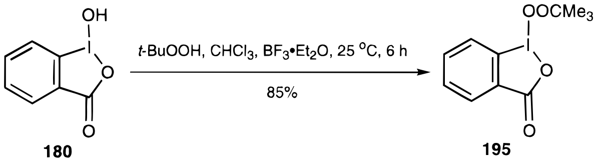


(96)

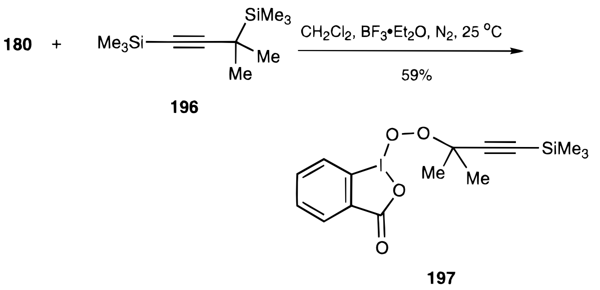


(97)

The stabilization effect due to the incorporation of the hypervalent iodine into a five-membered heterocycle made possible the isolation of several otherwise unstable iodine(III) derivatives. Bromoiodanes **64** and **66** (eqs 40 and 41; see Section III.B.3) represent typical examples of such a stabilization. Recently Ochiai and co-workers reported the preparation, X-ray structural investigation, and some chemical properties of (alkylperoxy)iodoxols **195** and **197** (eqs 98 and 99).[296,297] *tert*-Butylperoxyiodoxol **195** was prepared in high yield by treatment of benziodoxole **180** with *tert*-butyl hydroperoxide (eq 98),[296] while compound **197** was formed in an unusual reaction of **180** with silylated acetylene **196** in the presence of $BF_3{\cdot}Et_2O$ (eq 99).[297]



(98)

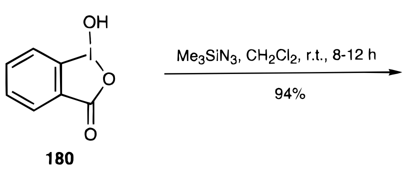


(99)

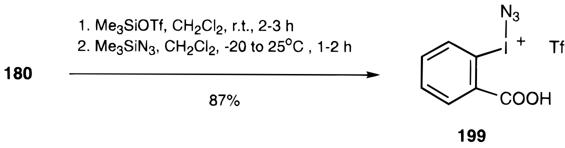
Both peroxides **195** and **197** are stable, crystalline products which can be stored at room temperature indefinitely. Peroxyiodane **195** is a strong oxidizer toward a variety of organic substrates, such as alkenes, organic sulfides, selenides, and phosphines.[296]

Azidoiodanes **198**, **199**, and **201** can be synthesized in one step by the reaction of iodoxoles **180** and **200** with trimethylsilyl azide in dichloromethane (eqs 100−102).[305]

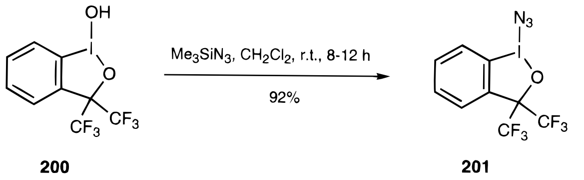
All three azides (**198**, **199**, and **201**) are thermally stable, nonexplosive crystalline solids; the molecular



(100)



(101)



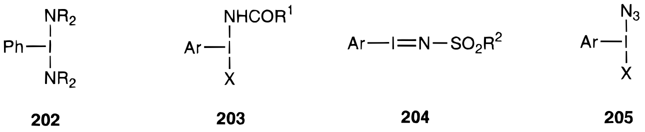
(102)

structure of compound **201** was confirmed by X-ray analysis.[298] These compounds are potentially useful reagents for direct azidonation of various organic substrates under free-radical conditions (see Section III.F.3).

The analogous cyanobenziodoxoles are prepared by treatment of benziodoxoles **180** and **200** with cyanotrimethylsilane and can serve as useful cyanating reagents (see Section IV.A).

## F. Derivatives with I−N Bonds

Iodanes with I−N bonds are generally less common than those with I−O bonds. Most of these compounds lack stability and are sensitive to moisture. In addition to the previously discussed benziodazoles **174** and benziodathiazoles **175** (see Section III.E), four more structural types of iodine(III) derivatives with one carbon ligand and one or two I−N bonds are known (structures **202**−**205**).

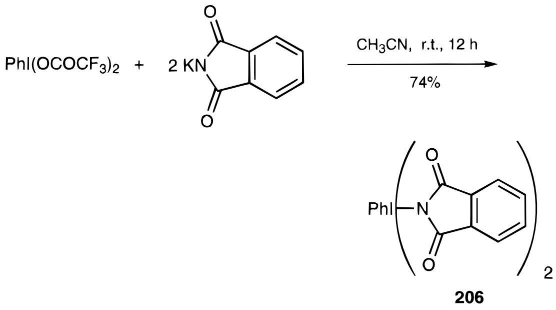


$NR_2$ = phthalimidate, succimidate, saccharinate;
$R^1$, $R^2$ = alkyl, aryl; X = OTs, OCOR, etc.; Ar = Ph, 2-$O_2CC_6H_4$

The first two structures (**202** and **203**) are amidoiodanes, the third (**204**) is an imidoiodane, an analogue of iodosylarenes, and the fourth (**205**) is an azide. One more representative, isocyanate PhI(NCO)OTf lacks stability, but may be generated from PhIO and appropriate trimethylsilyl derivatives (eq 2, see Section III.A.1).[59]

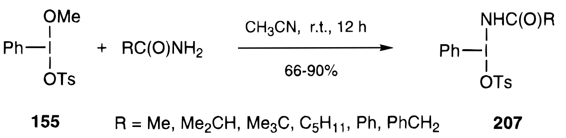
### 1. Amidoiodanes

The only known amidoiodanes with two *N*-ligands at iodine (**202**) are derivatives of cyclic imides, such as phthalimide, succinimide, glutarimide, and saccharine.[306,307] For example, the thermally stable, but water-sensitive, bis(phthalimidate) **206** can be prepared by the treatment of [bis(trifluoroacetoxy)iodo]benzene with potassium phthalimidate in acetonitrile (eq 103).[306]



(103)

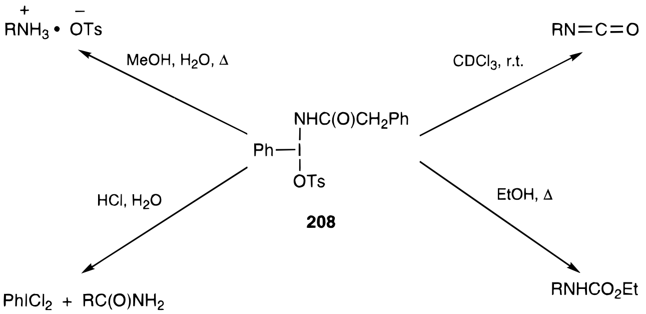
Amidoiodanes bearing one *N*-ligand at iodine (**203**) are plausible intermediates in the Hofmann-type degradation of amides with [bis(acyloxy)iodo]arenes or [hydroxy(tosyloxy)iodo]benzene (see Section III.D.1).[259] In most cases, these intermediates are highly unstable and instantaneously rearrange at room temperature with loss of iodobenzene to give isocyanates. However, *N*-phenyliodonio carboxamide tosylates **207** can be isolated as relatively stable, crystalline products in the reaction of [methoxy(tosyloxy)iodo]benzene (**155**) with amides (eq 104).[261]



(104)

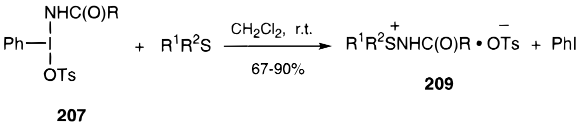
Koser and co-workers have investigated some chemical reactions of amidoiodane **208** (Scheme 8).

**Scheme 8**



In particular, it decomposes in a $CDCl_3$ solution under anhydrous conditions at room temperature with the formation of benzyl isocyanate or gives the ammonium salt upon decomposition in the presence of water. Concentrated hydrochloric acid converts compound **208** to dichloroiodobenzene and the respective amide.[261]

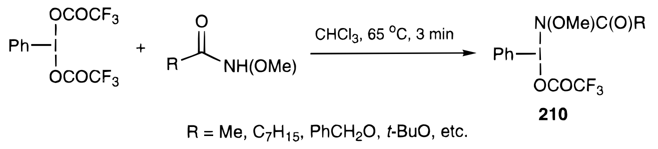
Amidoiodanes **207** react with organic sulfides to afford amidosulfonium tosylates **209** in good yield (eq 105).[278]



(105)

R = Me, Ph, $PhCH_2$, 4-$MeC_6H_4$; $R^1$,$R^2$ = Me, 4-$BrC_6H_4$

The unstable amidoiodanes **210** can be generated by the reaction of BTI with *N*-methoxyamides (eq 106).[279]



(106)

These species (**210**) react with arenes in situ to afford the respective *N*-aryl-*N*-methoxyamides in high yield.[279]

## 2. Iminoiodanes

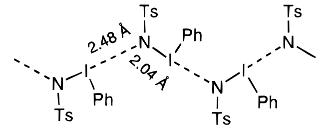
Iminoiodanes, ArI=NR, are formal analogues of iodosylbenzene. Several examples of [imino(iodo)]-arenes were reported in the literature—*N*-tosyl-,[308,309] *N*-(methylsulfonyl)oxy-,[310] and *N*-(trifluoroacetyl)- derivatives.[311] All known iminoiodanes were prepared by the reaction of (diacetoxyiodo)arenes with the respective amides under basic conditions. For example, the *N*-trifluoroacetyl derivative **211** precipitates from a basic methanolic solution of the amide and DIB at −40 °C (eq 107).[311]

$$PhI(OAc)_2 + CF_3C(O)NH_2 \xrightarrow{\text{KOH, MeOH, -40 °C}} PhI{=}NC(O)CF_3 \quad (107)$$

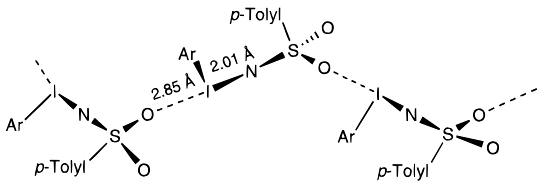
**211**

*N*-(Trifluoroacetyl)iminoiodane **211** and *N*-(methylsulfonyl)iminoiodanes are relatively unstable and explosive; however, the tosylate derivatives are stable, crystalline compounds which can be stored for extended periods.

Single-crystal X-ray structural data have recently been reported for several *N*-tosyliminoiodanes, namely, $PhI{=}NTs$,[309] 2,4,6-$Me_3C_6H_2I{=}NTs$,[309] and 2-$MeC_6H_4I{=}NTs$.[312] Similar to iodosylarenes (structure **6**, see Section III.A.), iminoiodanes have a linear polymeric, asymmetrically bridged structure with the expected T-shaped geometry around the iodine centers. In the case of PhINTs, the monomeric units are bridged by I−N interactions (structure **212**), while in the more sterically hindered 2,4,6-$Me_3C_6H_2INTs$ the bridging atom is the oxygen of the tosyl group (structure **213**).[309] The structure of 2-$MeC_6H_4I{=}NTs$ is intermediate between the structures **212** and **213**: it can form two different polymorphic modifications, one with nitrogen and the second with oxygen as the bridging atom in the polymeric chain.[312] A polymeric, nitrogen-bridged structure was determined for amorphous 4-$MeC_6H_4I{=}NTs$ by X-ray powder diffraction and EXAFS analyses.[43]

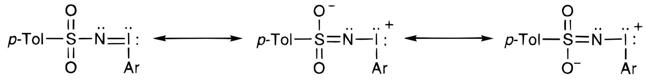


**212**



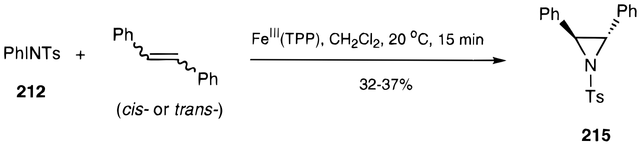
**213**, Ar = 2,4,6-$Me_3C_6H_2$

The intramolecular I−N distance of 2.01−2.04 Å in *N*-tosyliminoiodanes is consistent with a single bond and the structures are probably best represented by resonance forms **214b** and **214c** with the positive charge at iodine and the negative charge at the oxygens.



**214a** **214b** **214c**

[[*N*-(*p*-Tolylsulfonyl)imino]iodo]benzene (**212**) has recently found some synthetic application mainly as a nitrene precursor in various reactions.[311,313−320] Mansuy and co-workers first described the aziridination of alkenes with iminoiodane **212** in the presence of iron- or manganese porphyrins. This reaction has a mechanism similar to the metal-catalyzed oxygen atom transfer reactions of iodosylbenzene (see Section III.A.2) and involves a metal−nitrene complex as the intermediate; however, the stereochemical result of aziridination is usually different from epoxidation of alkenes with PhIO. For example, the aziridination of both *cis*- or *trans*-stilbenes gives exclusively the same *trans*-diphenylaziridine **215** (eq 108), while the epoxidation of *cis*-stilbene under similar conditions is a stereospecific *syn*-addition.[311]



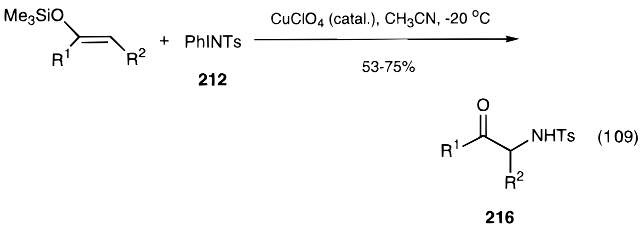
TPP = tetraphenylporphyrin

(108)

Evans and co-workers have further investigated the aziridination of alkenes using copper salts as catalysts.[313−315] Both electron-rich and electron-deficient alkenes react with iminoiodane **212** in the presence of copper(I) perchlorate or copper(II) acetylacetonate in acetonitrile at room temperature to afford the respective aziridines in yields ranging between 55 and 95%.[313] The stereochemical result of these reactions varies depending both on the nature of the alkene and the copper catalyst employed. For example, the aziridination of *cis*-$\beta$-methylstyrene with **212** in the presence of $Cu(ClO_4)_2$ gives exclusively the *cis*-aziridine, while the same reaction catalyzed by $CuBr_2$ affords predominantly the *trans*-adduct. In general, the reactions of unfunctionalized alkyl substituted alkenes in the presence of an appropriate copper catalyst proceed as a stereospecific *syn*-addition, which supports the concerted mechanism for the aziridination.[314,315]

Under similar conditions, silyl enol ethers react with iminoiodane **212** in the presence of copper(I) perchlorate to afford $\alpha$-tosylamino ketones **216** in good yield (eq 109).[313,314]

Reactions of iminoiodane **212** with alkenes can also be catalyzed by Lewis acids, such as boron trifluoride. Reaction of polycyclic triene **217** with reagent **212** in the presence of $BF_3$−etherate affords products **218** and **219** (eq 110), the structures of which were determined by X-ray analysis.[321,322] The formation

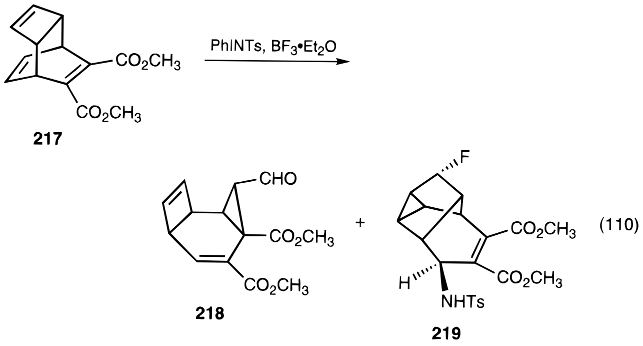


(109)

**212** **216**

$R^1, R^2$ = H, Me, Ph, Bu; $R^1 + R^2 = (CH_2)_4$, etc.

of products of skeletal rearrangement under these conditions supports the carbocationic mechanism of the reaction.



(110)

**217** **218** **219**

Trialkylboranes **220** react with iminoiodane **212** to give tosylamines **221** in good to excellent yields (eq 111).[323]

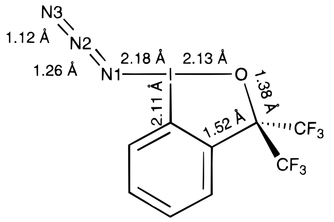
$$\underset{\mathbf{212}}{\mathrm{PhINTs}} + \underset{\mathbf{220}}{\mathrm{R_3B}} \xrightarrow[\text{60-99\%}]{\text{1. THF, r.t., 3 h; 2. } H_2O} \underset{\mathbf{221}}{\mathrm{RNHTs}} + \mathrm{PhI} \qquad (111)$$

### 3. Azidoiodanes

Azidoiodanes, $PhI(N_3)X$ (X = OAc, Cl, OTMS, etc.) or $PhI(N_3)_2$, were proposed as reactive intermediates in the widely used azidonation reactions involving the combination of PhIO or $PhI(OAc)_2$ with trimethylsilyl azide or $NaN_3$.[324-337] Attempts to isolate these intermediates always resulted in fast decomposition at −25 to 0 °C with the formation of iodobenzene and dinitrogen; however, low-temperature spectroscopy and the subsequent chemical reactions in situ provided some experimental evidence toward the existence of these species.

The first systematic study of the structure and reactivity of the unstable, acyclic azidoiodanes was attempted by Zbiral and co-workers in the early 1970s.[324,325] In particular, the IR spectroscopic measurements at −60 to 0 °C indicated the existence of $PhI(OAc)_{2-n}(N_3)_n$ species in the mixture of $PhI(OAc)_2$ with trimethylsilyl azide.[324] Interestingly, the absorption band of 2040 $cm^{-1}$ for the azido group in $PhI(OAc)_{2-n}(N_3)_n$ is very close to the absorption stretch of 2046−2048 $cm^{-1}$ in the stable, heterocyclic azidoiodanes **198** and **201** (eqs 100 and 102; see Section III.E).

The structure of the heterocyclic azidoiodane **201** was unambiguously established by a single-crystal X-ray analysis.[298] The structural data revealed the expected hypervalent iodine, distorted T-shaped geometry, with the N1−I−O bond angle of 169.5(2) degrees. The lengths of the bonds to the iodine atom, I−N (2.18 Å), I−O (2.13 Å), and I−C (2.11 Å), all have similar values, and generally are within the range of typical single covalent bonds in organic derivatives of polyvalent iodine. For example, the endocyclic I−N bond length in benziodazoles **174** is 2.06−2.14 Å,[289] while the I−O bond length in benziodoxoles **173** varies in a wide range from 2.11 Å to 2.48 Å (see Section III.E).



**201**

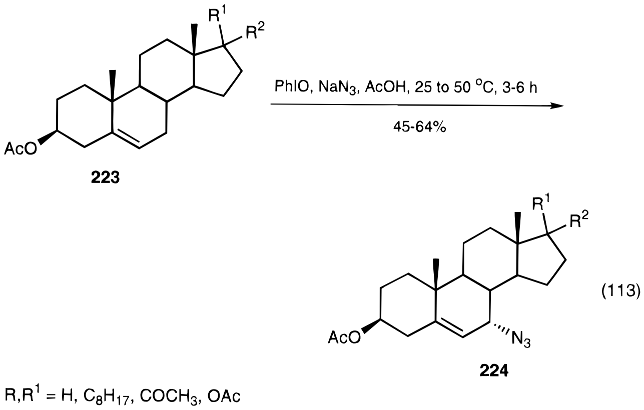
The unstable and highly reactive azidoiodanes generated in situ from $PhIO/TMSN_3$, $PhI(OAc)_2/NaN_3$, or $PhI(OAc)_2/TMSN_3$ have found some practical application as efficient reagents for the introduction of the azido function into organic molecules.[50-56,324-337] Zbiral and co-workers first investigated the reactions of the $PhI(OAc)_2/TMSN_3$ system with alkenes leading to diazides, α-azido ketones, or nitriles.[324,325] Later, Moriarty and co-workers developed a convenient experimental procedure for the preparation of vicinal diazides **222** from alkenes by reaction with $PhIO/NaN_3$ in acetic acid (eq 112).[326]

$$\mathrm{RCH{=}CHR^1} + \mathrm{PhIO} + \mathrm{NaN_3} \xrightarrow[\text{34-85\%}]{\text{AcOH, 25 to 50 °C, 2-3 h}} \underset{\mathbf{222}}{\mathrm{RCH(N_3)CH(N_3)R^1}}$$

$R,R^1$ = H, Ph, Me, $(CH_2)_4$, etc.

(112)

This reaction (eq 112) has predominantly *anti*-stereoselectivity; in several cases α-azido ketones were isolated as byproducts.[326] Steroids **223** under the same conditions gave exclusively allylic azides **224** (eq 113).[327]



(113)

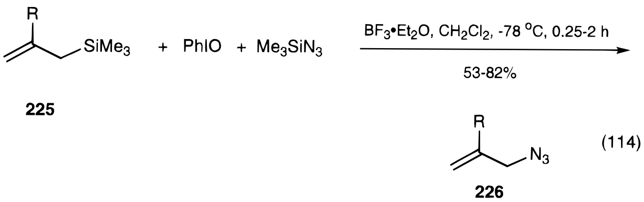
**223** **224**

$R,R^1$ = H, $C_8H_{17}$, $COCH_3$, OAc

Ochiai and co-workers developed a simple method for the synthesis of allyl azides **226** from allyltrimethylsilanes **225** utilizing the $PhIO/TMSN_3/BF_3 \cdot Et_2O$ combination (eq 114).[54]

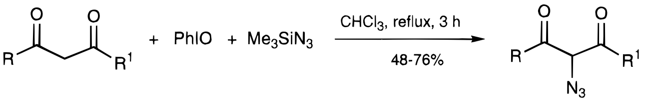
Treatment of β-dicarbonyl compounds **227** with $PhIO/TMSN_3$ in chloroform at reflux affords azides **228** in moderate to good yield (eq 115).[55] Under similar conditions, 2-(trimethylsiloxy)furan gives azidofuranone **229** as the main product (eq 116).[56]

Aromatic compounds, such as anisoles and alkylbenzenes, can be azidated in the ring by treatment

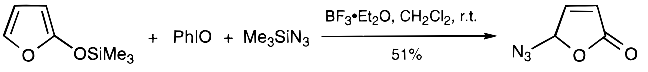


**225** **226** (114)

R = alkyl, cycloalkyl

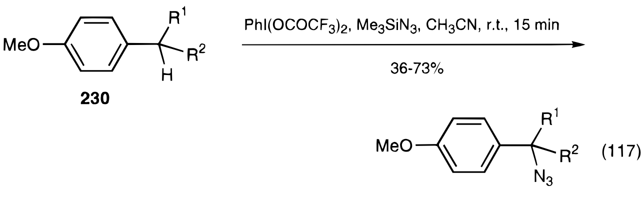


**227** R = Me, Ph; R1 = Me, OMe, OEt **228** (115)



**229** (116)

with $PhI(OCOCF_3)_2/TMSN_3$ in hexafluoropropanol.[328] This reaction does not involve azidoiodanes as reactive intermediates, but proceeds via cation radicals generated by single-electron transfer from a charge-transfer complex of the aromatic substrate with $PhI(OCOCF_3)_2$.[329] However, it is possible to change the course of this reaction by using acetonitrile instead of hexafluoropropanol as a solvent. Treatment of *p*-alkylanisols **230** with $PhI(OCOCF_3)_2/TMSN_3$ under these conditions affords arylalkyl azides **231** in reasonable yields (eq 117).[330]

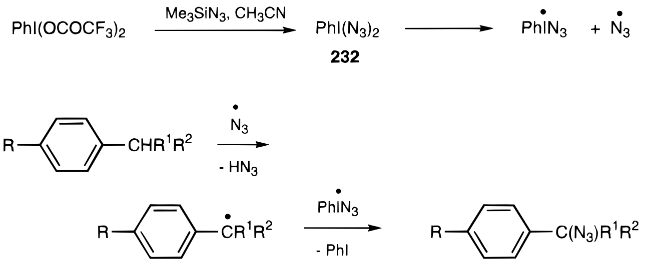


**230** **231** (117)

$R^1,R^2$ = H, alkyl, cycloalkyl, CN, SMe, $CO_2CH_3$, etc.

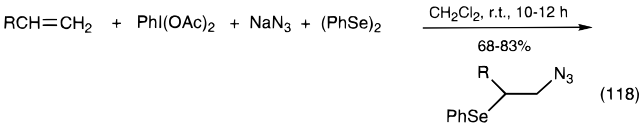
Kita and co-workers proposed a free-radical mechanism for this reaction (eq 117) involving the initial formation of azidoiodane **232** and its subsequent homolytic decomposition (Scheme 9).[330] Additional

**Scheme 9**



experimental evidence supporting the generation of azide radicals in the thermal decomposition of azidoiodanes formed from $PhI(OAc)_2/NaN_3$ was reported by Fontana and co-workers.[331]

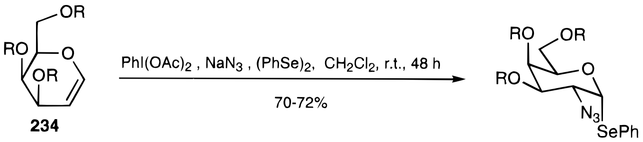
Alkenes react with $PhI(OAc)_2/TMSN_3$ in the presence of diphenyl diselenide to produce vicinal azido selenides **233** in good yield (eq 118).[332] This azido–phenylselenation reaction proceeds with complete anti-Markovnikov regioselectivity, which can be explained by assuming that the addition process is initiated by the azido radicals.



**233** (118)

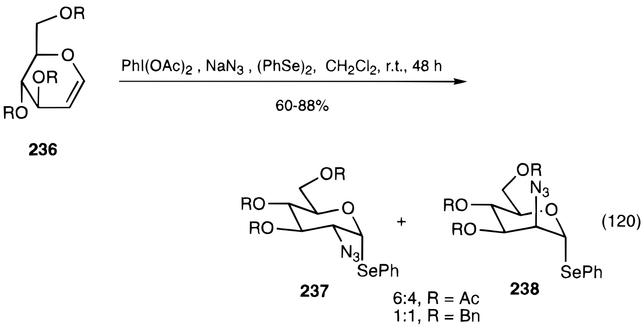
R = alkyl, aryl, cycloalkyl, etc.

The anti-Markovnikov azido–phenylselenation of protected galactals **234** under similar conditions proceeds as a stereospecific *anti*-addition to afford exclusively α-galacto isomer **235** (eq 119), while the analogous glucals **236** give both products of *anti*- and *syn*-addition (**237** and **238**) (eq 120).[333]



**234** **235** (119)

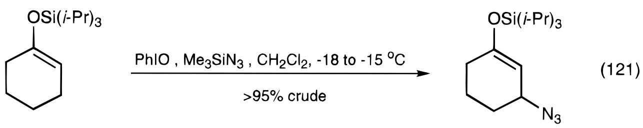
R = Ac, Bn



**236** **237** **238** (120)

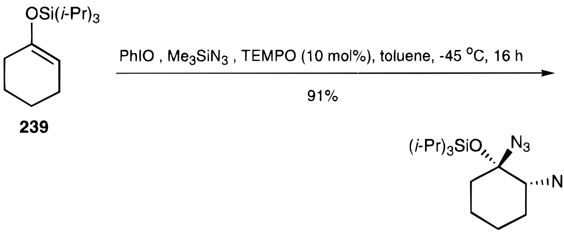
R = Ac, Bn

Recently Magnus and co-workers reported several new, synthetically useful azidonations with the PhIO/$TMSN_3$ combination, which presumably serves as the source of nonisolable azidoiodanes $PhI(N_3)_2$ or $PhI(N_3)OTMS$.[50−53,334−336] Various triisopropylsilyl enol ethers **239** react with this reagent at −15 to −18 °C to give the β-azido adducts (**240**) in excellent yields (eq 121).[52,53]



**239** **240** (121)

While examining the scope of the β-azidonation of triisopropylsilyl enol ethers, Magnus and co-workers found a dramatic effect of temperature on this reaction. The same reaction of silyl ether **239** with PhIO/$TMSN_3$ at lower temperatures (−78 °C) gave vicinal *trans*-diazide **241** as the major product.[52,53] Further examination of this reaction revealed that the addition of catalytic amounts of the stable radical TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) can be used to increase the yield of vicinal diazides (eq 122).[335] The effect of TEMPO on the outcome of this reaction (eqs 121 and 122) was explained by the change of the mechanism from ionic dehydrogenation to a radical addition process in the presence of TEMPO.[335]



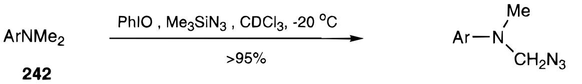
239

241

(122)

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

*N*,*N*-Dimethylarylamines **242** are cleanly converted into azidomethylene derivatives **243** with the PhIO/ $TMSN_3$ reagent combination (eq 123).[51]



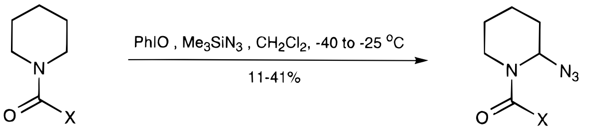
242

243

(123)

Ar = Ph, 3-$MeOC_6H_4$, 4-$MeC_6H_4$, 2,4,6-$Me_3C_6H_4$, etc.

Amides, carbamates, and ureas can also be α-azidated under similar conditions; however, the yields of azides in this case are generally lower.[50,336] For example, the piperidine derivatives **244** are converted to the azides **245** at −40 to −25 °C in only moderate yield (eq 124) with some starting material remaining in the reaction mixture.



244

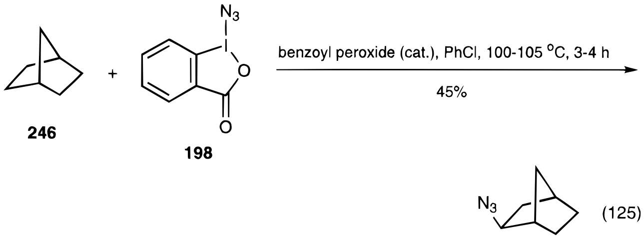
245

(124)

X = Me, *t*-BuO, Ph, $NPh_2$, OPh, 4-$NO_2C_6H_4$, etc.

Raising the temperature in this reaction (eq 124) above −20 °C leads to even lower yields of products due to the rapid destruction of the intermediate azidoiodanes. The problem of instability of the reactive intermediates in azidonation reactions can be overcome by the use of more stable azidoiodanes, such as azidobenziodoxoles (**198** and **201**). Magnus and co-workers first reported that the 2-iodosylbenzoic acid/$TMSN_3$ combination can be used as an azidating reagent even under reflux conditions in $CH_2Cl_2$ due to the greater stability of the reactive intermediates. Carrying out azidonations with 2-iodosylbenzoic acid/$TMSN_3$ at higher temperatures generally leads to a significant improvement of the yield of azidonation products in the reactions of amides and other deactivated substrates.[50]

The thermally stable azidobenziodoxoles **198** and **201** are especially useful reagents for the azidonation of generally unreactive substrates. These reagents at high temperatures can even be applied to polycyclic hydrocarbons. Norbornane (**246**) reacts with azidoiodane **198** in the presence of a radical initiator to afford *exo*-2-azidonorbornane (**247**) as the principal product (eq 125).[338] Similar reactions of adamantane (**248**) and 1,3-dimethyladamantane (**250**) with reagents **198** or **201** afford the respective tertiary azidoadamantanes **249** and **251** in good yield (eq 126).[338]

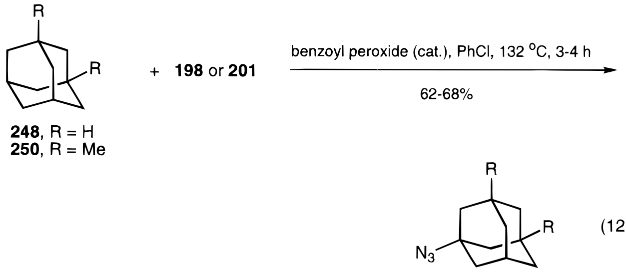


246

198

247

(125)



**248**, R = H
**250**, R = Me

**249**, R = H
**251**, R = Me

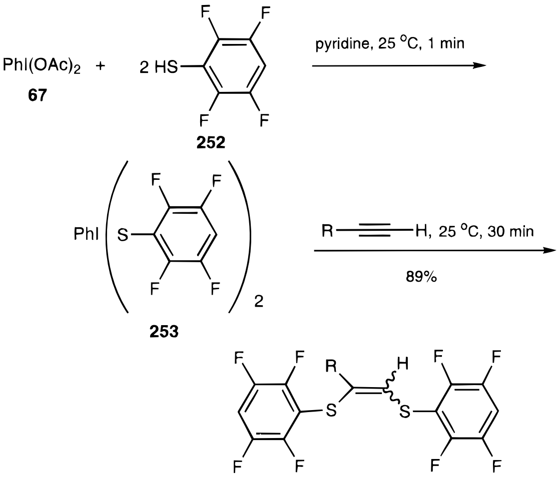
(126)

## G. Derivatives with Other Iodine–Element Bonds

The overwhelming majority of the known organic compounds of polyvalent iodine have halogen, oxygen, or nitrogen attached to the organoiodine fragment. To our knowledge, the only other elements, which can form relatively stable organoiodine derivatives are boron in the carborane ligand and divalent sulfur.

Carboranyl(aryl)iodonium derivatives having one I−C and one I−B bond are generally very similar to diaryl iodonium salts. The preparation and chemistry of carboranyliodonium salts was recently reviewed by Grushin.[339]

No organoiodine derivative $ArIX_2$ with an I−S bond was isolated as a stable compound. However, such species were proposed as reactive intermediates in several reactions.[13,135,340] In a recent example, Kita and co-workers generated bis(arylthio)iodobenzene **253** from 2,3,5,6-tetrafluorothiophenol **252** and DIB (**67**) in pyridine at room temperature. A sequential reaction of **253** with alkynes afforded 1,2-bis(arylthio)ethenes **254** as a mixture of (*E*) and (*Z*)-isomers (eq 127).[340]



67

252

253

254

(127)

R = EtO, *t*-BuO, PhS, Ph, $C_6H_{13}$

Only electron-deficient thiophenol **252** can form a relatively stable iodine(III) derivative, while a similar reaction of DIB with nonsubstituted PhSH affords only diphenyl disulfide.[340] The recently reported direct sulfenylation of phenol ethers using $PhI(OCOCF_3)_2$/ArSH in hexafluoropropanol does not involve bis(arylthio)iodobenzene, but proceeds via a nucleophilic attack of thiophenol on a cation radical intermediate.[341a]

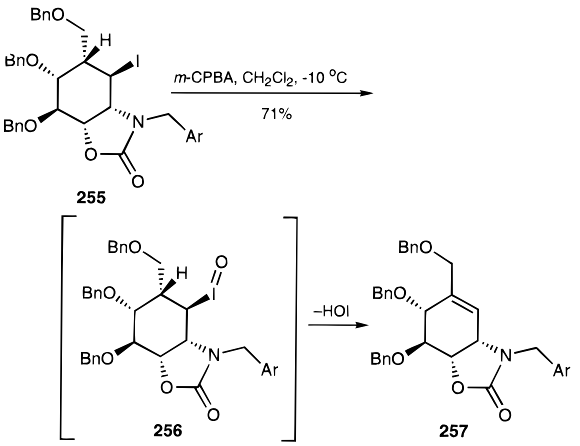
A number of stable iodonium salts, $Ar_2IX$, with a sulfur ligand X are also known.[341b,c]

## H. Iodine(III) Species with One $sp^3$-Carbon Ligand

Derivatives of polyvalent iodine with an alkyl (R) substituent at iodine, $RIX_2$, generally are highly unstable and can exist only as short-lived reactive intermediates in the oxidations of alkyl iodides. For example, the low-temperature reaction of iodomethane with chlorine results in the formation of a yellow precipitate of (dichloroiodo)methane which rapidly decomposes above −28 °C.[5] However, the introduction of an electron-withdrawing substituent, such as perfluoroalkyl- or sulfonyl- groups, into the alkyl moiety leads to a significant stabilization of the molecule. For example, 1-(dichloroiodo)-1*H*,1*H*-perfluoroalkanes, $R_fCH_2ICl_2$,[342,343] and (dichloroiodo)methyl sulfones, $RSO_2CH_2ICl_2$,[344] are known, stable representatives of this structural type. A higher thermal stability was also reported for *cis*-iodosylcyclopropanecarboxylic acid, in which the trivalent iodine is stabilized due to incorporation into a five-membered ring.[345]

### *1. Alkyl Iodosyl Derivatives as Intermediates in the Oxidation of Alkyl Iodides*

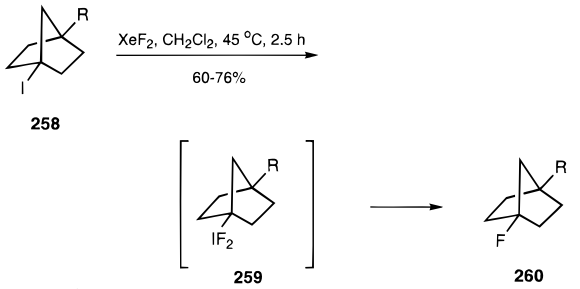
Alkyl iodides can be readily oxidized with a variety of oxidizing agents to afford either products of elimination, or the products of oxidatively assisted nucleophilic substitution of iodine. Both pathways involve alkyl iodosyl derivatives as reactive intermediates. The elimination pathway generally occurs in reactions of alkyliodides with peracids in a nonnucleophilic solvent, such as dichloromethane.[346−348] Reich and Peake first demonstrated that the elimination proceeds with *syn*-stereochemistry and have also proposed iodosylalkanes as reactive intermediates in this reaction.[346] Recently, the Reich iodosyl *syn*-elimination was used in several syntheses as a very mild and selective alternative elimination method to the standard selenoxide and sulfoxide protocols. Knapp and co-workers applied iodosyl elimination to prepare unsaturated oxazolidinone **257** (eq 128), the key intermediate in the synthesis of valienamine.[347] This reaction proceeds via oxidation of starting iodide **255** to the intermediate iodosyl compound **256**, which spontaneously eliminates HOI to afford product **257**.



(128)

Kim and Fuchs applied the Reich iodosyl *syn*-elimination for the preparation of intermediate steroidal units of cephalostatin 7.[348]

The second pathway of oxidative deiodination of alkyliodides involves nucleophilic substitution of the oxidized iodine moiety. In fact, functionalities containing polyvalent iodine (e.g. $-IX_2$) are among the best leaving groups.[349] For example, the normally unreactive 1-iodonorbornane can be readily transformed into 1-bromonorbornane by reaction with bromine via $S_N1$ substitution in the intermediate $RIBr_2$.[349] Recently, Della and Head developed a convenient procedure for the preparation of bridgehead fluorides **260** by the analogous fluorodeiodination of 1-iodonorbornanes **258** and other bridgehead iodides by reaction with xenon difluoride (eq 129).[350] A plausible mechanism of this reaction involves the intermediate formation of unstable difluoroiodides **259** and its subsequent decomposition by an $S_N1$ mechanism.



(129)

R = H, $CO_2Me$

Even very weak nucleophiles, such as perchlorate and triflate anions, can participate in the oxidatively assisted nucleophilic substitution of iodine.[351−353] Oxidation of alkyl iodides **261** in the presence of lithium perchlorate or tetrabutylammonium sulfonates in nonnucleophilic solvents affords the respective alkyl perchlorates or sulfonates **262** as principal products (eq 130).[256]

$$\underset{\mathbf{261}}{\mathrm{RI}} + \mathrm{M^+X^-} \xrightarrow[\text{30-96\%}]{\text{Oxidant, CH}_2\text{Cl}_2\text{ or AcOEt, −78 to 40 °C, 0.1 to 24 h}} \underset{\mathbf{262}}{\mathrm{RX}} \qquad (130)$$

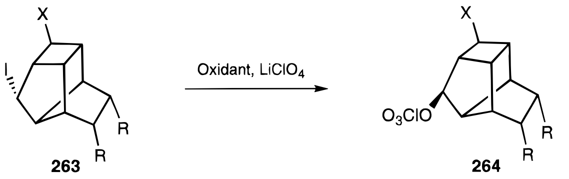
RI = MeI, $C_6H_{13}I$, 2-$C_3H_7I$, $CH_2I_2$, $I(CH_2)_6I$, $PhCOCH_2I$, $ICH_2CO_2H$, $ICH_2CO_2Me$, *cyclo*-$C_6H_{11}I$

$M^+X^-$ = $LiClO_4$, $Bu_4NClO_4$, $Bu_4NOTf$, $Bu_4NOTs$, $Bu_4NOSO_2Me$, $Bu_4NOSO_2F$

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

The oxidatively assisted nucleophilic substitution of iodine with perchlorate anion in primary and secondary substrates most likely has an $S_N2$ mechanism as indicated by the stereochemistry of this reaction in the polycyclic substrates **263** (eq 131).[353]

Treatment of alkyl iodides with peracids in the presence of water results in oxidatively assisted hydrolysis and the formation of alcohols.[346] This reaction can be applied as a useful synthetic method for the mild hydrolysis of iodides; for example, iodide

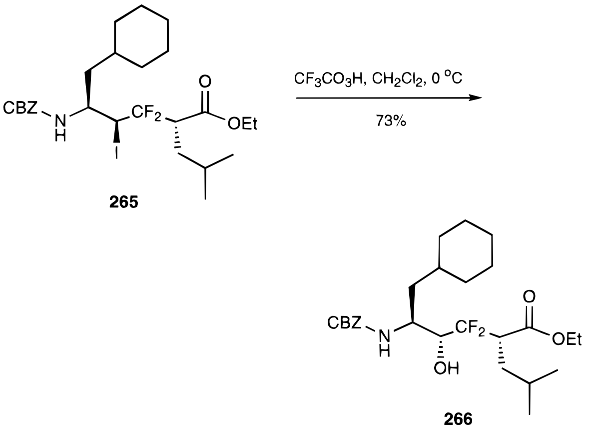


**263** **264** (131)

X = Br, 2,4-$(NO_2)_2C_6H_3S$, 2,4-$(NO_2)_2C_6H_3SO_2$, 2,4-$(NO_2)_2C_6H_3SO$; R = Me, $CO_2Me$

Oxidant = $Cl_2$, $NO_2BF_4$, $PhI(OCOCF_3)_2$

**265** undergoes facile stereospecific hydrolysis to the protected amino alcohol **266** under neutral conditions upon exposure to 10 equiv of buffered peroxytrifluoroacetic acid (eq 132).[354]



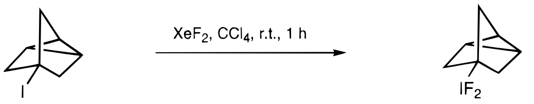
**265** **266** (132)

CBZ = benzyl carbamate

Similar to the oxidatively assisted nucleophilic substitution of iodine with perchlorate anion (eq 131), the oxidatively assisted hydrolysis of alkyl iodides (eq 132) results in a complete inversion of configuration, which indicates an $S_N2$ mechanism of substitution in the iodine(III) intermediate in this reaction.

## 2. Stable Alkyl and Fluoroalkyl Iodosyl Derivatives

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. A typical example of such a stabilization due to structural features is illustrated by the preparation of 4-(iodosyl)tricyclene derivatives by Morris and co-workers.[355,356] Difluoride **268** was prepared in the form of a pale yellow solid by treatment of a solution of 4-iodotricyclene **267** in carbon tetrachloride with an excess of xenon difluoride followed by removal of solvent (eq 133).[356]

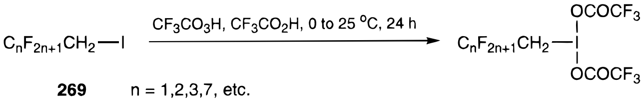


**267** **268** (133)

Similarly, reaction of 4-iodotricyclene with *m*-CPBA affords the respective 4-[bis-[(*m*-chlorobenzoyl)oxy]iodo]tricyclene as a stable, microcrystalline compound.[355]

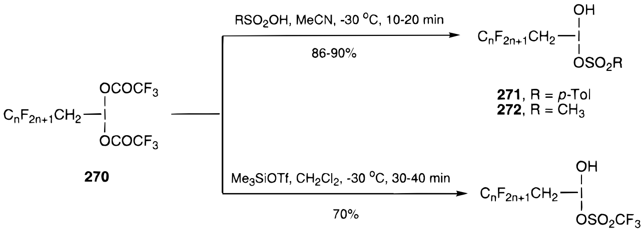
Historically, the first example of a stable alkyliodosyl derivative was represented by (dichloroiodo)methyl sulfones, $RSO_2CH_2ICl_2$, the stability of which was explained by the strong electron-withdrawing properties of the sulfonyl group combined with its bulk.[344] More recent examples of alkyliodosyl derivatives, stabilized due to electron-withdrawing substituents, include the derivatives of 1-iodo-1*H*,1*H*-perfluoroalkanes, $R_fCH_2IX_2$,[342,343,357–360] and 1-iodoperfluoroalkanes, $R_fIX_2$.[361–366]

Four types of derivatives of 1-iodo-1*H*,1*H*-perfluoroalkanes are known: bis(trifluoroacetates) $R_fCH_2I(CO_2CF_3)_2$,[357–359] difluorides $R_fCH_2IF_2$,[358] dichlorides $R_fCH_2ICl_2$,[342,343] and hydroxysulfonates, $R_fCH_2I(OH)OSO_2R$.[360] Bis(trifluoroacetates) **270** are prepared in almost quantitative yield by the oxidation of 1-iodo-1*H*,1*H*-perfluoroalkanes **269** with peroxytrifluoroacetic acid (eq 134).[357,359]



**269** **270** (134)

Trifluoroacetates **270** can be converted to sulfonates **271** and **272** (eq 135) by treatment with *p*-toluenesulfonic or methanesulfonic acid, respectively.[360] In contrast to the starting trifluoroacetates **270**, sulfonates **271** and **272** have a substantially higher thermal stability with a melting point at about 124 °C without decomposition. Both tosylate **271** and mesylate **272** are not water sensitive, can be purified by crystallization from acetonitrile, and can be stored for several months in a refrigerator. The analogous triflate **273** was prepared in a 70% yield by the reaction of trifluoroacetate **270** with trimethylsilyl triflate in dichloromethane (eq 135) and isolated as a colorless, stable, nonhygroscopic solid.[360]

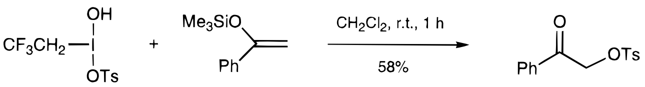


**270**

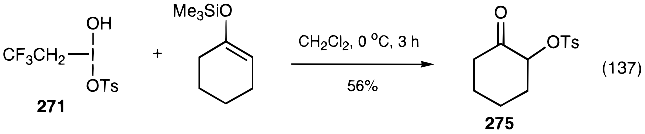
**271**, R = *p*-Tol
**272**, R = $CH_3$

**273** (135)

The reactivity pattern of sulfonates **271**–**273** is analogous to Koser's reagent, PhI(OH)OTs. Similar to its phenyl-substituted analogue, compound **271** is highly reactive toward electron-rich organic substrates, such as silyl enol ethers. Reactions of tosylate **271** with silyl enol ethers of acetophenone and cyclohexanone afford α-tosyloxy ketones **274** (eq 136) and **275** (eq 137) as major products.[360]



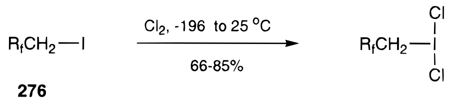
**271** **274** (136)



**271** **275** (137)

Triflate **273** can serve as a convenient precursor to trifluoroethyl(aryl)iodonium salts by reaction with trimethylsilylarenes under very mild conditions (see Section IV.E).[360,367]

Montanari and DesMarteau recently reported the synthesis of stable 1-(dichloroiodo)-1*H*,1*H*-perfluoroalkanes **277** by the direct chlorination of the respective iodides **276** (eq 138).[342,343]

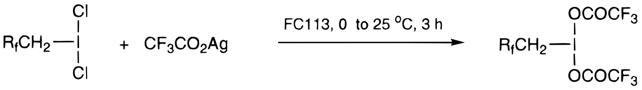


$$R_fCH_2{-}I \xrightarrow[66\text{-}85\%]{Cl_2,\ -196\ \text{to}\ 25\ ^\circ C} R_fCH_2{-}ICl_2 \qquad (138)$$

**276** **277**

$R_f = CF_3, C_2F_5, C_3F_7, H(CF_2)_6$

Dichlorides **277** show low sensitivity to moisture or light and can be stored for two to three weeks at room temperature in the dark. Treatment of chlorides **277** with silver trifluoroacetate affords the respective bis(trifluoroacetates) **278** in good yield (eq 139).[342,343]



$$R_fCH_2{-}ICl_2 + CF_3CO_2Ag \xrightarrow{FC113,\ 0\ \text{to}\ 25\ ^\circ C,\ 3\ h} R_fCH_2{-}I(OCOCF_3)_2$$

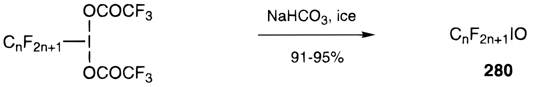
**277** $R_f = CF_3, C_2F_5, C_3F_7, H(CF_2)_6$ **278**

(139)

Like the analogous (dichloroiodo)benzene (see Section III.B.2), dichlorides **277** are effective chlorinating reagents. They convert unhindered alkenes into the respective vicinal dichlorides with *syn* stereochemistry; $\beta$-diketones and $\beta$-keto esters are also readily chlorinated by these reagents at room temperature in chloroform.[343]

Another important structural class of stable alkyliodosyl compounds is represented by the derivatives of 1-iodosylperfluoroalkanes, $R_fIX_2$.[361−366] Four types of these compounds are known: difluorides $R_fIF_2$,[74,366] bis(trifluoroacetates) $R_fI(CO_2CF_3)_2$,[361,372] hydroxy sulfonates $R_fI(OH)OSO_2R$,[363−365] and iodosylperfluoroalkanes $R_fIO$.[74,367]

Bis(trifluoroacetates), $R_fI(CO_2CF_3)_2$, were originally prepared by Yagupolskii and co-workers in almost quantitative yield by oxidation of 1-iodoperfluoroalkanes with peroxytrifluoroacetic acid.[361] These compounds have found practical application for the preparation of perfluoroalkyl(phenyl)iodonium salts, which are used as electrophilic fluoroalkylating reagents (FITS reagents).[368] Bis(trifluoroacetates) **279** can be converted to difluorides $R_fIF_2$ by reaction with $SF_4$, or hydrolyzed to iodosylperfluoroalkanes **280** (eq 140).[74,367]

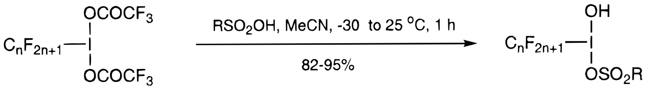


$$C_nF_{2n+1}{-}I(OCOCF_3)_2 \xrightarrow[91\text{-}95\%]{NaHCO_3,\ ice} C_nF_{2n+1}IO \qquad (140)$$

**279** n = 2, 3, 4, 6 **280**

Iodosylperfluoroalkanes **280** are yellow, amorphous solids, insoluble in water and common organic solvents, which is most likely explained by a polymeric structure similar to iodosylbenzene. Similar to iodosylbenzene, they can be used for the preparation of iodonium salts; however, their low thermal stability restricts their practical application.[367]

[Hydroxy(sulfonyloxy)iodo]perfluoroalkanes **281** and **282** are conveniently prepared by treatment of trifluoroacetates **279** with methanesulfonic acid or with the monohydrate of *p*-toluenesulfonic acid in acetonitrile (eq 141).[363−365]



$$C_nF_{2n+1}{-}I(OCOCF_3)_2 \xrightarrow[82\text{-}95\%]{RSO_2OH,\ MeCN,\ -30\ \text{to}\ 25\ ^\circ C,\ 1\ h} C_nF_{2n+1}{-}I(OH)OSO_2R$$

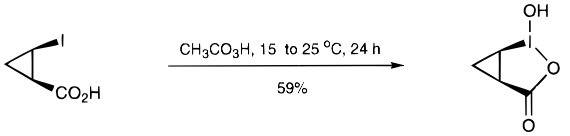
**279** n = 2-8

**281**, R = *p*-Tol
**282**, R = $CH_3$

(141)

In contrast to the starting trifluoroacetates **279**, products **281** and **282** have substantially higher thermal stability. These compounds are not water sensitive, can be purified by crystallization from acetonitrile, and can be stored indefinitely at room temperature. The analogous triflates can be prepared in high yields by the reaction of trifluoroacetates **279** with trimethylsilyltriflate in trifluoroacetic acid and isolated as white, hygroscopic solids. [Hydroxy(sulfonyloxy)iodo]perfluoroalkanes **281** and **282** are useful reagents for the preparation of perfluoroalkyl(aryl)iodonium sulfonates by the reaction with arylsilanes (see Section IV.E).[363−365]

A new, interesting example of a stable aliphatic iodosyl compound, *cis*-iodosylcyclopropanecarboxylic acid **284**, was reported by Moss and co-workers.[345] This moderately stable, but hygroscopic product is best prepared by oxidation of *cis*-iodosylcyclopropanecarboxylic acid (**283**) with peracetic acid (eq 142).[345]



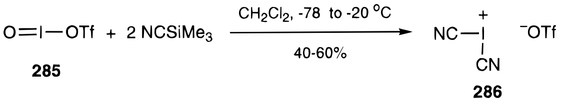
**283** **284** (142)

## IV. Derivatives of Iodine(III) with Two Carbon Ligands

According to conventional classification iodonium salts are defined as positively charged 8-I-2 species with two carbon ligands and a negatively charged counter ion, $R_2I^+ X^-$. A large variety of such compounds are known and an overwhelming majority of them have at least one aryl group as a ligand. The most common and well investigated class of these compounds are diaryliodonium salts, known for over 100 years and extensively covered in previous reviews.[5−8,11] In the last 10−15 years several new structural classes of iodonium species have been synthesized, most important of these are the aryliodonium derivatives bearing cyano-, alkynyl-, alkenyl-, or fluoroalkyl groups as the second ligand.

## A. Cyanoiodonium Salts

Three structural types of cyanoiodanes are known (dicyano)iodonium triflate, $(CN)_2IOTf$,[369,370] [cyano[(organosulfonyl)oxy]iodo]arenes, $ArI(CN)OSO_2R$,[59,151,371] and 1-cyanobenziodoxoles.[304,372] (Dicyano)iodonium triflate **286** can be prepared by the reaction of iodosyl triflate **285** with cyanotrimethylsilane in methylene chloride (eq 143). Crystalline **286** is thermally unstable and air sensitive; it completely decomposes at room temperature in 2–5 min with the formation of cyanogen iodine, ICN, and explodes when exposed to air. However, it can be stored at −20 °C under nitrogen for several days.[369]

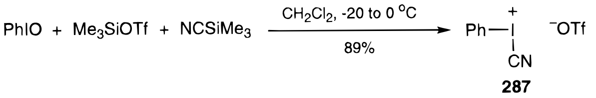


$$O{=}I{-}OTf + 2\,NCSiMe_3 \xrightarrow[\text{40-60\%}]{CH_2Cl_2,\ -78\ \text{to}\ -20\ ^{\circ}C} NC{-}\overset{+}{\underset{CN}{I}}\ {}^{-}OTf \qquad (143)$$

**285** **286**

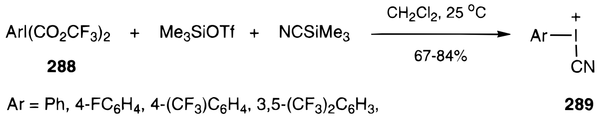
Despite its high instability, cyanide **286** can be used in situ for the very mild and efficient preparation of various bis(heteroaryl)iodonium salts by an iodonium transfer reaction with the respective stannylated heteroarenes (see Section IV.D.1).[369]

[Cyano[(organosulfonyl)oxy]iodo]arenes **287** and **289** are generally prepared by reactions of iodosylbenzene or bis(trifluoroacetates) **288** with trimethylsilyl triflate and cyanotrimethylsilane (eqs 144 and 145). Cyanides **289** are relatively stable, white microcrystalline solids that decompose over several days at room temperature, but may be stored for extended periods in a refrigerator without change.[59,151]



$$PhIO + Me_3SiOTf + NCSiMe_3 \xrightarrow[\text{89\%}]{CH_2Cl_2,\ -20\ \text{to}\ 0\ ^{\circ}C} Ph{-}\overset{+}{\underset{CN}{I}}\ {}^{-}OTf \qquad (144)$$

**287**



$$ArI(CO_2CF_3)_2 + Me_3SiOTf + NCSiMe_3 \xrightarrow[\text{67-84\%}]{CH_2Cl_2,\ 25\ ^{\circ}C} Ar{-}\overset{+}{\underset{CN}{I}}\ {}^{-}OTf$$

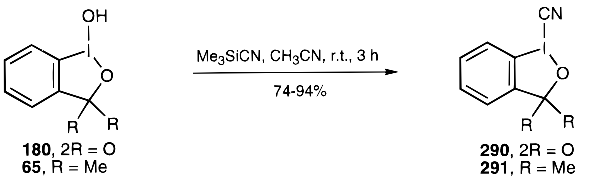
**288** **289**

Ar = Ph, 4-FC$_6$H$_4$, 4-(CF$_3$)C$_6$H$_4$, 3,5-(CF$_3$)$_2$C$_6$H$_3$,

(145)

Recently, phenyl(cyano)iodonium triflate **287** has found practical application as especially useful iodonium-transfer reagent in the synthesis of various alkynyliodonium and alkenyliodonium salts (see Sections IV.B and C).

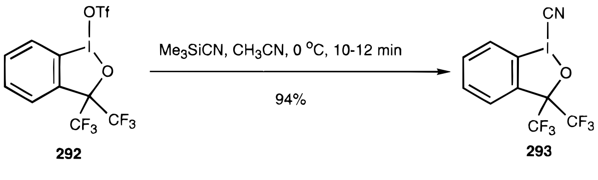
Cyanobenziodoxoles **290**, **291**, and **293** represent the most stable structural type of cyanoiodanes. Compounds **290** and **291** can be prepared in one step by the reaction of cyanotrimethylsilane with the respective 1-hydroxybenziodoxoles **180** or **65** (eq 146), while cyanoiodane **293** is best prepared starting from triflate **292**, which in turn is easily synthesized from trimethylsilyl triflate and the appropriate benziodoxole (eq 147).[372]



**180**, 2R = O
**65**, R = Me

**290**, 2R = O
**291**, R = Me

(146)

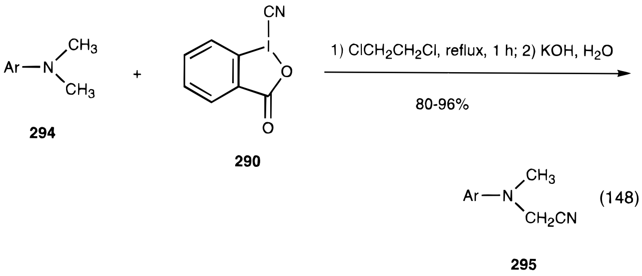


**292** **293**

(147)

All three adducts (**290**, **291**, and **293**) were isolated as thermally stable white, microcrystalline solids. The structure of heterocyclic cyanoiodane **293** was unambiguously established by a single-crystal X-ray analysis.[373] The structural data revealed a distorted T-shaped geometry expected for hypervalent iodine with a NC–I–O bond angle of 169.5°. The lengths of the bonds to the iodine atom, I–CN (2.167 Å), I–O (2.117 Å), and I–Ph (2.112 Å), all have similar values and generally are within the range of typical single covalent bond lengths in organic derivatives of polyvalent iodine. However, the endocyclic I–O bond in **293** is significantly shorter than usual in C-substituted benziodoxole derivatives, while the I–CN bond is slightly longer.

The reactivity pattern of cyanobenziodoxoles is different from cyanoiodonium salts **286** and **289**. In particular, cyanobenziodoxoles **290**, **291**, and **293** generally do not react as iodonium transfer reagents, but serve as efficient cyanating reagents. For example, cyanobenziodoxole **290** reacts with *N*,*N*-dimethylanilines (**294**) in dichloroethane at reflux to afford the respective *N*-(cyanomethyl)-*N*-methylanilines (**295**) in excellent yields (eq 148).[372]



**294** **290** **295**

Ar = Ph, 4-BrC$_6$H$_4$, 4-MeC$_6$H$_4$, 1-naphthyl

This reactivity pattern (eq 148) is similar to that of azidoiodanes, which can serve as efficient azidonating reagents toward a variety of organic substrates including *N*,*N*-dimethylanilines (see Section III.F.3).

## B. Alkynyliodonium Salts

Alkynyl(phenyl)iodonium salts **296** are relatively recent members of the family of polyvalent organic iodine species.[11,24,25] Beringer and Galton[374] first attempted to prepare these salts via interaction of PhICl$_2$ with lithium phenylacetylide (eq 149). However, due to the relative nucleophilicity of the chloride counterion in **296**, it decomposed in a few hours at room temperature into 1:1 mixture of iodobenzene and phenyl chloroacetylene. Merkushev and coworkers[168] reported the formation of the crystalline, stable, albeit hygroscopic, species **297** but characterized it only by its infrared absorption and hydrolysis product **298** (eq 150).

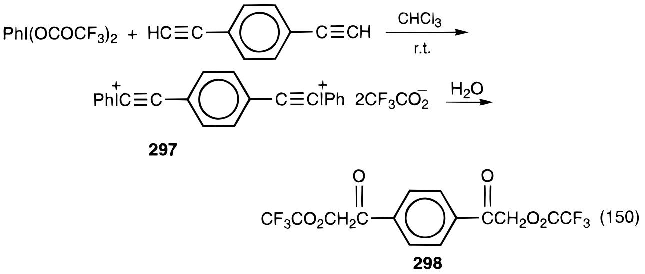
$$RC{\equiv}C\overset{+}{I}Ph\ X^{-}$$

**296**: X = OTs, OTf, BF$_4$

$$PhC{\equiv}CLi + PhICl_2 \xrightarrow{-LiCl} PhC{\equiv}C\overset{+}{I}Ph\ Cl^{-} \qquad (149)$$

**296**

The first[235] preparation of fully characterized, stable alkynyliodonium salts was Koser and coworkers' report[243–245] of the formation of tosylates **296** (X = OTs) via the interaction of HTIB with terminal alkynes (eq 72, see Section III.D.1) in the early 1980s.



From then on this area developed rapidly and alkynyl(phenyl)iodonium salts **296** have become "electrophilic acetylene" equivalents par excellence.

### 1. Preparation, Structure, and Properties

An improved, modified[375,376] variant of Koser's procedure allows the preparation of alkynyliodonium tosylates in better yields. However, the most efficient and common way of preparing[60−68,377−380] alkynyliodonium salts **296** is interaction of a sila- or stannaacetylene with an electrophilic iodine reagent. Key reagents are PhIO, HTIB, the $\mu$-oxo-bridged species **9** and the cyano(phenyl)iodonium triflate **287**.

Interaction of a large variety of $\beta$-functionalized alkynylstannanes[381,382] with **287** provides ready access to diverse $\beta$-functionalized alkynyliodonium salts **299** (eq 151) in 42−89% isolated yields.[66] This procedure allows the preparation[60,61] of the novel bisiodonium species **300** and **301** (eqs 152 and 153).

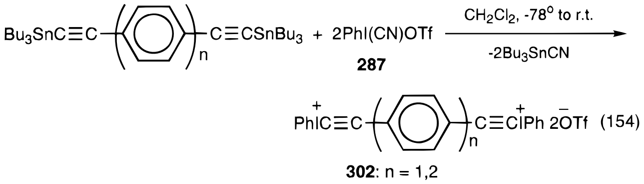
$$\mathrm{YC{\equiv}CSnR_3 + \underset{\mathbf{287}}{PhI(CN)OTf} \xrightarrow[-42^\circ\ to\ 20^\circ\ C]{CH_2Cl_2} \underset{\mathbf{299}}{YC{\equiv}C\overset{+}{I}Ph\ \overset{-}{O}Tf} + R_3SnCN} \qquad (151)$$

Y = CN, Cl, ArSO$_2$, RC(O)-, R$_2$NC(O)-, etc.

$$\mathrm{Bu_3SnC{\equiv}CSnBu_3 + 2\underset{\mathbf{287}}{PhI(CN)OTf} \xrightarrow[-30^\circ\ to\ -20^\circ C]{CH_2Cl_2,\ N_2} \underset{\mathbf{300}}{Ph\overset{+}{I}C{\equiv}C\overset{+}{I}Ph\ 2\overset{-}{O}Tf}} \qquad (152)$$

$$\mathrm{Me_3SnC{\equiv}C{-}C{\equiv}CSnMe_3 + 2\underset{\mathbf{287}}{PhI(CN)OTf} \xrightarrow[-30\ ^\circ C]{CH_2Cl_2,\ N_2} \underset{\mathbf{301}}{Ph\overset{+}{I}C{\equiv}C{-}C{\equiv}C\overset{+}{I}Ph\ 2\overset{-}{O}Tf}} \qquad (153)$$

Likewise, this procedure is applicable to the synthesis[63] of both conjugated **302** (eq 154) and unconjugated **303** (eq 155) bisiodonium salts. Diynyl(phenyl)iodonium triflates **304** (eq 156) have also been prepared[68] by the use of **287**. In contrast, reaction of either **9** or activated PhIO with silaacetylenes afford[377−380] only $\beta$-alkyl- or aryl-substituted alkynyliodonium salts **305** and **306** (eqs 157 and 158).



**302**: n = 1,2

$$\mathrm{Bu_3SnC{\equiv}C{-}\!\left(CH_2\right)_n\!{-}C{\equiv}CSnBu_3 + 2\underset{\mathbf{287}}{PhI(CN)OTf} \xrightarrow[-2Bu_3SnCN]{CH_2Cl_2,\ -78^\circ\ to\ r.t.} Ph\overset{+}{I}C{\equiv}C{-}\!\left(CH_2\right)_n\!{-}C{\equiv}C\overset{+}{I}Ph\ 2\overset{-}{O}Tf} \qquad (155)$$

**303**: n = 2, 4, 5, 6, 8

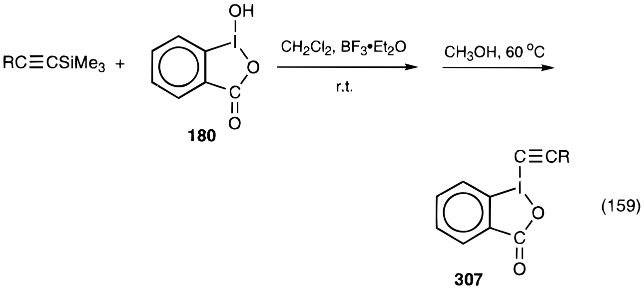
$$\mathrm{RC{\equiv}C{-}C{\equiv}CSnBu_3 + \underset{\mathbf{287}}{PhI(CN)OTf} \xrightarrow[-40\ ^\circ C]{CH_2Cl_2} \underset{\mathbf{304}}{RC{\equiv}C{-}C{\equiv}C\overset{+}{I}Ph\ \overset{-}{O}Tf}} \qquad (156)$$

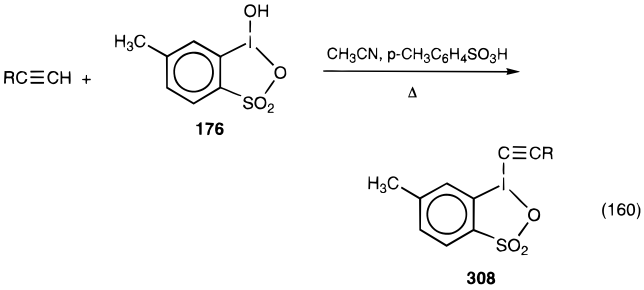
R = Me, *n*-Bu, *t*-Bu, Ph, Me$_3$Si

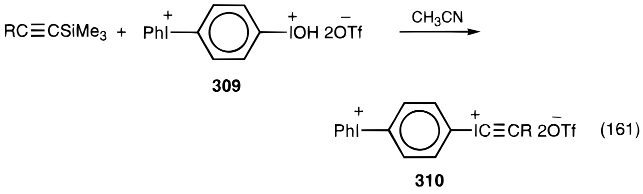
$$\mathrm{RC{\equiv}CSiMe_3 + \underset{\mathbf{9}}{Ph\overset{OTf}{\overset{|}{I}}{-}O{-}\overset{OTf}{\overset{|}{I}}Ph} \xrightarrow{CH_2Cl_2\ 0\ ^\circ C\ to\ r.t.} \underset{\mathbf{305}}{RC{\equiv}C\overset{+}{I}Ph\ \overset{-}{O}Tf}} \qquad (157)$$

$$\mathrm{RC{\equiv}CSiMe_3 + PhIO \xrightarrow[or\ Et_2OBF_3,\ NaBF_4]{Et_3O^+BF_4^-,\ CH_2Cl_2} \underset{\mathbf{306}}{RC{\equiv}C\overset{+}{I}Ph\overset{-}{B}F_4}} \qquad (158)$$

Heterocyclic alkynyliodonium species have been reported. Reaction of silaalkynes with **180** in CH$_2$Cl$_2$ in the presence of BF$_3$−etherate, followed by heating in CH$_3$OH at 60° affords[295] the stable cyclic salts **307** (eq 159). Likewise, reaction of just terminal alkynes with **176** in the presence of *p*-toluenesulfonic acid gives[291] the intramolecular, alkynyliodonium salts **308** (eq 160). Treatment of silaalkynes with **309** (prepared from PhIO + 2CF$_3$SO$_3$H) in CH$_3$CN results[383] in the bis-iodonium *p*-phenylene ditriflate **310** (eq 161). The preparation of dialkynyliodonium **311** salts has also been reported[384] (eq 162).







$$\mathrm{2RC{\equiv}CSiMe_3 + O{=}IOSO_2CF_3 \xrightarrow[-\ (Me_3Si)_2O]{CH_2Cl_2,\ -78^\circ\ to\ r.t.} \left(RC{\equiv}C\right)_2\overset{+}{I}\ \overset{-}{O}Tf} \qquad (162)$$

**311** R = *t*-Bu, Me$_3$Si, *i*-Pr$_3$Si

Several X-ray molecular structure determinations for alkynyliodonium salts have been reported.[66,247,295,378,384,385] The data are all consistent with the pseudo-trigonal bipyramidal, or T-shaped geometry, of 8-I-2 species discussed in section II. In all known cases the aryl group occupies an equatorial positions whereas the alkynyl moiety and the counterion occupy apical positions. The alkynyl−I bond length is 2.0 ± 0.01 Å. The I−O distances vary from 2.34 to 2.69 Å. The $C_{sp}$−I−O bond angles vary from 166° to 172° and the $C_{sp^2}$−I−$C_{sp}$ bond angles are between 90° and 95°.

Alkynyliodonium salts **296** also have very characteristic spectral features. They show weak IR absorption due to the C≡C bond between 2120 and 2190 $cm^{-1}$. Most diagnostic are the C-13 signals with the $C_\alpha$ resonances between 20 and 40 ppm (due to the heavy atom effect of iodine) and the $C_\beta$ resonances between 110 and 120 ppm compared to the usual acetylenic carbon signals of 60−90 ppm. The downfield shift of the $C_\beta$ signals is due to the resonance induced electron deficiency by the $I^+Ar$ moiety: $RC\equiv C-I^+Ar \leftrightarrow RC^+=C=IAr$. Likewise, the carbon signals of the aromatic group in **296** are affected by the iodonium moiety. Specifically, the ipso-carbon is shifted upfield in the range of 110 ppm due again to the heavy atom effect of the I atom, whereas the remaining carbon signals are downfield shifted by 20−30 ppm compared to iodobenzene.

Pure alkynyliodonium salts are microcrystalline solids soluble only in nonnucleophilic polar solvents, the best being acetonitrile. Their stability is dependent upon both the counterions and the β-substituent on the alkyne. The less nucleophilic the counterion the more stable the alkynyl iodonium species. Hence, the order of stability of alkynyliodonium salts, as a function of counter ion is approximately: $CH_3CO_2^- < C_6H_5CO_2^- < Cl^- < (RO)_2PO_2^- < CF_3CO_2^- < CH_3SO_3^- \cong ArSO_3^- < ClO_4^- \cong BF_4^- \cong CF_3SO_3^-$. Therefore, the most commonly used and stable species are the alkynyliodonium triflates, tetrafluoroborates, and tosylates.

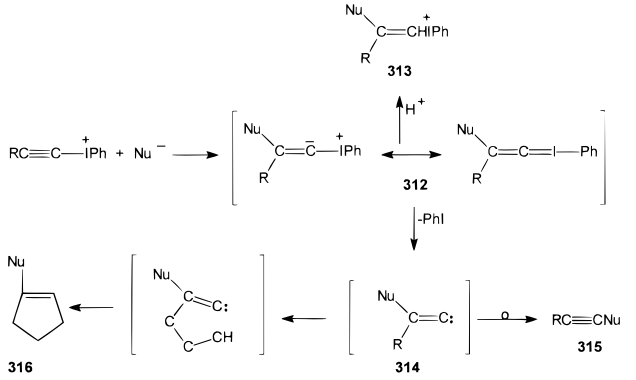
The parent ethynyliodonium salts and alkyl-substituted ones are the most stable and may be stored indefinitely as pure solids in a refrigerator. The β-functionalized, **299**, and bis-iodonium species **302** and **303** are somewhat less stable, but can be isolated, fully characterized and stored cold (in pure form) for several days. The stability of **304** and **311** are strongly dependent on the steric bulk of R, with the bulkier R the most stable. The least stable species is the 1,4-bis-iodonium butadiyne **301** that rapidly decomposes above −20° and hence is best used in situ.

### 2. Reactions and Uses

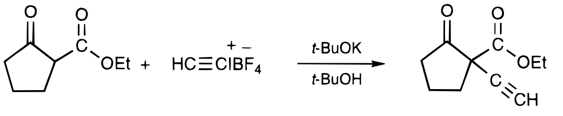
The inductive electron-withdrawing ability of iodine, as measured by the Taft inductive parameter, is $\sigma_I = 0.39$. In contrast $\sigma_I = 0.85$ for $-I(OAc)_2$, $\sigma_I = 1.17$ for $-ICl_2$ and $\sigma_I = 1.24$ for $PhI^+BF_4^-$ (with $PhI^+OTf^-$ similar).[386] The powerful inductive electron-withdrawing ability of the iodonium moiety imparts unique reactivity to alkynyliodonium salts **296**. Specifically, alkynyliodonium salts serve as electrophilic acetylene equivalents in reactions with a wide variety of nucleophiles, as well as excellent cycloaddition partners in Diels−Alder and 1,3-dipolar cycloaddition processes.

Only “soft” nucleophiles react well with alkynyliodonium salts **296**; “hard” nucleophiles such as simple enolates, alkoxides, alkyllithiums, etc., give only decomposition products. Although the reasons for these empirical observations are not yet understood a possible rationalization may be that hard nucleophiles attack directly on the positive iodine moiety or react by some yet unknown process, whereas soft nucleophiles react via an acetylene addition−elimination process. In the case of “soft” nucleophiles all available evidence indicates that the first step of the reaction is a Michael addition to the electron-deficient β-carbon to form an ylide **312** (Scheme 10).[24] In the presence of a ready proton source ylide **312** may be protonated to yield the stable vinyliodonium salt **313**. In most cases ylide **312** undergoes loss of iodobenzene (analogous to loss of $N_2$ from diazonium ions) to give the well-known[387,388] alkylidenecarbene **314** as an intermediate (Scheme 10). If either of the two β-substituents of **314** is an atom or group with a high migratory aptitude, such as a hydrogen, the alkylidenecarbene **314** undergoes a rearrangement to the alkyne **315**. As seen in Scheme 10, the final result is a nucleophilic acetylenic substitution reaction ($S_N$−A) via an addition−elimination−rearrangement process. Alternatively, if both the β-substituent R and the nucleophile Nu are groups or atoms with a poor migratory aptitude, such as a carbonyl, and in the *absence* of a viable external trap, carbene **314** undergoes intramolecular insertion into any available 1,5-carbon−hydrogen bond resulting in a substituted cyclopentene **316** as the final product. The exact product distribution depends both on the specific reaction conditions and the nucleophile employed.

**Scheme 10**

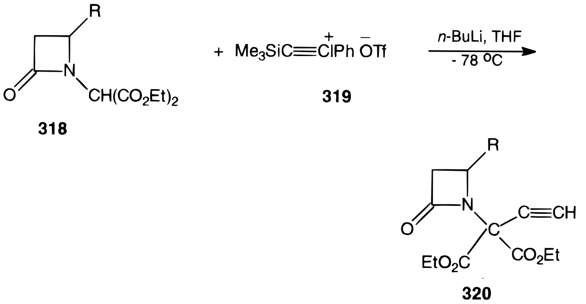


The parent ethynyliodonium salt gives[380] exclusively rearranged (alkynylation) products **317** with diverse β-dicarbonyl nucleophiles in yields of 63−78% as illustrated in eq 163. Similarly, reaction of (2-oxoazetidinyl)malonates **318** with alkynyliodonium triflate **319** affords[389] after workup the corresponding ethynylmalonates **320** in 92% yield (eq 164). Reaction of a variety of alkynyliodonium triflates with 2-aminomalonate **321** gave[377] alkynylation products **322** in 33−95% yield (eq 165). Whereas, reaction of alkynyliodonium salts, **324** substituted with an alkyl group possessing a 1,5-C−H bond, with a range of β-dicarbonyl enolates **323** result[390] in the carbene insertion derived cyclopentene products **325** (eq 166). Bis-iodonium salts **303** provide[391] bis-cyclopentene



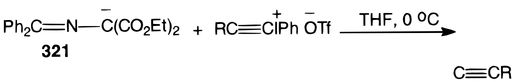
**317**

(163)



**318** **319** **320**

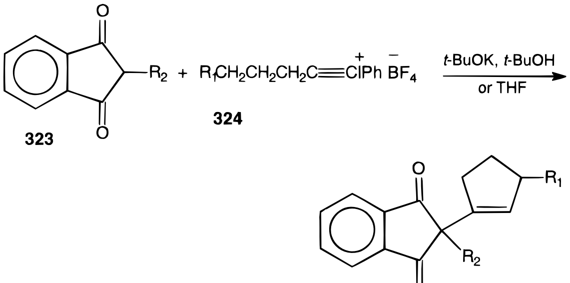
(164)



**321**

**322**: R=Me$_3$Si, Ph, n-Bu, t-Bu

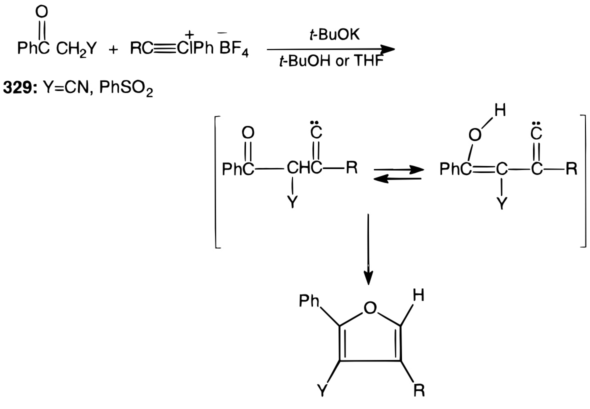
(165)



**323** **324** **325**

(166)

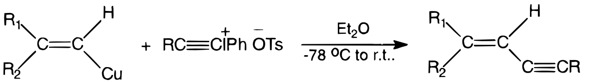
products **326**–**328** as summarized in Scheme 11. When activated carbonyl compounds, with acidic hydrogens, **329**, are used as nucleophiles, furans **330** (eq 167) are obtained via insertion of the carbene into the enolic-O-H bond.



**329**: Y=CN, PhSO$_2$

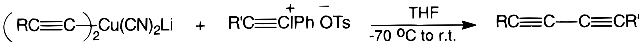
**330**: R=Me, n-C$_8$H$_{17}$

(167)



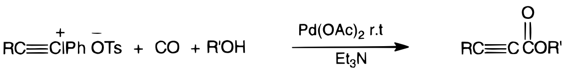
**331** **332**

(168)



**333** **334**

(169)



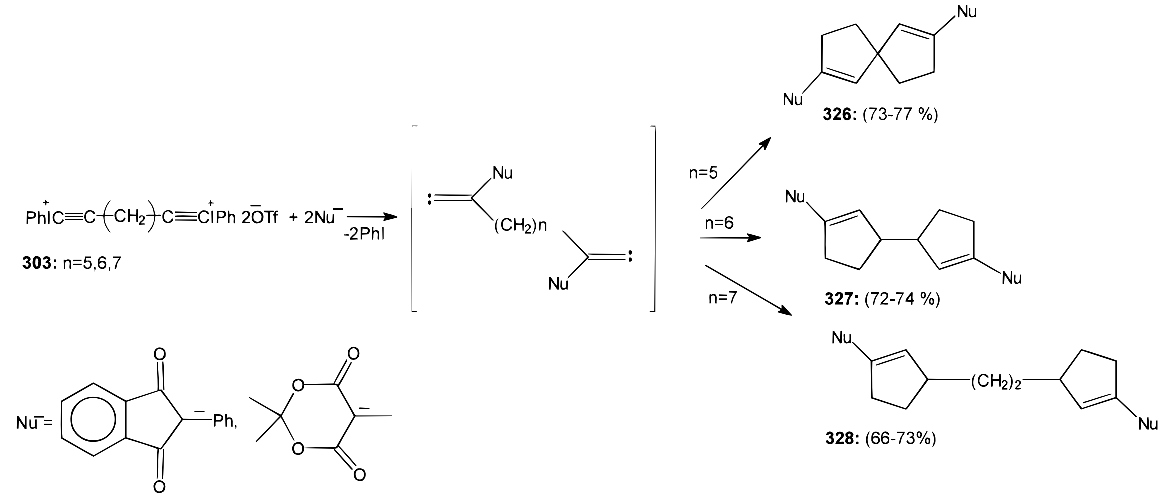
**335**

(170)

The reaction of alkynyliodonium tosylates with vinylcopper reagents **331** is stereospecific, with retention of olefin geometry, in the formation[392] of conjugated enynes **332** (eq 168). Dialkynylcuprates **333** give[393] conjugated diynes **334** as products (eq 169). Recently this methodology was employed[394] to form liquid-crystalline diacetylenes. Alkynyliodonium tosylates **296** may be carbonylated[395] under very mild conditions to yield alkynoic esters **335** (eq 170).

Nitrogen and phosphorus nucleophiles may be reacted with alkynyliodonium salts as well. Reaction of $LiNPh_2$ with functionalized alkynyliodonium triflates **299** results in push–pull ynamines[396] **336** (eq 171). Treatment of **296** with $Me_3SiN_3$ results[397] in the stereoselective formation of (*Z*)-β-azidovinyliodonium salts **337** (eq 172) via protonation of the intermediate ylide (see Scheme 10) by the in situ-generated $HN_3$. A β-azidovinyliodonium salt is also formed in the reaction of $PhC{\equiv}CI^+Ph\ OTs^-$ with $NaN_3$ in $CH_2Cl_2$ in the presence of 18-crown-6,[398] whereas reaction of the *tert*-butyl congener **338** in the

**Scheme 11**



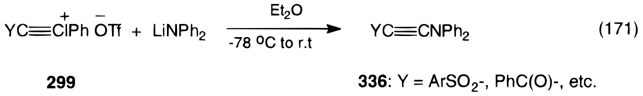
**303**: n=5,6,7

**326**: (73-77 %)

**327**: (72-74 %)

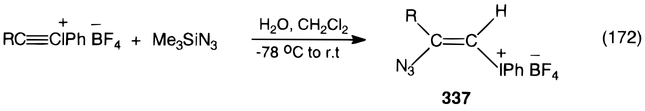
**328**: (66-73%)

presence of $Et_3SiH$ forms the $\beta$-azidovinylsilane **339** (eq 173). This latter reaction is further evidence for the formation of alkylidenecarbenes **312** (Scheme 10) in these reactions.



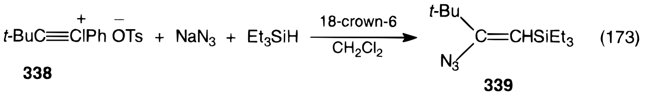
$$YC{\equiv}\overset{+}{I}Ph\ \overset{-}{O}Tf + LiNPh_2 \xrightarrow[-78\ ^oC\ to\ r.t]{Et_2O} YC{\equiv}CNPh_2 \quad (171)$$

**299** **336**: Y = $ArSO_2$-, PhC(O)-, etc.



$$RC{\equiv}\overset{+}{I}Ph\ \overset{-}{B}F_4 + Me_3SiN_3 \xrightarrow[-78\ ^oC\ to\ r.t]{H_2O,\ CH_2Cl_2} (R)(N_3)C{=}C(H)\overset{+}{I}Ph\ \overset{-}{B}F_4 \quad (172)$$

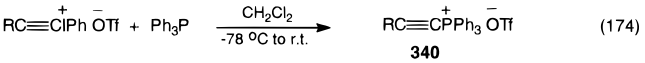
**337**



$$t\text{-}BuC{\equiv}\overset{+}{I}Ph\ \overset{-}{O}Ts + NaN_3 + Et_3SiH \xrightarrow[CH_2Cl_2]{18\text{-crown-6}} (t\text{-}Bu)(N_3)C{=}CHSiEt_3 \quad (173)$$

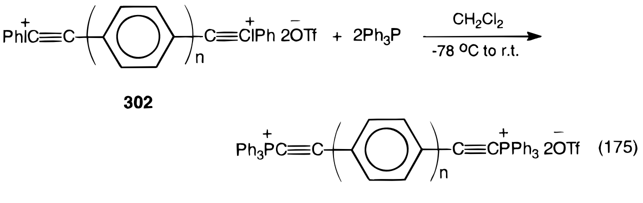
**338** **339**

Reaction of $Ph_3P$ with **296** affords[399] alkynylphosphonium salts **340** in essentially quantitative yields (eq 174). Similarly reaction of **302** and **303**, respectively, give[63] bisphosphonium diynes **341** and **342** (eqs 175 and 176). Phosphacubane **343** may be alkynylated with **296** to give[400] alkynylphosphacubanes **344** (eq 177).



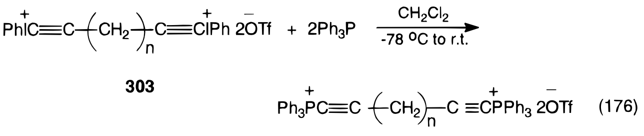
$$RC{\equiv}\overset{+}{I}Ph\ \overset{-}{O}Tf + Ph_3P \xrightarrow[-78\ ^oC\ to\ r.t.]{CH_2Cl_2} RC{\equiv}\overset{+}{C}PPh_3\ \overset{-}{O}Tf \quad (174)$$

**340**



**302**

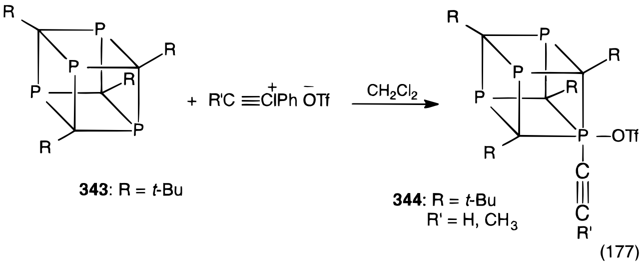
**341**: n = 1,2



$$Ph\overset{+}{I}C{\equiv}C{-}(CH_2)_n{-}C{\equiv}\overset{+}{I}Ph\ 2\overset{-}{O}Tf + 2Ph_3P \xrightarrow[-78\ ^oC\ to\ r.t.]{CH_2Cl_2} Ph_3\overset{+}{P}C{\equiv}C{-}(CH_2)_n{-}C{\equiv}\overset{+}{C}PPh_3\ 2\overset{-}{O}Tf \quad (176)$$

**303**

**342**: n = 2, 4, 5

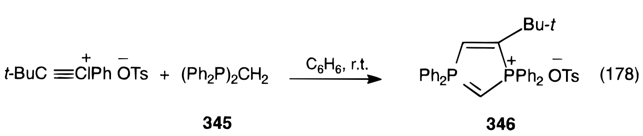


**343**: R = *t*-Bu

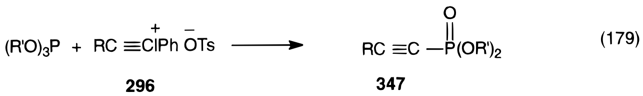
**344**: R = *t*-Bu
R' = H, $CH_3$

Reaction[401] of *t*-$BuC{\equiv}CI^+Ph\ OTs^-$ with bis(diphenylphosphino)methane **345** gives the previously unknown diphospholium ion **346** (eq 178). Trialkyl phosphites react[245] with **296** to give dialkyl alkynylphosphonates **347** via an Arbuzov-type process (eq 179).

A wide range of oxygen and sulfur nucleophiles react with alkynyliodonium salts. However, both alkoxides $RO^-$ and siloxides $R_3SiO^-$ give only decomposition products rather than the desired alkoxy- and siloxyacetylenes. The softer sulfonate, carboxylate, and phosphate anions all readily react with **296** to



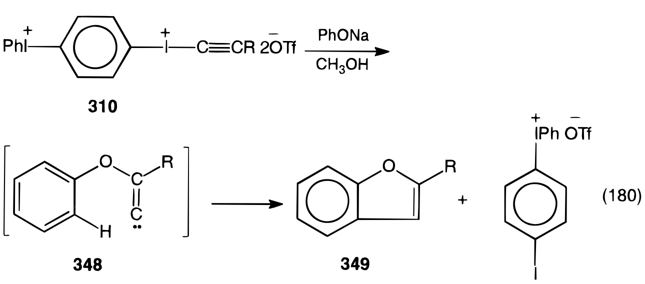
**345** **346**



$$(R'O)_3P + RC{\equiv}\overset{+}{I}Ph\ \overset{-}{O}Ts \longrightarrow RC{\equiv}C{-}P(O)(OR')_2 \quad (179)$$

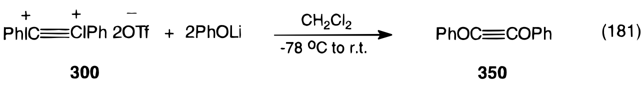
**296** **347**

give[402] hitherto unknown alkynyl sulfonate, carboxylate, and phosphate esters. Likewise, phenoxide ions react with **310** to give[403] furans **349** (eq 180) via carbenes **348**. Bisiodonium ethyne **300** gives[60,61] bisphenoxide **350** via reaction with 2 equiv of phenoxide (eq 181).



**310**

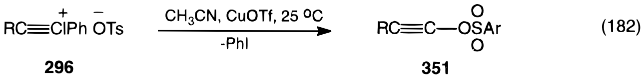
**348** **349**



$$Ph\overset{+}{I}C{\equiv}C\overset{+}{I}Ph\ 2\overset{-}{O}Tf + 2PhOLi \xrightarrow[-78\ ^oC\ to\ r.t.]{CH_2Cl_2} PhOC{\equiv}COPh \quad (181)$$

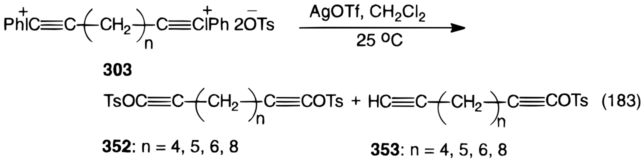
**300** **350**

Reaction of alkynyliodonium tosylates **296** in dry $CH_3CN$ with catalytic amounts of CuOTf or AgOTs leads[246,247] to the formation of alkynyl sulfonate esters **351** (eq 182) and **303** results[65] in modest yields of bis-tosylates **352** along with some monotosylates **353** (eq 183).



$$RC{\equiv}\overset{+}{I}Ph\ \overset{-}{O}Ts \xrightarrow[-PhI]{CH_3CN,\ CuOTf,\ 25\ ^oC} RC{\equiv}C{-}OS(O_2)Ar \quad (182)$$

**296** **351**



$$Ph\overset{+}{I}C{\equiv}C{-}(CH_2)_n{-}C{\equiv}\overset{+}{I}Ph\ 2\overset{-}{O}Ts \xrightarrow[25\ ^oC]{AgOTf,\ CH_2Cl_2} TsOC{\equiv}C{-}(CH_2)_n{-}C{\equiv}COTs + HC{\equiv}C{-}(CH_2)_n{-}C{\equiv}COTs \quad (183)$$

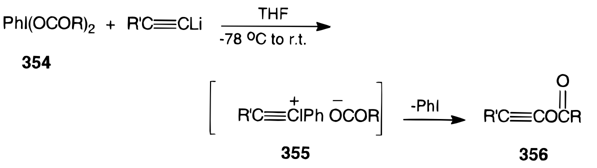
**303**

**352**: n = 4, 5, 6, 8 **353**: n = 4, 5, 6, 8

Alkynyl carboxylate esters **356** are obtained[404] via the intermediacy of **355** in the reaction of bis(acyloxyiodo) benzene **354** with lithium acetylides (eq 184). All alkynyl esters are sensitive to moisture and readily undergo hydration.[405] As a consequence bisalkynyl benzoates **357** can only be isolated in 6−15% yields from the reaction[65] of **303** with sodium benzoates (eq 185). Alkynyl benzoates, **356**, R=$C_6H_5$, are potent protease inhibitors.[406]

Sequential reaction of silaacetylenes with PhIO and $Et_2OBF_3$ followed by aqueous dialkyl sodium phosphate yields[284] alkynyl phosphate esters **358** (eq 186) that are excellent inhibitors of bacterial phosphotriesterase.[407−409]

Reaction of alkynyliodonium salts **296** with aqueous NaSCN in $CH_2Cl_2$ affords[382] alkynyl thiocyanates **359** in high yields (eq 187), whereas dithiocyanates **360** and **361** are obtained[65] in the reactions of bisiodoniumdiynes **302** and **303** (eq 188, 189), re-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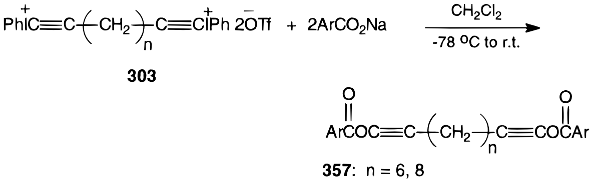
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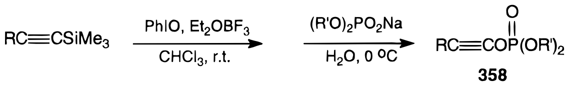
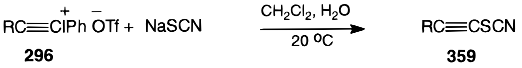
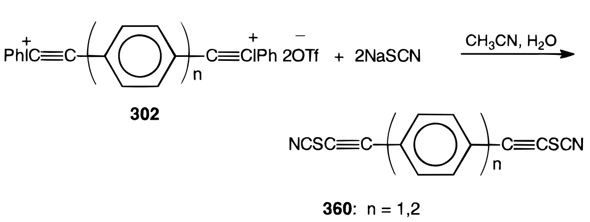
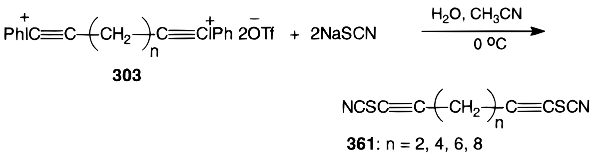

(186)

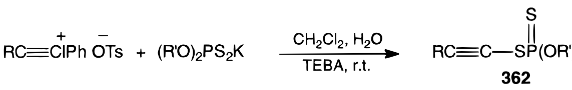
spectively. Likewise, alkynyl thiocyanates **359** are also obtained in the reaction of **310** with KSCN in DMF.


(187)


(188)


(189)

The reaction of $(R'O)_2PS_2K$[410] and $ArS(O)_2SK$,[411] respectively, with **296** results in alkynylphosphorodithioates **362** and **363** (eqs 190 and 191) in good yields. Hitherto unknown alkynyl thiocarboxylates **364** are obtained[412] in the reaction of **296** with $PhCS_2^-Na^+$ (eq 192).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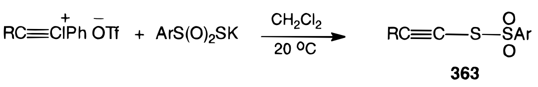
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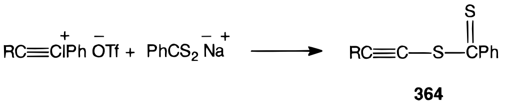
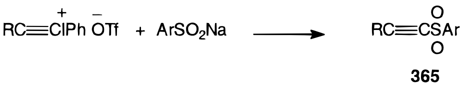

(192)

The interaction of arylsulfinate with alkynyliodonium salts **296** is particularly interesting and useful. When R in **296** lacks a 1,5-C−H bond, alkynyl sulfones **365** and **366** are formed[413] in excellent yields (eq 193, 194). If 1,5-C−H bonds are available in the R group of **296**, the intermediate carbene (**314**, Scheme 10) preferentially undergoes[414] insertion rather than rearrangement, and as a consequence cyclopentenyl sulfones **367** predominate, accompanied by minor amounts of alkynyl sulfones (eq 195). As a consequence of the poor migratory aptitudes of sulfones, carbonyls and amido moieties exclusive cyclopentenone formation is observed[64] in the reaction of $\beta$-keto- and $\beta$-amido-functionalized alkynyliodonium triflates **299** with $ArS(O)_2Na$ in $CH_2Cl_2$. The full synthetic potential of this reaction is summarized in Table 1 where it is seen that not only simple cyclopentenones but also fused bicyclic systems and alkaloids are readily accessible by this new methodology,[64] which nicely complements the Pauson−Khand[415−418] Co-mediated as well as Nazarov[419,420] and related cationic cyclizations.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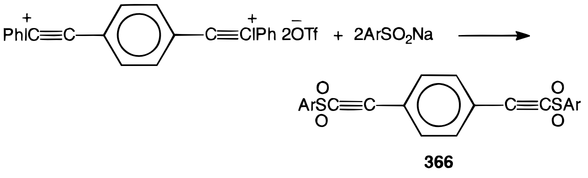
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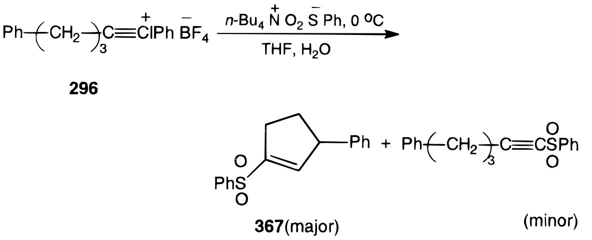
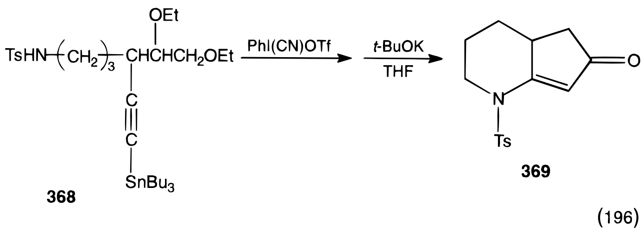

(195)

Recently, a related methodology, employing tosylamides **368** as nucleophiles and proximal 1,5-intramolecular C−H insertion, was developed by Feldman and co-workers[421] to form polycyclic alkaloids **369** as illustrated in eq 196. In contrast to reaction with $ArS(O)_2Na$, phenylsulfinic acid, **370**, itself in methanol, traps[414] the initially formed ylide (**312**, Scheme 10) to give high yields of (*Z*)-$\beta$-sulfonylvinyliodonium salts **371** (eq 197). Bisthio-diynes **372** are obtained[60,61] in the reactions of **300** and **301** with PhSNa, respectively (eq 198).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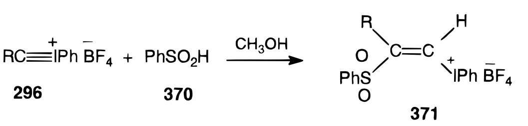
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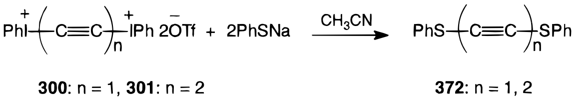
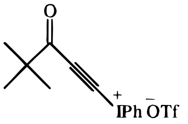
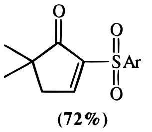
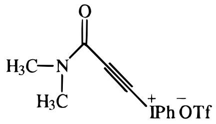
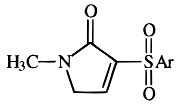
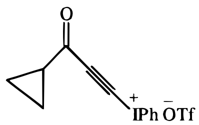
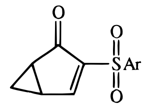
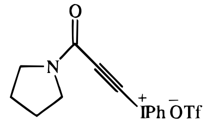
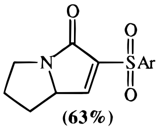
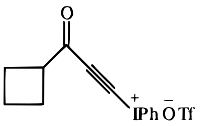
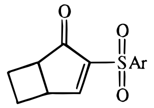
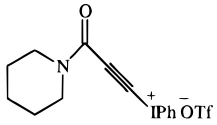
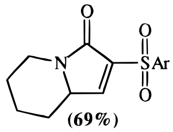
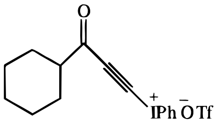
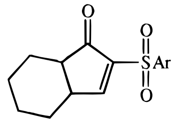
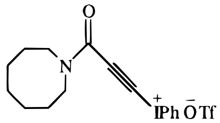
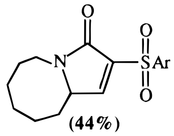
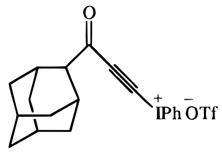
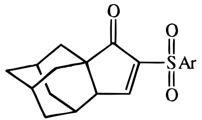
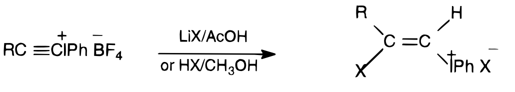

(198)

Halogens may serve as nucleophiles in the reaction with alkynyliodonium salts **296**. Either LiX (X = Br,

**Table 1. Cyclopentenones and $\gamma$-Lactams via the Reaction of $NaO_2SC_6H_4CH_3$ with $\beta$-Keto and $\beta$-Amidoethyliodonium Triflates**

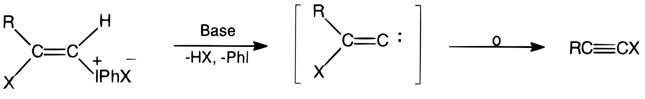
| Starting Iodonium Salt | Product, Yield | Starting Iodonium Salt | Product, Yield |
|---|---|---|---|
|  |  (72%) |  |  (63%) |
|  |  (53%) |  |  (63%) |
|  |  (75%) |  |  (69%) |
|  |  (57%) |  |  (44%) |
|  |  (82%) | | |

Cl) in acetic acid or HX in methanol results[422] in the stereoselective formation of ($Z$)-$\beta$-halovinyliodonium halides **373** (eq 199) via protonation of the ylide resulting from the Michael addition of the halide to **296** (Scheme 10). Vinyliodonium salts **373** serve as carbene, **374**, progenitors that lead[423] to haloalkynes **375** (eq 200).



373: X = Br, Cl

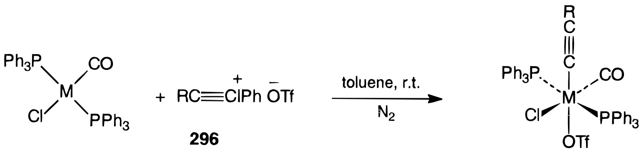
(199)



373 374 375

(200)

Transition metal complexes can behave as nucleophiles toward alkynyliodonium species and thereby provide an alternative for the formation of $\sigma$-alkynyl transition metal systems from the usual reaction of $RC{\equiv}C^-$ with metal halides. Reaction[424] of the square planar Ir, **376**, and Rh, **377**, with **296** results in the respective hexacoordinate $\sigma$-alkynyl complexes, **378**, **379** (eq 201). The full scope of this reaction[425] is illustrated in Scheme 12 in the formation of highly conjugated complexes, **380**, **381**, **383**, and **385** that are of considerable interest from a materials science[426,427] perspective.



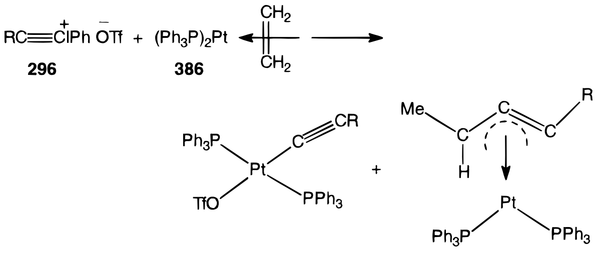
296

376: M = Ir
377: M = Rh

378: M = Ir
379: M = Rh

(201)

Reaction of alkynyliodonium salts **296** with the Pt(0) complex **386** can lead[428] to either $\sigma$-alkynyl–Pt(II) complexes **387** or the $\eta^3$-propargyl/allenyl–Pt(II) complexes **388** depending upon both the exact reaction conditions and the size of R in **296** (eq 202).



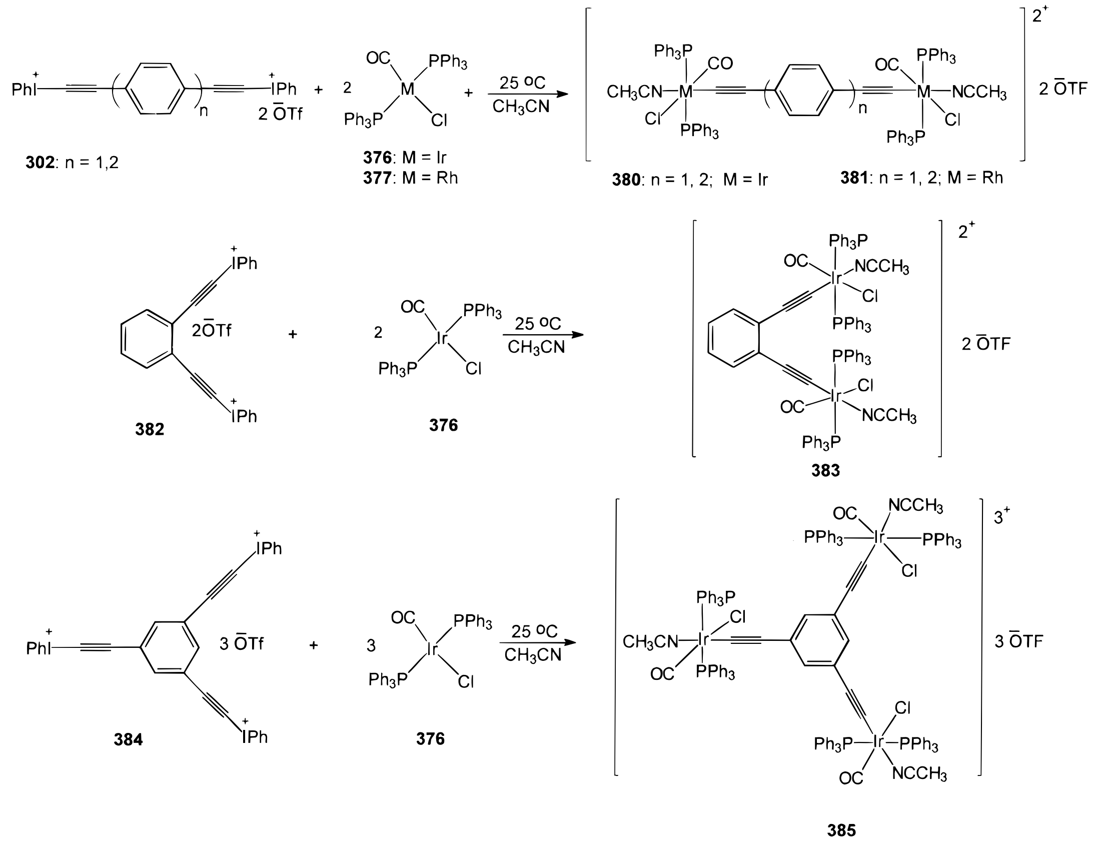
296 386

387 388

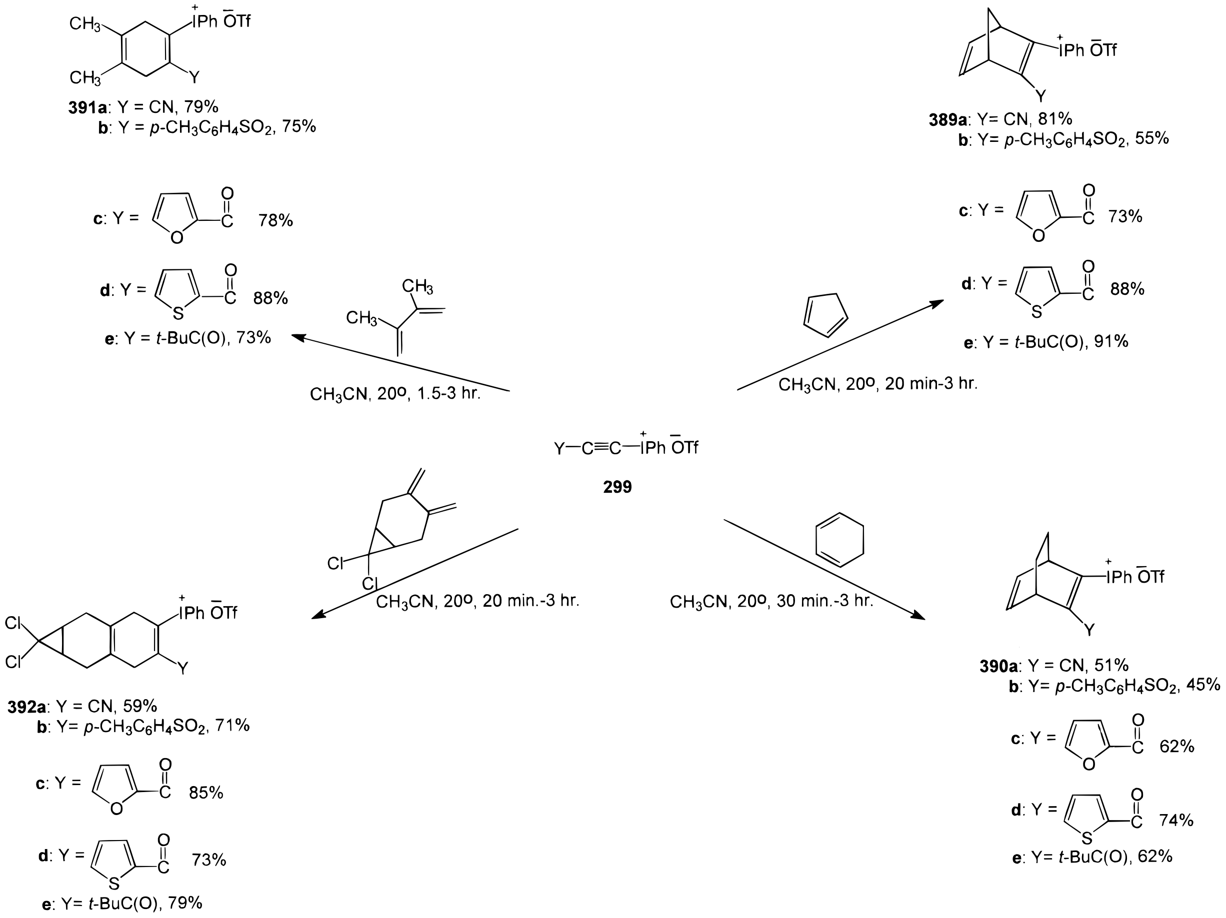
(202)

Alkynyliodonium salts functionalized with deactivating substituents in the $\beta$-position, **299**, readily undergo[66] Diels–Alder cycloadditions with a wide range of dienes as summarized in Scheme 13. All adducts **389**–**392** are stable microcrystalline solids

**Scheme 12**



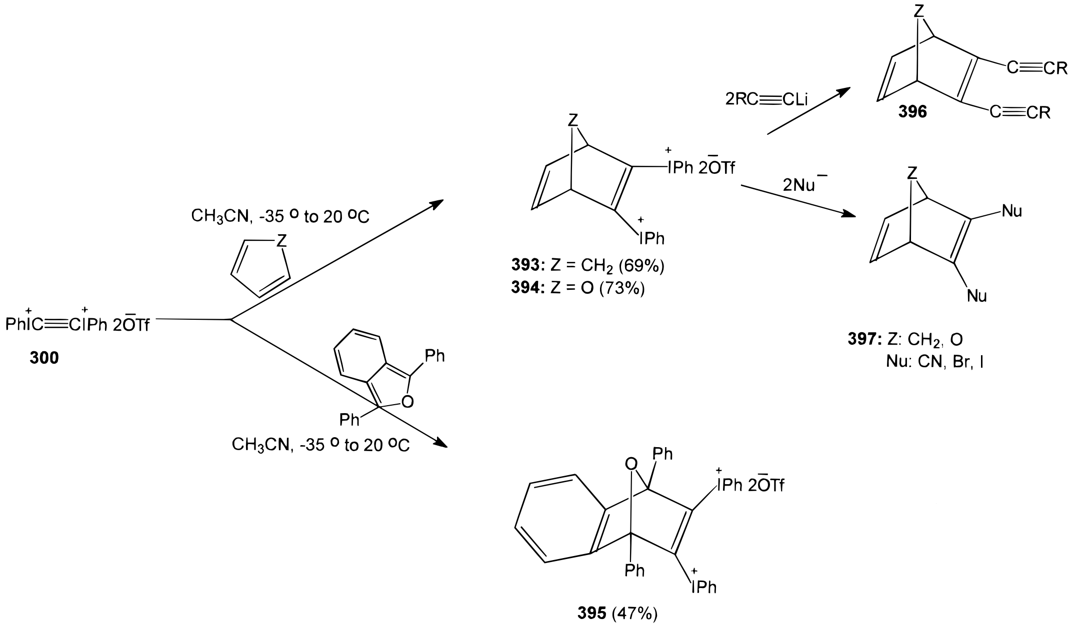
**Scheme 13**



with two functionalities, the iodonium moiety and Y, that may be used for further synthetic elaboration.

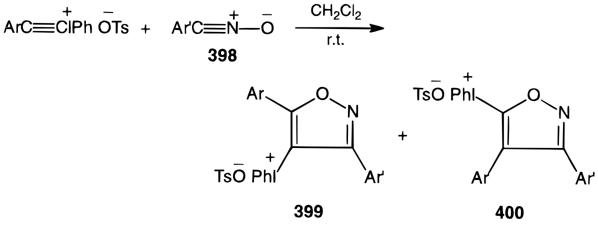
The bisiodonium ethyne **300** undergoes Diels−Alder reaction even more readily than **299** as summarized

**Scheme 14**

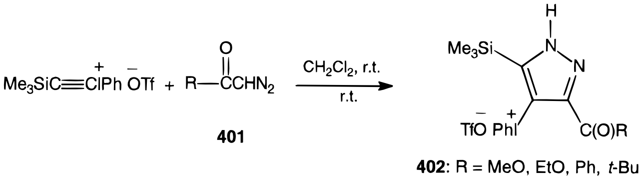


in Scheme 14. The structure of adduct **393** was established by X-ray data.[61] Products **393** and **394** can be reacted further[429,430] with RC≡CLi to give enediynes **396** or with nucleophiles to give dienes **397** (Scheme 14).

Finally, alkynyliodonium salts readily undergo reaction with 1,3-dipolar reagents: arenenitrile oxides **398** give[431] a mixture of cycloadducts **399** and **400** (eq 203), whereas diazocarbonyl compounds **401** afford[432] heterocycles **402** (eq 204) and organoazides give[432] triazines **403** (eq 205).

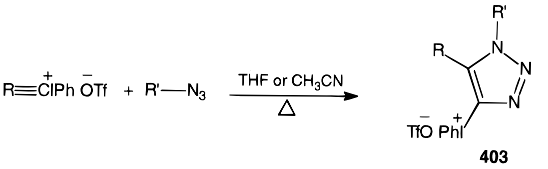


(203)



**402**: R = MeO, EtO, Ph, *t*-Bu

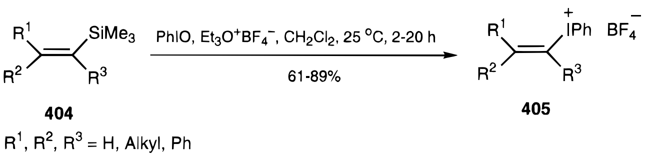
(204)



(205)

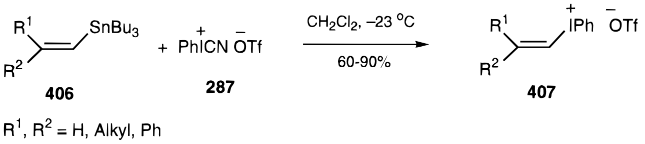
## C. Alkenyliodonium Salts

Several examples of alkenyliodonium salts have been known for many years, but only in the last decade have these compounds become readily available and found some synthetic application. The first general method of synthesis of alkenyliodonium species was developed by Ochiai in the mid-1980s.[93,433] This method is based on the reaction of silylated alkenes **404** with iodosylbenzene in the presence of Lewis acids leading to the stereoselective formation of various alkenyliodonium tetrafluoroborates **405** in good yield (eq 206).



(206)

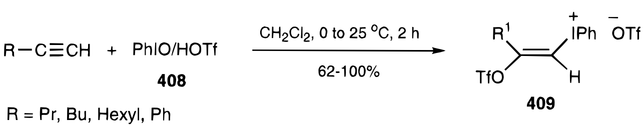
A very general and mild procedure for stereospecific synthesis of alkenyliodonium triflates **407** involves phenyl(cyano)iodonium triflate **287** as an iodonium-transfer reagent in reactions with stannylated alkenes **406** (eq 207).[434,435] This method was also applied to the preparation of the parent vinyliodonium triflate from tributyl(vinyl)tin.[67]



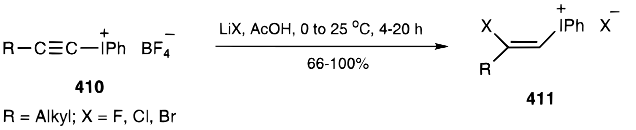
(207)

A variety of alkenyliodonium salts were synthesized via electrophilic addition of aryliodosyl derivatives to alkynes or allenes.[47,57,70−72,137,243] Reactions of terminal alkynes with phenyliodosyl triflate **408** proceeds as a highly stereoselective *anti*-addition to afford (*E*)-([[[(β-trifluoromethyl)sulfonyl]oxy]vinyl]-iodonium triflates **409** in high yield (eq 208).[71,72] Similar products were obtained from internal alkynes and ethyne.[72]

(*Z*)-β-Substituted vinyliodonium salts **411** can be prepared by a Michael-type nucleophilic addition of nucleophiles to alkynyliodonium salts **410** (eq 209).[422,436]



(208)

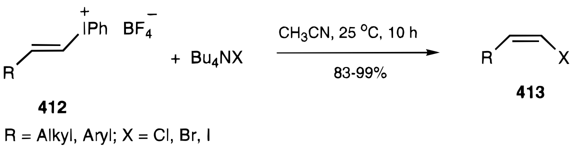


(209)

A number of iodonium- and bis(iodonium) norbornadienes and other polycyclic adducts were synthesized by [2 + 4] cycloaddition reactions of alkynyliodonium triflates with 1,3-dienes (see Section IV.B).

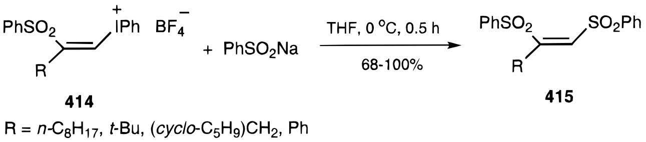
Several single-crystal X-ray structures of alkenyliodonium salts have been reported in the literature.[57,61,93,137,437] These structures generally can be considered as ionic with a typical distance between iodine and the nearest anion of 2.8−3.0 Å. However, with consideration of the anionic part of the molecule, the overall experimentally determined geometry is T-shaped similar to the 10-I-3 species. The C−C double bonds in alkenyliodonium salts have normal lengths of 1.31−1.34 Å, the $C_{sp^2}$−I distances can vary from 2.07 to 2.13 Å, and the C-I-C angles are in the range of 91−99°.

Alkenyl(phenyl)iodonium salts are highly reactive in vinylic nucleophilic substitution reactions because of the excellent leaving group ability of phenyliodonium moiety. Ochiai and co-workers first described reactions of alkenyl(phenyl)iodonium tetrafluoroborates with a number of nucleophiles, such as organocuprates, thiolates, sodium nitrite, copper halides, etc., leading to the respective products of nucleophilic substitution.[93] Further detailed study of this reaction revealed that the stereochemistry of substitution strongly depends on the structure of the substrate and reaction conditions.[436,438−440] In particular, nucleophilic substitution at vinylic carbons of (*E*)-($\beta$-alkylvinyl)iodonium salts **412** with halide anions proceeds with complete inversion of configuration (eq 210), presumably via an S$_N$2 transition state.[438]



(210)

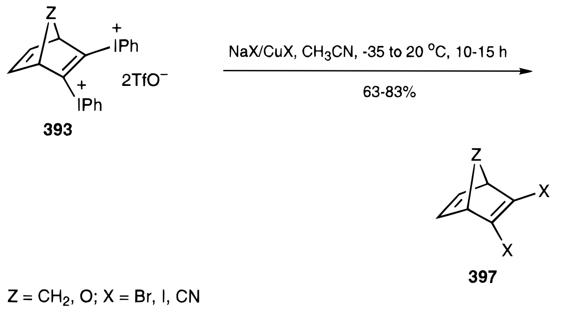
The same reaction, but in the presence of copper salts results in exclusive retention of configuration at the sp$^2$ carbon.[438] Retention of configuration is also observed in the reactions of (*Z*)-[($\beta$-phenysulfonyl)vinyl]iodonium salts **414** with benzenesulfinate anion (eq 211) and some other reactions.[436,439−441]



(211)

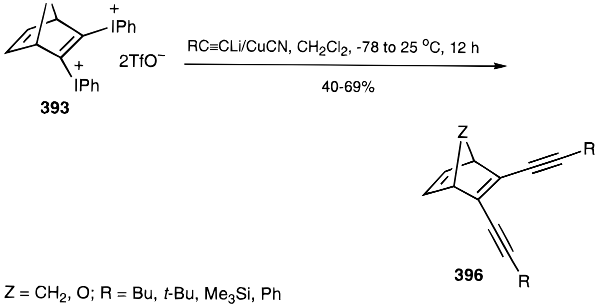
Retention of configuration is generally observed in the reactions of alkenyliodonium salts implying an addition−elimination or a ligand coupling mechanism.[439−441] In some cases alkynes or products of *ipso*-substitution at the phenyl carbon are isolated as byproducts in these reactions.[438,441]

Bicycloalkenyldiiodonium salts **393** can react with a variety of nucleophiles to afford the respective products of vinylic nucleophilic substitution.[429,430] The yields of substitution products **397** can be substantially improved by carrying out reactions with anionic nucleophiles in the presence of copper(I) salts (eq 212).[430]



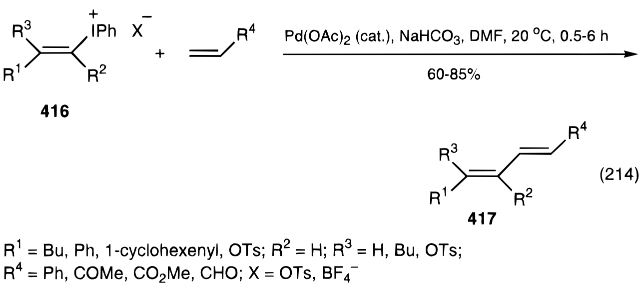
(212)

Similarly, the reactions of diiodonium salts **393** with lithium alkynyl cuprates afford enediynes **396** as major products (eq 213).[429]



(213)

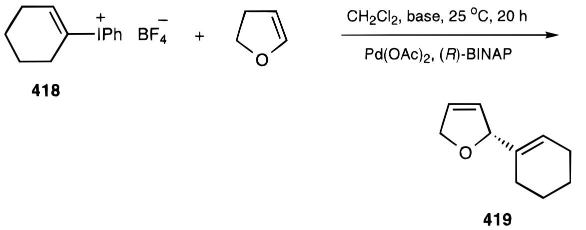
Alkenyliodonium salts can serve as highly reactive substrates for Heck-type olefination and similar palladium-catalyzed coupling reactions.[434,442−444] Moriarty and co-workers have developed a very mild and stereoselective procedure of palladium-catalyzed coupling of alkenyliodonium salts **416** with various alkenes (eq 214).[442]



(214)

Recently, a similar procedure was employed in asymmetric Heck-type coupling of iodonium salt **418** with 2,3-dihydrofuran (eq 215).[443] When carried out in the presence of the chiral bidentate ligand (*R*)-

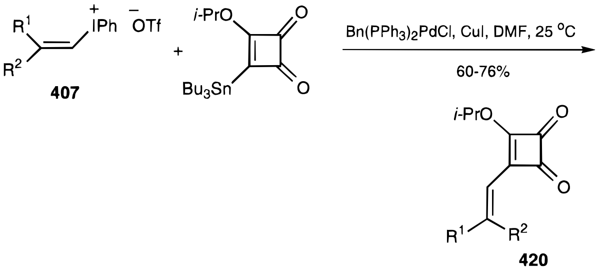
BINAP, this reaction (eq 215) afforded optically active (up to 78% ee) coupling product **419** in moderate yield.



(215)

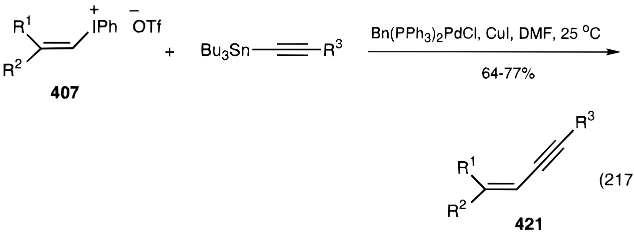
(*R*)-BINAP = (*R*)-2,2'-bis(diphenylphosphino)-1.1'-binaphthyl

Even better results are obtained in the palladium-catalyzed coupling of alkenyliodonium salts with organotin compounds.[434,444] For example, palladium/copper-cocatalyzed coupling of the readily available trisubstituted alkenyl(phenyl)iodonium triflates **407** with alkynyl- and alkenylstannanes proceeds under exceedingly mild conditions with retention of geometry of the alkenyl ligand of the iodonium salt (eqs 216 and 217).[434]



(216)

$R^1, R^2$ = Me, Et, Bu

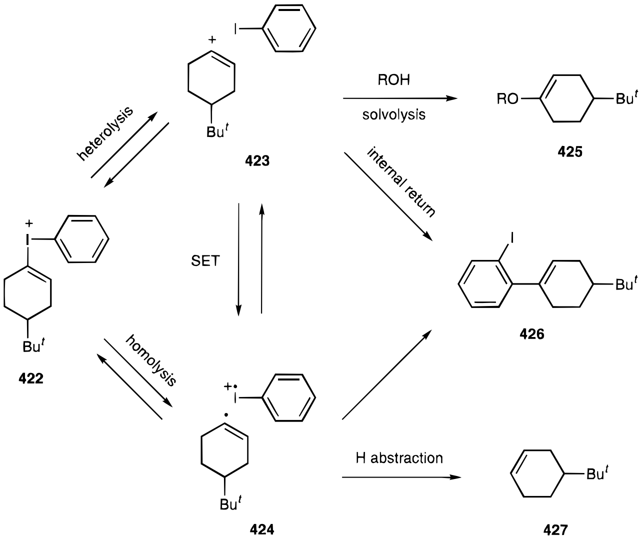


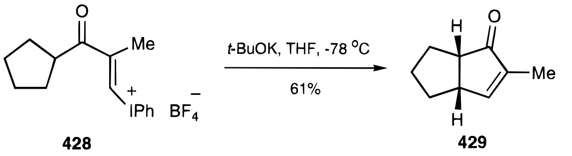
(217)

Recently, Okuyama, Ochiai, and co-workers investigated mechanistic details of the solvolysis of alkenyliodonium salts **422** in alcohol and aqueous solutions.[445a] In particular, the phenyliodonio group was found to be a remarkably good leaving group, $10^6$ times more reactive than triflate. In addition to the expected products **425** and iodobenzene, the solvolysis afforded 13–40% of the internal return products **426** and small amounts of a free-radical product **427**. A proposed mechanism involves mainly the initial heterolysis to form the intimate ion pair **423** with accompanying single electron transfer to lead to a free-radical intermediate **424** (Scheme 15).[445a]

Reactions of alkenyliodonium salts with strong bases may lead to the generation of an alkylidene carbene via base-induced α-elimination.[444,445b] Alkylidene carbenes generated by this method can undergo a 1,5-carbon–hydrogen insertion, providing a useful route for the construction of substituted cyclopentenes.[414,423,444] In a typical example, reaction of alkenyliodonium tetrafluoroborate **428** with potassium *tert*-butoxide affords bicyclic product **429** in high yield (eq 218).[444]

**Scheme 15**

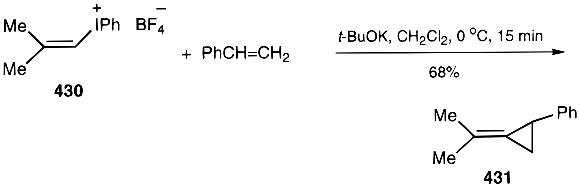




(218)

In some cases, such a cyclization is accompanied by alkyne formation due to 1,2-migration of a substituent in the intermediate alkylidenecarbene.[414,423,444]

The alkylidene carbenes generated via base-induced α-elimination can also be trapped by cycloaddition with external alkenes. For example, the treatment of alkenyliodonium salt **430** with a strong base in the presence of excess styrene gives methylenecyclopropane **431** in good yield (eq 219).[445b]



(219)

## D. Aryl- and Heteroaryliodonium Salts

Aryliodonium as well as heteroaryliodonium, salts belong to the most common, stable, and well-investigated class of polyvalent iodine compounds. The chemistry of aryliodonium salts was extensively covered in previous reviews,[5−8,11] so in this section we will discuss only the important recent developments in this area.

### *1. Preparation and Structure*

Aryliodonium salts are usually prepared by reaction of arenes or silylated arenes with electrophilic aryliodosyl derivatives.[5−8,11] A similar approach was used recently for the preparation of various aryliodonium triflates, sulfates, and other derivatives.[152,153,164,446−449] Iodosylbenzene or [(diacetoxy)iodo]benzene **67** react with aromatic compounds in the presence of trifluoromethanesulfonic acid to afford diaryliodonium triflates **432** in good yield (eq 220).[446]

$$\underset{\mathbf{67}}{\mathrm{PhI(OAc)_2}} + 2\mathrm{TfOH} + \mathrm{ArH} \xrightarrow[\text{74-98\%}]{\mathrm{CH_2Cl_2},\ 0\text{ to }25\ ^\circ\mathrm{C},\ 1\text{ h}} \underset{\mathbf{432}}{\overset{+}{\mathrm{PhI}}\mathrm{Ar}\ {}^{-}\mathrm{OTf}} \qquad (220)$$

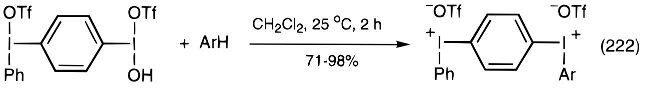
Ar = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 4-$ClC_6H_4$, 4-$BrC_6H_4$, 4-$IC_6H_4$, 4-*t*-$BuC_6H_4$, 2,5-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 5-indanyl

Phenyliodosyl sulfate **12** reacts with arenes under similar conditions to give the respective diaryliodonium hydrosulfates **433** (eq 221).[447]

$$\underset{\mathbf{12}}{\overset{+}{\mathrm{PhI}}\text{-}\mathrm{OSO_3^-}} + \mathrm{ArH} \xrightarrow[\text{54-84\%}]{\mathrm{CH_2Cl_2},\ -50\text{ to }20\ ^\circ\mathrm{C},\ 1\text{-}3.5\text{ h}} \underset{\mathbf{433}}{\overset{+}{\mathrm{PhI}}\mathrm{Ar}\ {}^{-}\mathrm{OSO_3H}} \qquad (221)$$

Ar = Ph, 4-$MeC_6H_4$, 4-$FC_6H_4$, 4-$IC_6H_4$, 4-*t*-$BuC_6H_4$, 2,4-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$ , 3-$NO_2C_6H_4$

(*p*-Phenylene)bis(aryliodonium) triflates **434** can be prepared similarly by reaction of reagent **10**, a product of the self-condensation of iodosylbenzene (see Section III.A.1), with arenes (eq 222).[70,448]

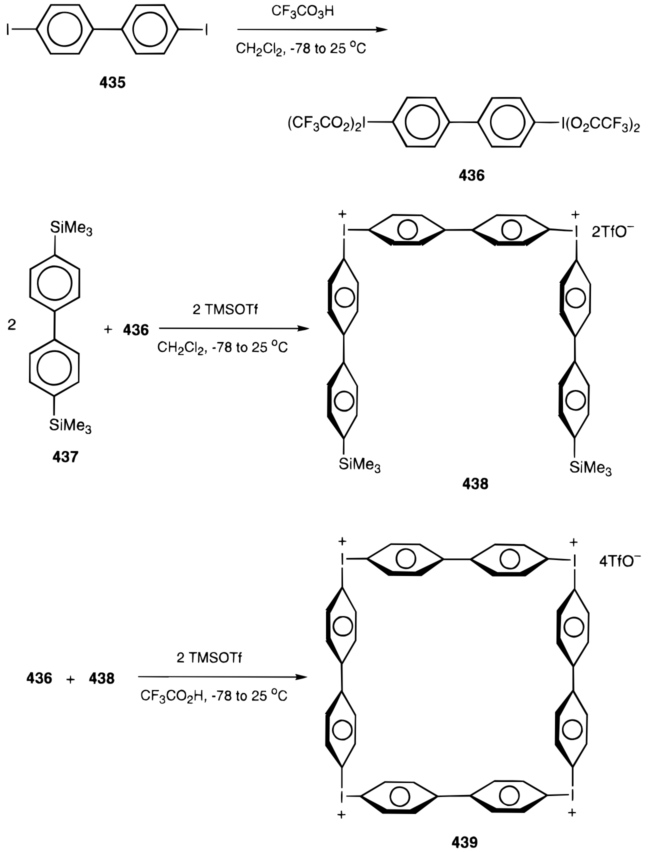


**10** **434**

Ar = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 4-$ClC_6H_4$, 4-$BrC_6H_4$, 4-$MeOCH_2C_6H_4$, 4-*t*-$BuC_6H_4$, 5-indanyl, etc.

A more general synthetic approach to bisiodonium salts **73** is based on reactions of *p*-bis[bis[(trifluoroacetyl)oxy]iodo]benzene **72** with trimethylsilylarenes (eq 45, see Section III.C.1).[153] An analogous reaction was applied to the synthesis of macrocyclic tetraaryltetraiodonium cationic molecular square **439** from diiodobiphenyl **435** (Scheme 16).[152]

**Scheme 16**



Inorganic iodosyl derivatives, such as iodosyl trifluoromethanesulfonate **440** and iodosyl fluorosulfate **442** react with arenes or trimethylsilylarenes under mild conditions to afford iodonium triflates **441** (eq 223) or hydrosulfates **443** (eq 224).[450,451]

$$\underset{\mathbf{440}}{\mathrm{O{=}IOTf}} + \mathrm{ArSiMe_3} \xrightarrow[\text{57-93\%}]{\mathrm{CH_2Cl_2},\ -78\text{ to }20\ ^\circ\mathrm{C},\ 30\text{ min}} \underset{\mathbf{441}}{\mathrm{Ar_2}\overset{+}{\mathrm{I}}\ {}^{-}\mathrm{OTf}} \qquad (223)$$

Ar = Ph, 4-$MeC_6H_4$, 2,4,6-$Me_2C_6H_2$, 4-$BrC_6H_4$, 4-(4'$BrC_6H_4$)$C_6H_4$, etc.

$$\underset{\mathbf{442}}{\mathrm{O{=}IOSO_2F}} + \mathrm{ArH} \xrightarrow[\text{53-95\%}]{\mathrm{CH_2Cl_2},\ -60\text{ to }20\ ^\circ\mathrm{C},\ 0.5\text{-}3\text{ h}} \underset{\mathbf{443}}{\mathrm{Ar_2}\overset{+}{\mathrm{I}}\ {}^{-}\mathrm{OSO_3H}} \qquad (224)$$

Ar = Ph, 4-$MeC_6H_4$, 4-*t*-$BuC_6H_4$, 2,4-$Me_2C_6H_3$, 4-$FC_6H_4$, 4-$ClC_6H_4$, 4-$BrC_6H_4$

Naumann and co-workers used a similar procedure for the preparation of bis(pentafluorophenyl)iodonium triflate **445** from iodine tris(trifluoroacetate) **444**, pentafluorobenzene, and the corresponding sulfonic acid (eq 225).[452]

$$\underset{\mathbf{444}}{\mathrm{I(OCOCF_3)_3}} + \mathrm{C_6F_5H} + \mathrm{RSO_3H} \xrightarrow[\text{80\%}]{\mathrm{CF_3CO_2H},\ 20\ ^\circ\mathrm{C},\ 72\text{ h}} \underset{\mathbf{445}}{\mathrm{(C_6F_5)_2}\overset{+}{\mathrm{I}}\ {}^{-}\mathrm{OSO_2R}}$$

R = $CF_3$; 2,4,6-$(NO_2)_3C_6H_2$

(225)

A very mild and general method for the preparation of aryl- and heteroaryliodonium triflates is based on iodonium transfer reactions of iodine(III) cyanides with the respective aryl- or heteroarylstannanes.[151,153,369,370] (Dicyano)iodonium triflate **286** generated in situ reacts with tributyltin derivatives of aromatic compounds **446** affording the corresponding diaryliodonium salts **441** (eq 226).[370]

$$\underset{\mathbf{286}}{\mathrm{(NC)_2}\overset{+}{\mathrm{I}}\bullet{}^{-}\mathrm{OTf}} + \underset{\mathbf{446}}{2\mathrm{ArSnBu_3}} \xrightarrow[\text{45-74\%}]{\mathrm{CH_2Cl_2},\ -40\text{ to }20\ ^\circ\mathrm{C}} \underset{\mathbf{441}}{\mathrm{Ar_2}\overset{+}{\mathrm{I}}\ {}^{-}\mathrm{OTf}} \qquad (226)$$

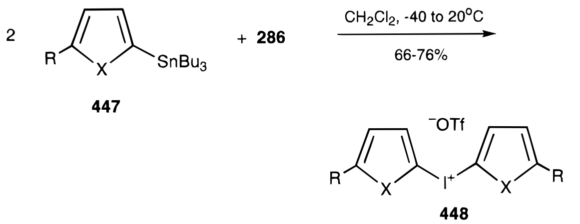
Ar = Ph, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, etc.

Since (dicyano)iodonium triflate (**286**) does not possess any pronounced electrophilic or oxidizing properties and is not acidic, it is especially useful for the synthesis of various bis(heteroaryl)iodonium salts from acid-sensitive substrates.[369] For example, reagent **286** reacts with stannylated derivatives of furan, thiophene, indole, and pyrazole under very mild condition to afford the respective iodonium salts **448**, **450**, and **452** in good yield (eqs 227−229).[369]

Aryl(cyano)iodonium triflates (**289**) can be used in a similar iodonium exchange with stannylated aromatic precursors **453** and **454** affording mixed diaryl (**432**) or aryl(heteroaryl) (**455**) iodonium salts (eqs 230 and 231).[151,153]

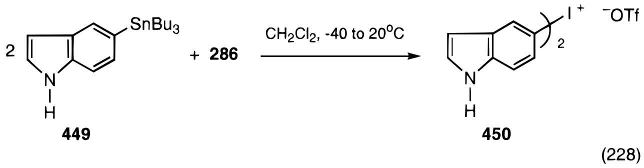
Another iodonium-transfer reagent, (chlorovinyl)iodonium dichloride **456**, is especially useful for the preparation of aryliodonium salts from lithiated arenes.[453] Recently this compound was applied as the iodonium transfer reagent in the synthesis of hybrid, iodonium−transition metal macrocyclic squares **459** (Scheme 17).[454]

A number of X-ray molecular structure determinations have been reported for aryl- and heteroaryliodonium salts with the structural features of the iodonium moiety generally similar to that previously



(227)

X = O, S; R = H, Br



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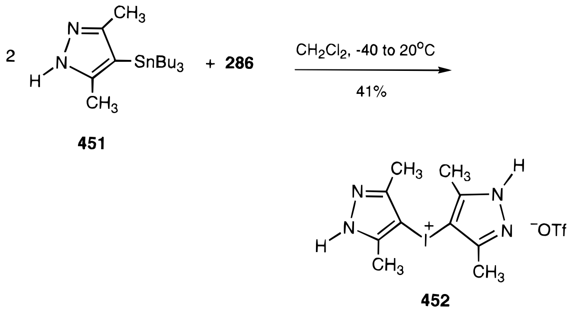
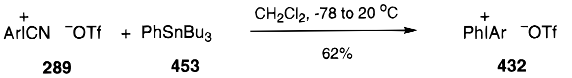


(229)



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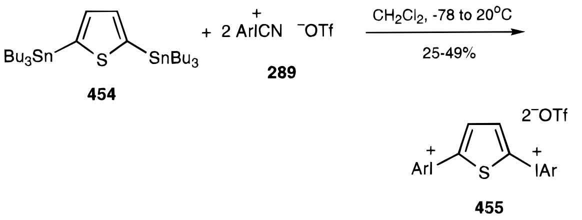


(231)

Ar = Ph, 4-FC6H4

described for the alkynyl and alkenyl species (see Sections IV.B.1 and C).[455]

### 2. Reactions

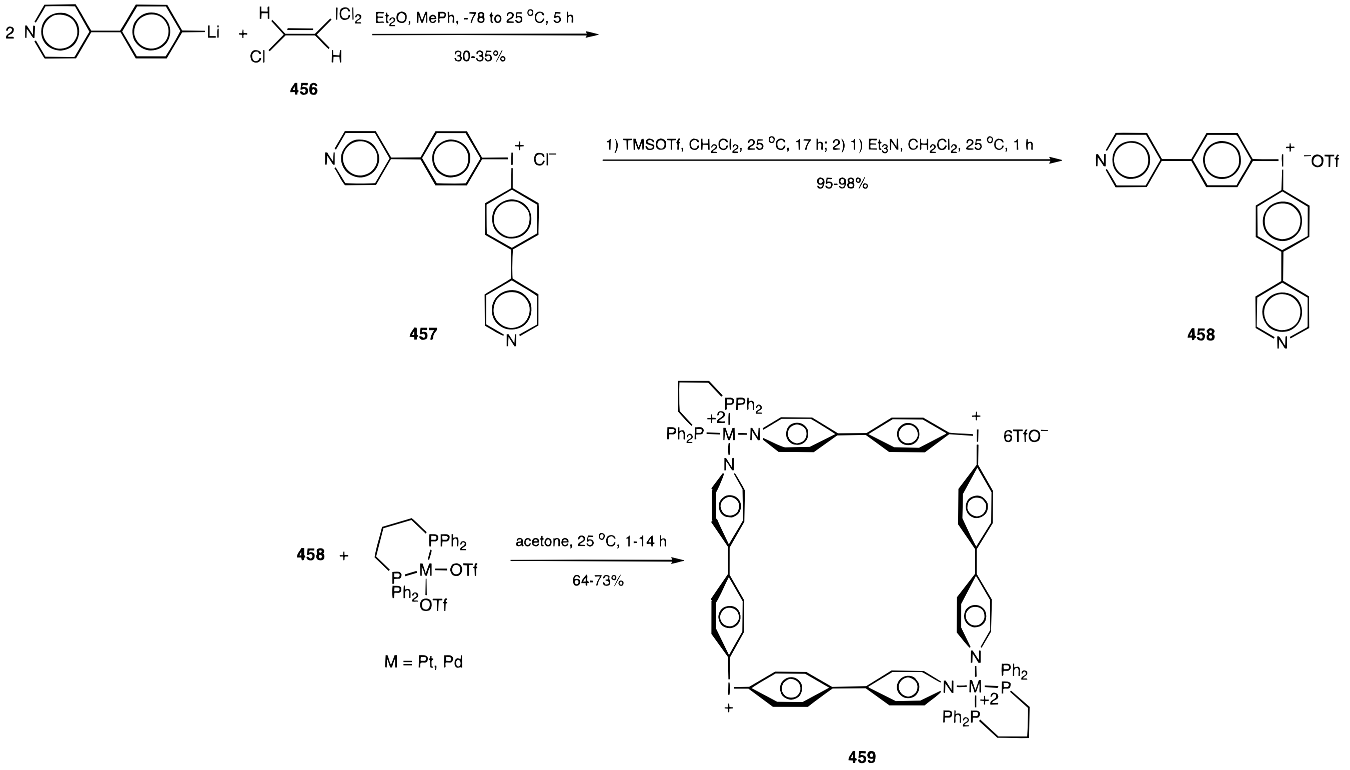
Diaryliodonium salts have found synthetic application as arylating reagents in reactions with various organic substrates under polar, catalytic, or photochemical conditions. Typical recent examples of the reactions with anionic nucleophiles under polar conditions include arylations of thiocarbamates **460** (eq 232),[456,457] thiocarboxylates **461** (eq 233),[458] thiophosphates **462** (eq 234),[459] dialkyl phosphites **463** (eq 235),[460] sodium telluride,[461] aryl selenides,[462] and aryl tellurides **464** (eq 236).[463]

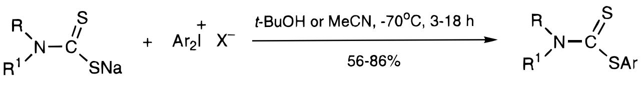
Arylations of carbon nucleophiles under polar conditions is illustrated by the reaction of Meldrum's acid derivatives **465** (eq 237)[464] and arylations of various silyl enol ethers, such as **466** (eq 238).[465]

An interesting example of the generation of benzyne **468** by the decomposition of iodonium triflate **467** under polar conditions was recently reported by Kitamura and Yamane (eq 239).[466]

The mechanistic aspects of the polar reactions of aryliodonium salts were recently discussed by Grushin, Demkina, and Tolstaya.[339,467] The authors[467] proposed a unified mechanism for the reactions of diaryliodonium salts with nucleophiles involving initial formation of a trigonal bipyramidal, 10-I-3 hypervalent intermediate (**469a,b**, Scheme 18) where the bulkier of the two aryl ligands and two lone electron pairs usually occupy the less encumbered equatorial positions. The 10-I-3 species can undergo synchronous (cheletropic) extrusion of an iodoarene during intramolecular rotation via tetragonal pyramidal intermediates **470a**−**c** in which the interaction Ar−Nu is symmetry allowed. The nucleophile prefers to bind to the more bulky ligand or

**Scheme 17**

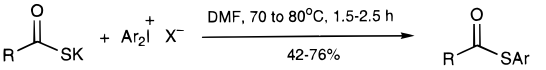




**460**

R = Me, Et, Ph, $PhCH_2$, etc.
Ar = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 4-$ClC_6H_4$, 3-$NO_2C_6H_4$, etc.
X = Cl, Br, I, OAc, OTf

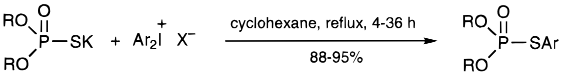
(232)



(233)

**461**

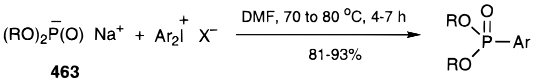
R = Me, Ph; Ar = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 4-$ClC_6H_4$, 3-$NO_2C_6H_4$; X = Cl, I



(234)

**462**

R = Et, Pr, i-Pr; Ar = Ph, 4-$MeC_6H_4$, 4-$ClC_6H_4$



(235)

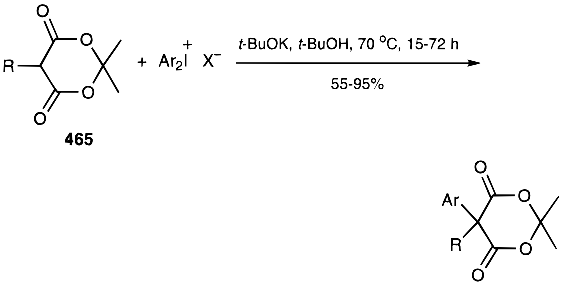
**463**

R = Et, Pr, i-Pr; Ar = Ph, 4-$MeC_6H_4$, 4-$ClC_6H_4$

$$\mathrm{Ar^1TeNa} + \mathrm{Ar^2{}_2\overset{+}{I}\;X^-} \xrightarrow[\text{46-81\%}]{\text{DMF, 70 to 80 °C, 4-7 h}} \mathrm{Ar^1TeAr^2} \qquad (236)$$

**464**

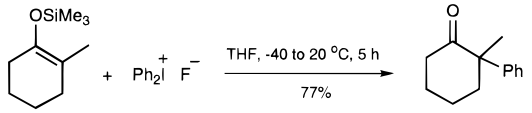
$Ar^1$ = Ph, 4-$ClC_6H_4$; 1-naphthyl;
$Ar^2$ = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 4-$ClC_6H_4$; X = Cl, I



**465**

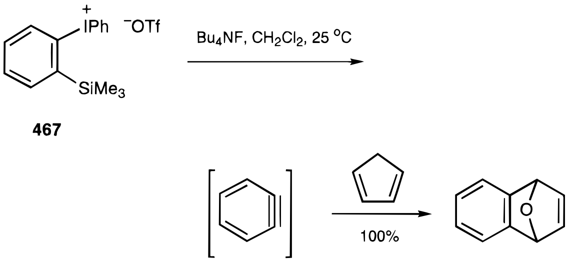
(237)

R = $PhCH_2$, i-Pr, etc.; Ar = Ph, 4-$MeC_6H_4$, 4-$ClC_6H_4$ 4-$MeOC_6H_4$, 3-$NO_2C_6H_4$;
X = Cl, Br, I



(238)

**466**



**467**

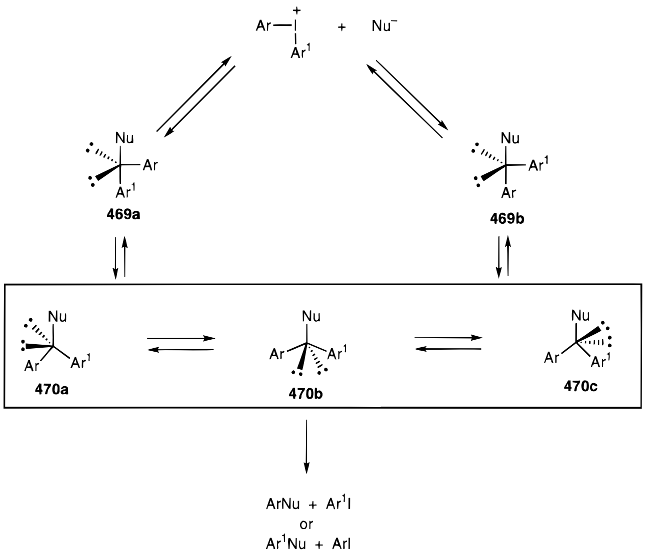
**468**

(239)

to the more electron-deficient one if both of the aryl groups are of similar effective bulk (Scheme 18).[339,467]

Arylations with aryliodonium salts can be effectively catalyzed by transition metals. Similar to alkenyliodonium salts (see Section IV.C), aryliodonium salts are highly reactive substrates in Heck-type olefination and other palladium-catalyzed coupling reactions. Bumagin, Beletskaya, and coauthors have recently reported that aryliodonium salts can serve as very efficient reagents in the palladium-catalyzed arylations of acrylic acid (eq 240),[468] organotin compounds (eq 241),[469] sodium tetraphenylborate (eq 242),[470] and copper acetylide (eq 243).[471]

**Scheme 18**



$$\mathrm{CH_2{=}CHCO_2H} + \mathrm{Ar_2\overset{+}{I}\;X^-} \xrightarrow[\text{50-97\%}]{\text{Pd(OAc)}_2\text{, H}_2\text{O, Na}_2\text{CO}_3\text{, 20 to 100 °C, 1-15 h}} \mathrm{ArCH{=}CHCO_2H} \qquad (240)$$

Ar = Ph, 3-$NO_2C_6H_4$, 4-$MeC_6H_4$, 4-$MeOC_6H_4$; X = $HSO_4$, $BF_4$

$$\mathrm{RSn(CH_3)_3} + \mathrm{Ar_2\overset{+}{I}\;X^-} \xrightarrow[\text{60-83\%}]{\text{Pd(OAc)}_2\text{, DMF, 60-70 °C, 2.5 h}} \mathrm{ArR} \qquad (241)$$

Ar = 3-$NO_2C_6H_4$; R = Me, 3-$MeC_6H_4$; X = $HSO_4$, $BF_4$, $CF_3CO_2$

$$\mathrm{Ph_4BNa} + \mathrm{Ar_2\overset{+}{I}\;X^-} \xrightarrow[\text{96-98\%}]{\text{PdCl}_2\text{, H}_2\text{O, Na}_2\text{CO}_3\text{, 80 °C, 1 h}} \mathrm{ArPh} \qquad (242)$$

Ar = 3-$NO_2C_6H_4$, etc.; X = $HSO_4$, $BF_4$, $CF_3CO_2$

$$\mathrm{PhC{\equiv}CCu} + \mathrm{Ar_2\overset{+}{I}\;X^-} \xrightarrow[\text{98\%}]{\text{PdCl}_2\text{, DMF, NaI}\cdot 2\text{H}_2\text{O, 20 °C, 1 h}} \mathrm{PhC{\equiv}CAr} \qquad (243)$$

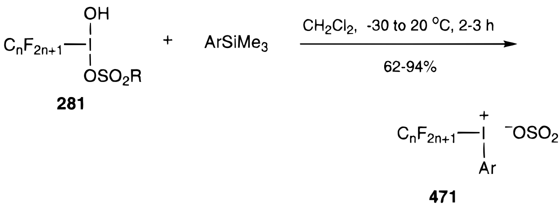
Ar = 3-$NO_2C_6H_4$; X = $HSO_4$, $BF_4$, $CF_3CO_2$

Under photochemical conditions diaryliodonium salts can decompose by a variety of pathways, which usually involve radical or radical cation intermediates. Due to this property they have found some practical application as photoinitiators for radical polymerizations.[11,472] The photoreactivity of aryliodonium salts was extensively covered in the book of Varvoglis.[19]

## E. 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 and some of them even were isolated in the form of labile crystalline salts.[11,19,473]

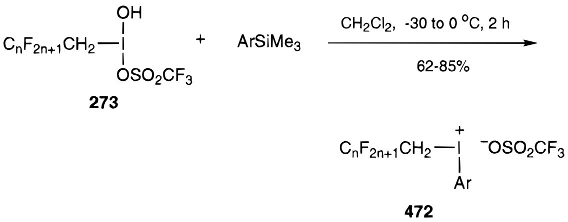
The presence of electron-withdrawing groups in the alkyl group of iodonium salts has a pronounced stabilizing effect. The most stable and important derivatives of this type are perfluoroalkyl(aryl)iodonium salts. These salts as chlorides were first prepared in 1971 by Yagupolskii and co-workers[474] and later widely applied as electrophilic fluoroalkylating reagents by Umemoto and co-workers.[368] The triflate salts, $PhIC_nF2_{n+1}OTf$, originally were synthesized by the reaction of [bis(trifluoroacetoxy)iodo]perfluoroalkanes with benzene in the presence of triflic acid.[362] A recent and more general method for the preparation of various perfluoroalkyl(aryl)iodonium sulfonates **471** involves the reaction of [hydroxy(sulfonyloxy)iodo]perfluoroalkanes **281** with arylsilanes under Lewis acid catalysis (eq 244).[363−365]



(244)

R = *p*-Tol, $CH_3$, $CF_3$; n = 4,6;
Ar = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 2-$MeC_6H_4$, 4-$Me_3SiC_6H_4$

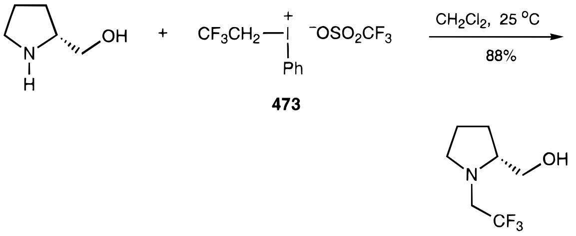
In a similar manner, 1*H*,1*H*-perfluoroalkyl(aryl)iodonium triflates **472** are best prepared by reaction of triflates **273** with trimethylsilylarenes under mild conditions (eq 245).[360,367]



(245)

n = 1,2; Ar = Ph, 4-$MeC_6H_4$, 2-$MeC_6H_4$, 4-$Me_3SiC_6H_4$, 4-$MeOC_6H_4$

Fluoroalkyl(aryl)iodonium triflates **471** and **472** have found practical application as electrophilic fluoroalkylating reagents toward a variety of organic substrates, such as arenes, carbanions, alkynes, alkenes, carbonyl compounds, amines, phosphines, and sulfides.[368] In a recent example, Montanari and co-workers used trifluoroethyl(phenyl)iodonium triflate (**473**) for the *N*-trifluoroethylations of amino alcohols (eq 246)[342] and 1,10-diaza-18-crown-6 (Kryptofix 22) **474** (eq 247).[475]



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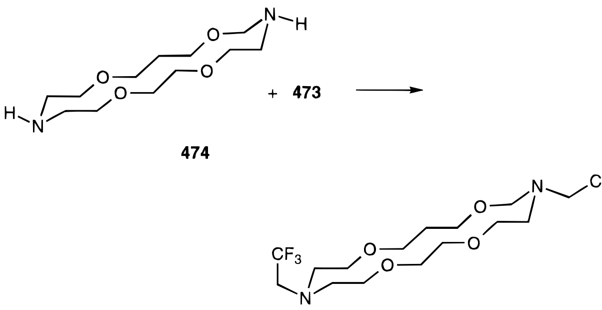
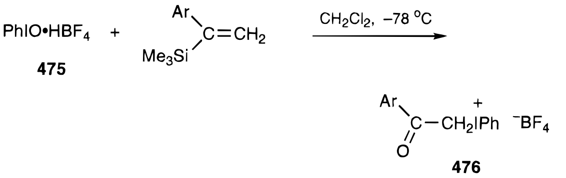


(247)

The unstable β-oxoalkyl(phenyl)iodonium salts **476** can be generated by a low-temperature reaction of silyl enol ethers with reagent **475** (eq 248).[106,107]



(248)

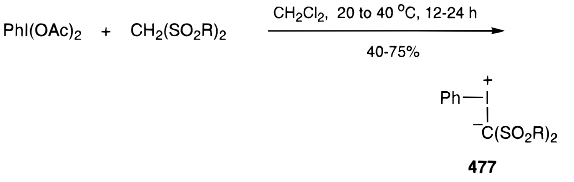
Ar = Ph, 4-$MeC_6H_4$, 4-$ClC_6H_4$, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$

These and similar species have been proposed as the reactive intermediates in synthetically useful carbon−carbon bond-forming reactions recently reviewed by Moriarty and Vaid.[18]

## F. Iodonium Ylides

The first preparation of an iodonium ylide by the reaction of dimedone and $PhIF_2$ was reported by Neiland and co-workers[476] in 1957. Since then a large number of stable iodonium ylides have appeared, and many synthetic applications have emerged. The chemistry of iodonium ylides was reviewed by Koser,[11] and more recently it was extensively covered in the book of Varvoglis.[19] In this section we will discuss only the most recent results on the preparation and chemistry of stable iodonium ylides, as well as several synthetic procedures based on the generation of iodonium ylides in situ as unstable reactive intermediates.

There is a significant current interest in phenyliodonium ylides stabilized by two organosulfonyl groups, $PhIC(SO_2R)_2$.[477−480] Zhu and Chen first reported the preparation of phenyliodonium bis(perfluoroalkanesulfonyl)methide (**477**) from DIB and bis[(perfluoroalkyl)sulfonyl]methane (eq 249).[477]



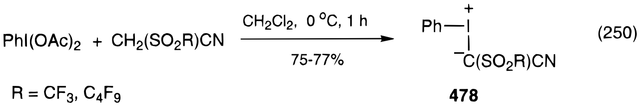
(249)

R = $CF_3$, $C_4F_9$ or 2R = $(CF_2)_3$

Ylides **477** have unusually high thermal stability; they can be stored without decomposition at room temperature for several months. The X-ray structural analysis for the trifluoromethanesulfonyl derivative **477** is normal for iodonium ylide structures with the ylide bond length about 1.9 Å and the C−I−C bond angle 98°.[479]

Hackenberg and Hanack reported the synthesis of similar, nonsymmetric cyano[(perfluoroalkyl)sulfonyl]-substituted ylides **478** by the analogous reaction (eq 250).[480]

Phenyliodonium bis(phenylsulfonyl)methide, $PhIC(SO_2Ph)_2$ and the dicarbonyl derivative $PhIC(COR)_2$



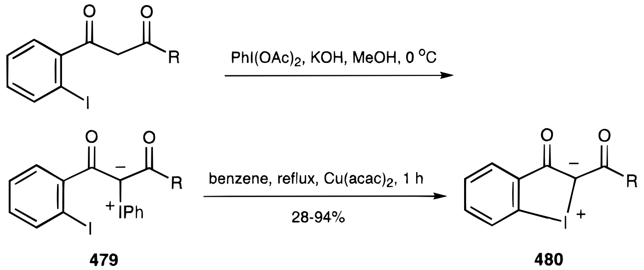
**478**

(250)

are generally prepared by a reaction of $PhI(OAc)_2$ with $H_2C(SO_2R)_2$ or $H_2C(COR)_2$ under basic conditions.[476,479,481,482] These two types of iodonium ylides usually have relatively low thermal stability; nevertheless, they have attracted significant recent research activity.[481−497]

The thermal stability of iodonium ylides can be substantially increased by the incorporation of the iodonium atom in a five-membered ring. Yang and co-workers recently reported the preparation of unusually stable cyclic iodonium ylides **480** via the intramolecular transylidation of a preformed acyclic ylide **479** (Scheme 19).[483]

**Scheme 19**

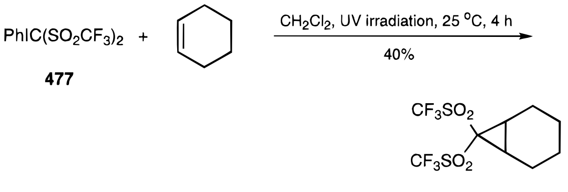


**479** **480**

R = Me, Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-PhOC$_6$H$_4$, α-naphthyl

The X-ray structural analysis for ylide **480** (R = Me) revealed a distorted five-membered ring in this molecule with the ylidic bond length about 2.1 Å and a C−I−C bond angle of 82°, which is smaller than the usual 90° one.[483]

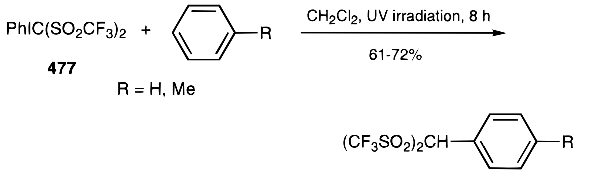
Iodonium ylides can serve as convenient precursors to the respective carbene intermediates under photochemical, thermal, or catalytic conditions. Zhu and Chen reported on the reactions of phenyliodonium bis(perfluoroalkanesulfonyl)methides **477** upon irradiation with UV light in the presence of various organic substrates.[477−479] For example, reaction with cyclohexene afforded cycloaddition product **481** (eq 251), the photolysis of **477** in benzene or toluene led to the C-H insertion products **482** (eq 252), and reaction in pyridine gave pyridinium ylide **483** (eq 253).[479]



**477**

**481**

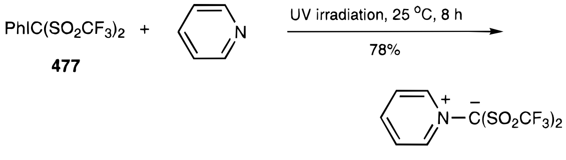
(251)



**477**

**482**

(252)



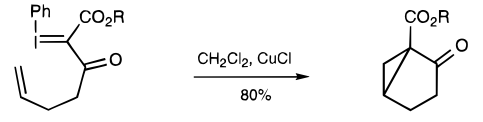
**477**

**483**

(253)

Hackenberg and Hanack found that similar reaction (eqs 251−253) of ylides **477** and **478** can also be carried out under thermal conditions or in the presence of catalytic amounts of Cu(acac)$_2$.[480] The carbenoid reactions of iodonium ylides can also be effectively catalyzed by rhodium(II) complexes.[484,485] The scope and mechanism of carbenoid reactions in the rhodium(II)-catalyzed decomposition of iodonium ylides was investigated recently by Müller and Fernandez.[484] The product composition in these reactions of iodonium ylides was found to be identical to that of the corresponding diazo compounds, which indicates that the mechanism of both processes is similar and involves metallocarbenes as key intermediates as it has been unequivocally established for the diazo decomposition.[484]

The catalytical decomposition of iodonium ylides is especially useful as a method of cyclization via intramolecular cycloaddition or bond insertion.[485,486] As a representative example, Moriarty and co-workers applied intramolecular cyclopropanation of ylide **484** (eq 254) in their synthesis of the 3,5-cyclovitamin D ring A synthon.[486]



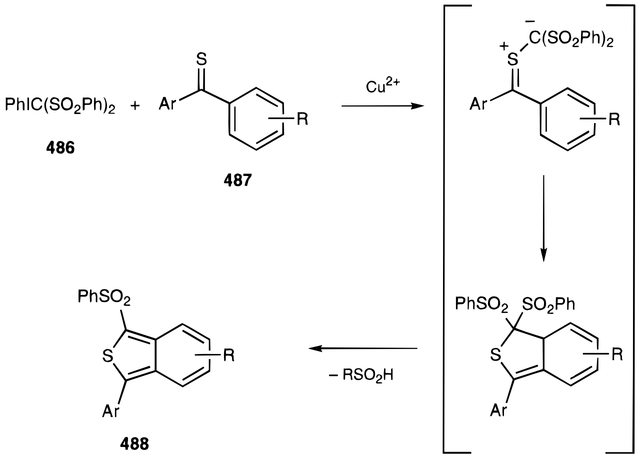
**484** **485**

(254)

R = 1-menthyl or 1(S)-3(S)-*exo*-hydroxy-2(S)-*exo*-naphthylbornane

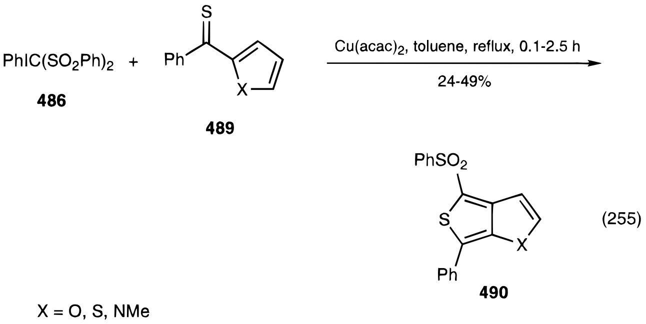
The transfer of the ylide moiety from iodine to an atom of nitrogen, phosphorus, sulfur, or selenium is a very typical reaction of iodonium ylides.[479,480,490,492,497] Recently, Saito and co-workers applied the transylidation reaction of ylide **486** with aromatic thioketones **487** in a new, efficient synthesis of thiophenes **488** (Scheme 20).[490,492]

**Scheme 20**



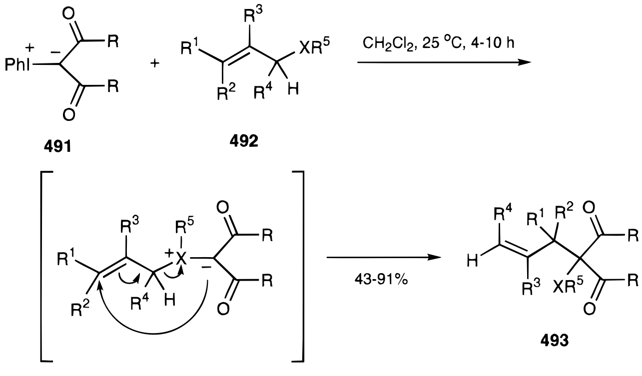
**486** **487** **488**

This approach is especially useful in the synthesis of heterocycle-fused [*c*]thiophenes **490** via reaction of heteroaromatic thioketones **489** with iodonium ylide **486** (eq 255).[492]



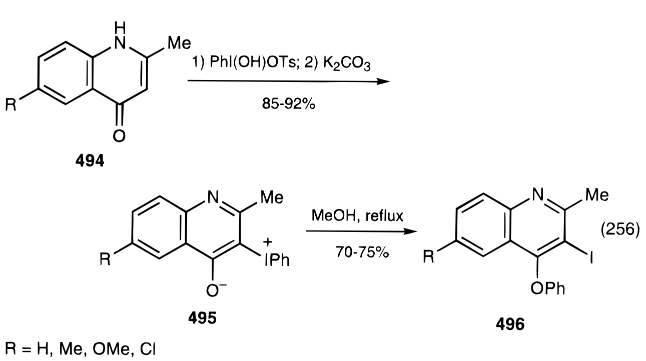
The transylidation reaction of ylides **491** with allylic sulfides or selenides **492** was applied as an efficient and mild method for the preparation of $\beta$-dicarbonyl derivatives **493** (Scheme 21).[497]

**Scheme 21**

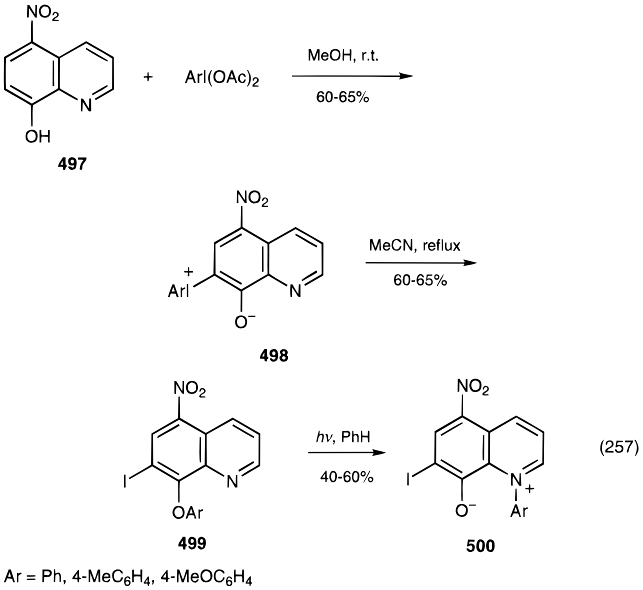


R = Me, Ph, OEt; $R^1$-$R^4$ = H, Alkyl; $R^5$ = Bn, *i*-Bu, *n*-$C_6H_{13}$, $CH_2Ph$, etc.; X = S, Se

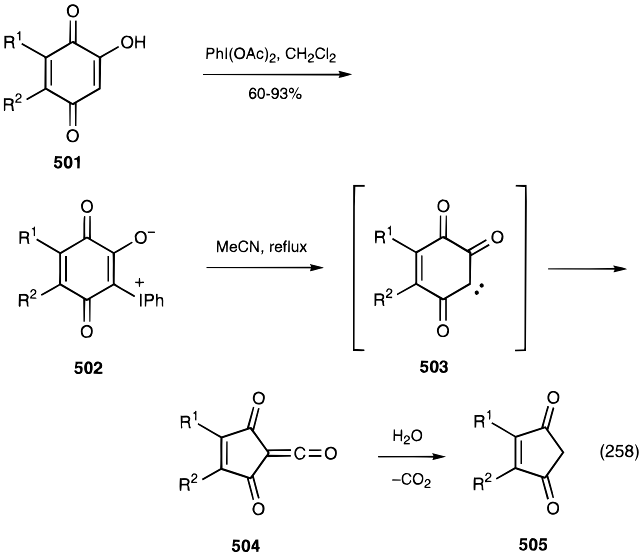
An important class of stable iodonium ylides is represented by (aryliodonio)phenolates, 1,4-dipoles with the negative charge on the oxygen atom of the phenolic group.[19,498−500] Several new examples of these synthetically useful compounds have been reported in recent papers.[498−500] Prakash and co-workers reported the preparation of novel, stable ylides **495** from quinolones **494** and HTIB. These ylides undergo intramolecular phenyl migration upon heating in methanol (eq 256).[498]



Spyroudis and co-workers prepared ylides **498** by the reaction of quinolines **497** with (diacetoxy)iodoarenes (eq 257). Heating and subsequent irradiation of ylides **498** results in a two-step aryl migration to afford products **500**.[499]



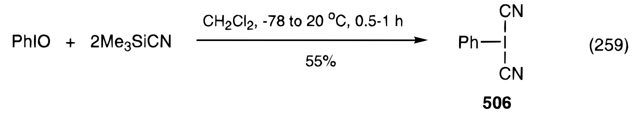
A different reactivity pattern is typical of ylides **502**—derivatives of benzoquinones **501**.[500] Heating of these compounds leads to a ketocarbene **503** which then undergoes ring contraction and gives a ketene **504**. In the presence of moisture ketene **504** spontaneously decarboxylates to afford the final isolated products **505** (eq 258).[500]



## V. Iodine(III) Species with Three Carbon Ligands

In general, iodine(III) species with three carbon ligands are unstable at room temperature. Only a few examples of isolable compounds of this type were reported in the earlier literature, namely, triphenyl iodine[501] and 5-aryl-5*H*-dibenziodoles.[502] All triaryliodanes are highly unstable and air sensitive.

A more recent example of a relatively stable, isolable compound of this type is (dicyanoiodo)benzene **506**, which can be prepared in good yield by the reaction of iodosylbenzene with trimethylsilyl cyanide in methylene chloride (eq 259).[49]

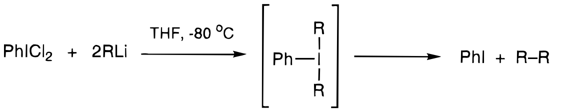


$$PhIO + 2Me_3SiCN \xrightarrow[55\%]{CH_2Cl_2,\ -78\ to\ 20\ ^\circ C,\ 0.5\text{-}1\ h} Ph{-}I(CN)_2 \qquad (259)$$

**506**

Cyanide **506** was isolated as an air-sensitive, crystalline solid, stable at room temperature under nitrogen for several weeks.

The intermediate formation of tricoordinated iodanes with three carbon ligands was also proposed in some carbon−carbon bond-forming reactions of iodonium reagents, but none of these intermediates have been isolated or observed by spectral methods.[18] Recently Barton and co-workers investigated a carbon−carbon bond-forming reaction of dichloroiodobenzene or (diacetoxy)iodobenzene with alkyllithiums.[503] One of the possible mechanistic descriptions of this reaction involves ligand coupling in the triorganoiodane intermediate **507** (eq 260). However, species **507** cannot be detected even at −80 °C, and an alternative explanation of this reaction via nucleophilic substitution in the intermediate alkyl(phenyl)iodonium salts is also possible.[503]



$$PhICl_2 + 2RLi \xrightarrow{\text{THF, -80 }^{\circ}\text{C}} \left[ Ph-\overset{R}{\underset{R}{I}} \right] \longrightarrow PhI + R-R \qquad (260)$$

**507**

## VI. Derivatives of Iodine(V)

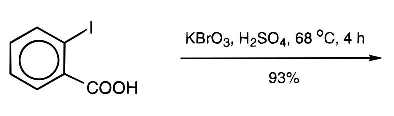
The first organic compound of pentavalent iodine, iodylbenzene $PhIO_2$, was prepared by Willgerodt nearly 100 years ago.[504] Since then a variety of structural classes of iodine(V) derivatives have appeared, and some of these compounds have found synthetic applications. However, in general the organic chemistry of iodine(V) is much less developed than the chemistry of iodine(III). The chemistry of organic compounds of pentavalent iodine was reviewed in the book of Varvoglis.[19]

### A. Preparation and Structure

The most common structural class of iodine(V) compounds is represented by iodylarenes, $ArIO_2$. Iodylarenes are generally prepared by direct oxidation of iodoarenes with strong oxidants, or by disproportionation of iodosylarenes. Iodylbenzene is a colorless, microcrystalline solid, which detonates violently upon heating. X-ray structural analysis for $PhIO_2$ revealed a distorted octahedral arrangement with three primary bonds to iodine with bond distances in the range of 1.92−2.01 Å and three secondary I−O bonds of 2.57−2.73 Å.[38]

There is a substantial current interest in the cyclic iodylarenes, which have better stability due to the incorporation of the pentavalent iodine into a five-membered ring.[37,40,505−518] Similar to 2-iodosylbenzoic acid (see Section III.E), 2-iodylbenzoic acid has the actual structure of the cyclic hydroxyiodane oxide (**508**), as determined by X-ray structural analysis.[36,37] It is most commonly prepared by oxidation of 2-iodobenzoic acid with potassium bromate in sulfuric acid (eq 261).[39,508,519]

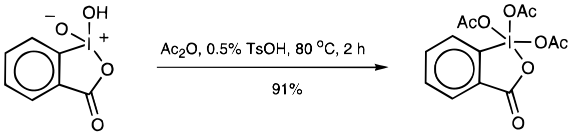
Oxide **508** was reported to be explosive under excessive heating or impact,[515] but Dess and Martin suggested that the explosive properties of some samples **508** were due to the presence of bromate or other impurities.[39] An alternative preparation of iodylbenzoic acids involve oxidation of the respective iodobenzoic acids with excess peracetic acid or aqueous sodium hypochlorite.[506]



(261)

**508**

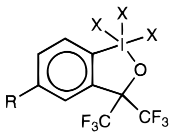
Benziodoxole oxide **508** is widely used as starting material for the preparation of triacetate **509**, the so called Dess−Martin periodane.[39,508−510] Recently Ireland and Liu reported an improved procedure for its preparation by the reaction of oxide **508** with acetic anhydride in the presence of *p*-toluenesulfonic acid (eq 262).[508]



(262)

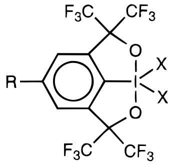
**508** **509**

In the early 1990s Martin and co-workers reported the synthesis, structure, and properties of several other, stable, cyclic periodanes **510**−**512**.[39,40,507]



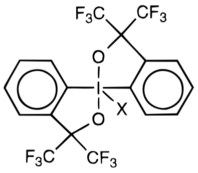
**510**

R = H, Me
X = F, OAc, OCOCF3, etc.



**511**

R = Me, *t*-Bu
2X = O or X= F, OTf, OCOCF3, etc.



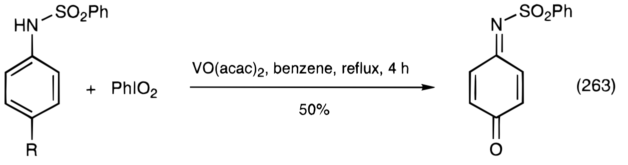
**512**

X = F, Cl, Br, O⁻, NHCMe3,
OTf, OCOCF3, etc.

### B. Reactions and Uses

Noncyclic iodylarenes have received only limited practical application because of their explosive properties. It was shown that iodylbenzene can oxidize alcohols to ketones[520] or it can be used to generate alkoxy radicals from alcohols under photochemical conditions.[521] In general, iodylbenzene has a relatively low reactivity as an oxidizing reagent and its reactions usually are conducted at high temperature or in the presence of a catalyst. Recently Barret and Daudon have found that vanadyl compounds can effectively improve the oxidizing properties of iodylbenzene toward aromatic amines.[522] For example, oxidation of sulfonamides **513** in the presence of vanadyl acetylacetonate proceeds under mild conditions to afford quinone imine **514** in moderate yield (eq 263).[522]

Another typical reaction pathway of iodylarenes includes nucleophilic substitution of the iodyl group

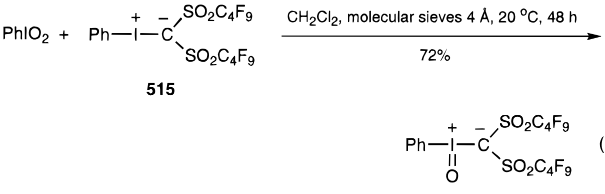


**513** R = H, OH **514** (263)

at an aromatic carbon with an external nucleophile. Recent examples of such reactions are represented by the hypochlorite-induced substitution of the iodyl group with chloride anion[523] and the palladium-catalyzed carbonylation of iodylarenes in water (eq 264).[524]

$$\mathrm{ArIO_2 + CO \xrightarrow[55\text{-}89\%]{H_2O,\ Na_2CO_3,\ 0.1\%\ Na_2[PdCl_4],\ 40\ ^{\circ}C,\ 1\ atm,\ 3\text{-}10\ h} ArCO_2Na} \qquad (264)$$

A novel pentavalent iodine ylide **516** was recently prepared via the transylidation reaction of iodylbenzene and iodonium ylide **515** (eq 265).[480]



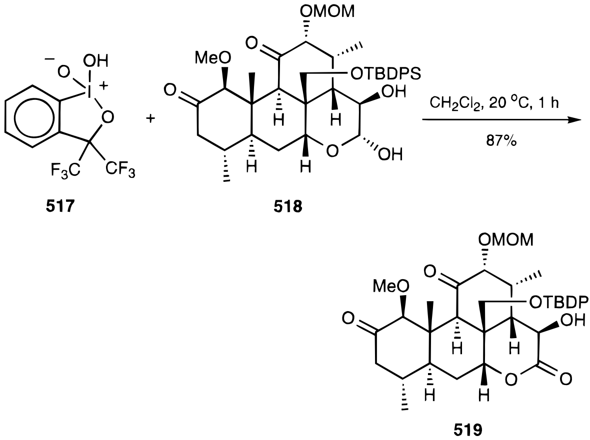
**515** **516** (265)

The cyclic derivatives of pentavalent iodine have attracted substantial recent attention as efficient and selective oxidizing reagents. Dess–Martin periodane **509** is especially useful as a reagent for the very selective oxidation of alcohols that gives excellent results even in the presence of the siloxy protective groups[525] or polypeptides.[39] In their 1991 paper Dess and Martin cited 74 references that described useful oxidations by reagent **509**.[39] More recently, Meyer and Schreiber[526] reported acceleration of the Dess–Martin oxidation, using **509**, by water.

Benziodoxole oxide **508** can also be applied for selective oxidations. Recently Frigerio and Santagostino reported its use for the oxidation of 1,2-diols to α-ketols or α-diketones without any cleavage of the glycol C–C bond.[511]

Another useful oxidizing reagent is benziodoxole oxide **517**. Grieco and co-workers have successfully applied this reagent in the oxidation of diol **518** to lactone **519** (eq 266), which was an important step in the total synthesis of (–)-glaucarubolone.[527] Attempts to use the Dess–Martin periodane, as well as many other oxidizing reagents, in this oxidation (eq 266) led only to cleavage products, but not the desired lactone **519**.

Similar to 1-hydroxy-1,2-benziodoxole-3(1*H*)-one **180** (see Section III.E), benziodoxole oxide **508** and its derivatives have attracted considerable research efforts due to its high catalytic activity in the cleavage of toxic phosphates and reactive esters.[301]



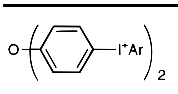
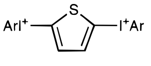
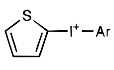
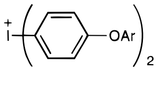
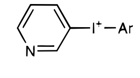
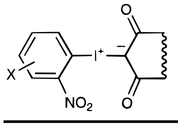
**517** **518** **519** (266)

## VII. Biological Properties of I(III) Species

In this section we present the biological properties of polyvalent organoiodine compounds. Of the different structural types of polyvalent organic iodine species discussed above, iodonium salts of various kinds have considerable biological activity.

Data in the patent literature[528] in the 1970's established the biocidal, antimicrobial activity of numerous diaryliodonium salts. Activity against a wide variety of both Gram positive and Gram negative bacterial species such as *Staphylococcus aureus*, *Mycobacterium phlei*, *Trichophyton mentagrophytes*, *Bacillus subtilis*, *Cephalvaucus fragons*, *Escherichia coli*, and others are described in these patents.[528] A brief description of the specific biological activity of several bisaryliodonium and bis-iodonium salts is summarized in Table 2. A more recent patent[528h] claims antimicrobial activity for a wide range of iodones (iodonium ylides), a typical example is given in Table 2. While exhibiting significant activity against microorganisms many iodonium salts have

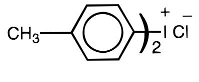
**Table 2. Biological Activity of Some Mono- and Bis(diaryl)iodonium Salts**

| Structure | Biological Activity | Ref. |
|---|---|---|
|  | Antimicrobial agents against bacteria, fungi, and organisms that attack seeds, roots and above-ground portions of plants, viricidal against small RNA viruses. | 528a |
|  | Antimicrobials for inhibition of the growth of many bacterial and fungal organisms that attack seeds, roots and above-ground portions of plants. | 528c |
|  | Control several bacterial organisms as well as molds, mildews, fungi, and slimes. | 528g |
|  | Anthelmintic agents that are active upon oral administration, active in vitro against gram negative and gram positive organisms. | 528d |
|  | Toxicity against growth of bacteria, fungi, organisms that attack seeds, roots and above-ground portions of plants, micro-organisms responsible for mold, mildew, rot, decay. | 528b |
|  | Active against Bacillus Subtilis, Pseudomonas species, Escherichia Coli, Staphylococcus species, fungi, algae, yeasts. | 528h |

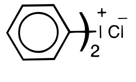
relatively low toxicity towards mammals: the $LD_{50}$ in mice for $Ph_2I^+Cl^-$ is 56 mg/kg of body weight, whereas for (*p*-chlorophenyl)(thienyl)iodonium chloride it is >4000 mg/kg.[528g]

Potential applications of iodonium salts, due to their potent antifungal and antimicrobial activity include[528] disinfectants as well as preservatives for diverse materials such as paints, adhesives, inks, paper, textiles, lubricants, cosmetics, etc.

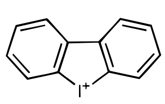
Ditolyliodonium chloride, **520**, is a potent inhibitor of microbes that deaminate amino acids in ruminating animals, thereby preventing maximum food utilization. Use of **520** as a food additive (~25 mg/kg), along with a methane inhibitor, in lambs[529] and steers[530,531] increased feed utilization efficiency by about 10%. Presumably the iodonium salt acts as a deaminase inhibitor. The parent diphenyliodonium salt (BPI), **521**, inhibits casein degradation at extremely low concentrations.[532]



**520**



**521**

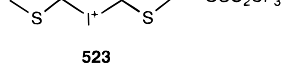


**522**

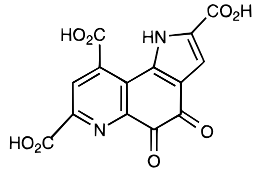
More recently, the physiological effects of several aryliodonium species and in particular bis(phenyl)-iodonium chloride (BPI), **521**, and diphenyleneiodonium (DPI), **522**, have been extensively explored.[533] Early work by Lardy[534] and co-workers established DPI as a potent hypoglycemic agent at a dose as low as 4 mg/kg body weight. It is believed that DPI binds covalently to a 23.5 kDa protein within complex I causing irreversible inhibition of NADH oxidation.[534,535] DPI inhibits gluconeogenesis in isolated rat hepatocyctes,[536] causes swelling of rat liver mitochondria,[537] and induces cardiomyopathy.[538] Both BPI and DPI induce mitochondrial myopathy[539,540] inhibit the superoxide production of neutrophiles[541−544] as well as nitric oxide synthase[545] and NADPH oxidase.[546−548] Diphenyl iodonium salts have been shown to be effective in the treatment of hypertension.[549]

The 1,3-dichloro isomer of DPI catalyzes the chloride exchange across the inner membrane of rat liver mitochondria, as well as inhibits succinate oxidation and stage 3 respiration.[550,551] Bis-iodonium salts of the type $PhI^+(CF_2)_nI^+Ph{\cdot}2BF_4^-$ possess anticholinesterase activity.[552]

BPI has also been shown to inhibit cytochrome P450 reductase.[553] Most recently Cohen, Gallop and co-workers demonstrated[554] that DPI as well as the bis-thiophenyl(iodonium) triflate **523** inhibit superoxide anion formation in vivo in rabbit aorta.



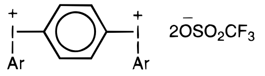
**523**



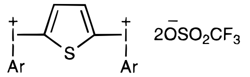
**524**

Gallop and co-workers have hypothesized[555,556] that the aforementioned physiological activity of iodonium species is due to their interaction with PQQ. Methoxatin, PQQ, (4,5-dihydro-4,5-dioxo-1*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylic acid), **524**, a pyrroloquinoline quinone is an organic cofactor, analogous to flavins, in an increasing number of biological redox processes.[557] It is widely distributed[558] in microorganisms, animal cells, tissues, and fluids and was first isolated from cultures of the methylotrophic soil bacterium *Pseudomonas* sp. in 1979.[559] An important role has also been suggested for PQQ as a growth or nutritional factor at critical stages in eukaryotic development.[560,561] However, its most important role remains in diverse redox cycling processes particularly in dehydrogenases and mitochondrial complex I.[562]

Supporting evidence[153] for this hypothesis comes from recent data demonstrating that a variety of iodonium salts are potent sequestering agents for PQQ. Specifically, bis-iodonium salts **525** and **526** inhibit PQQ at a nanomolar level (7−13 nM) and are nearly a 1000 times better inhibitors of PQQ than BPI and DPI. At the moment the exact mode of action of iodonium species in biological processes and PQQ inhibition is not yet understood. Nevertheless it is obvious from the foregoing brief summary that iodonium salts have an active role and a bright future in biological processes. Particularly intriguing is the potent PQQ inhibition by certain bis-iodonium salts[153] and the potential implications of this in the possible uses of bis-iodonium salts as biocides and in particular as a new class of antimicrobial agents.



**525:** Ar = $C_6H_5$, *p*-$FC_6H_4$



**526:** Ar = $C_6H_5$, *p*-$FC_6H_4$

## VIII. Conclusions

The preceding survey and review of the chemistry of polyvalent organic iodine species reflects an active resurgence of interest in these compounds although they have been known for a century. In just the last dozen years a wide variety of new reagents has been introduced and polyvalent iodine chemistry is employed increasingly in synthetic transformations, natural product synthesis as well as biochemical processes. Major advances have been made in the preparation and uses of alkynyl- and alkenyliodonium salts, azido-, amido-, imino-, and cyanoiodanes as well as perfluoroalkyliodonium derivatives.

There is a major surge of activity in pentavalent I(V) species. This is likely due to the increasing popularity and uses of the Dess−Martin reagent **509** since its introduction in 1983. The Dess−Martin periodane was recently characterized as "one of the mildest and most convenient reagents available for the oxidation of alcohols".[526] This characterization (i.e. mild and convenient) applies to many of the polyvalent iodine species discussed above. They are easily made from readily available commercial precursors, tend to be selective in their reactions, and can be used under mild reaction conditions (i.e. common solvents, at or near room temperature). Iodine (III) reagents resemble the reactivity characteristics of Hg(II), Tl(III), and Pb(IV) cognates without the toxic and environmental problems associated with the heavy metal species. Moreover, the mode of reaction of I(III) compounds, ligand exchange, reductive elimination etc. show similarities with transition metal species and in particular with the Ni-triad. Hence, much of the early, well-developed chemistry of Hg(II), Tl(III), and Pb(IV) as well as some of the rich, more recent, chemistry of the Pt and Pd metal systems may be carried out with the less expensive, less toxic, readily available iodine congeners. It is then evident that this analogy, albeit clearly limited, opens up an entire new vista and new opportunities for polyvalent iodine chemistry.

Likewise, the discovery that certain aryliodonium salts are PQQ sequestering agents may shed new light upon the well-established known antimicrobial properties of these polyvalent iodine compounds. The insights gained from the interaction of aryliodonium salts with PQQ might provide an understanding of the wide ranging biological activity of I(III) species briefly summarized in section VII.

The preparation of the unique macrocyclic molecular squares **439** and **459**, and related species, adds a new dimension to supramolecular chemistry[563,564] and in particular possible host−guest interactions, catalyses, noncovalent interactions, etc. involving these aryliodonium species.

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

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## X. References

(1) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford England, 1984; Chapter 17, pp 925−926.
(2) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 154.
(3) Willgerodt, C. *Chem. Ber.* **1892**, *25*, 3494.
(4) Hartmann, C.; Meyer, V. *Chem. Ber.* **1894**, *27*, 426.
(5) Willgerodt, C. *Die Organischen Verbindungen mit Mehrwertigen Jod*; Ferdinand Enke Verlag: Stuttgart, 1914.
(6) Sandin, R. B. *Chem. Rev.* **1943**, *32*, 249.
(7) Beringer, F. M.; Gindler, E. M. *Iodine Abstract Rev.* **1956**, *3*, 70.
(8) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.
(9) Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10,* 7099.
(10) Umemoto, T. *Yuki Gosei Kagaku Kyokai Shi* **1983**, *41,* 251.
(11) (a) Koser G. F. In *The Chemistry of Functional Groups, Suppl. D*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1983; Chapters 18 and 25, pp 721−811 and 1265−1351. (b) Koser G. F. In *The Chemistry of Halides, Pseudo-Halides and Azides, Suppl. D2*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1995; Chapter 21, pp 1173−1274.
(12) Nguyen, T. T.; Martin, J. C. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 1, p 563.
(13) Varvoglis, A. *Synthesis* **1984**, 7099.
(14) Ochiai, M.; Nagao, Y. *Yuki Gosei Kagaku Kyokai Shi* **1986**, *44*, 660.
(15) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244.
(16) Merkushev, E. B. *Russ. Chem. Rev.* **1987**, *56*, 826.
(17) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365.
(18) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431.
(19) Varvoglis A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers, Inc.: New York, 1992.
(20) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274.
(21) Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, 221.
(22) Prakash, O.; Saini, N.; Sharma, P. K. *Heterocycles* **1994**, *38*, 409.
(23) (a) Prakash, O.; Singh, S. P. *Aldrichimica Acta* **1994**, *27*, 15. (b) Prakash, O. *Aldrichimica Acta* **1995**, *28*, 63.
(24) Stang, P. J. In *The Chemistry of Triple-Bonded Functional Groups, Supplement C2*; Patai, S., Ed.; John Wiley & Sons, Ltd.: Chichester, 1994; Vol. 2, Chapter 20, pp 1164−1182.
(25) Stang, P. J. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH Publishers: Weinheim, 1995; Chapter 3, pp 67−98.
(26) Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Law, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.
(27) Archer, E. M.; van Schalkwyk, T. G. D. *Acta. Crystallogr.* **1953**, *6*, 88.
(28) Alcock, N. W.; Countryman, R. M.; Esperas, S.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1979**, 854.
(29) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 65.
(30) Martin, J. C. *Science* **1983**, *221*, 509.
(31) Reed, A. E.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.
(32) Burbank, R. D.; Jones, G. R. *Inorg. Chem.* **1974**, *13*, 1071.
(33) Edwards, A. J.; Taylor, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2174.
(34) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 902.
(35) Bozopoulos, A. P.; Rentzeperis, P. J. *Acta Crystallogr.* **1987**, *C43*, 142.
(36) Gougoutas, J. *Cryst. Struct. Commun.* **1981**, *10*, 489.
(37) Katritzky, A. R.; Savage, J. P.; Palenic, G. J.; Quian, K.; Zhang, Z.; Durst, H. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1657.
(38) Alcock, N. W.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1980**, 115.
(39) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277.
(40) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 2488.
(41) Saltzman, H.; Sharefkin, J. G. *Org. Syn.* **1963**, *43*, 60; *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 658.
(42) Zhdankin, V. V. Unpublished observations.
(43) Carmalt, C. J.; Crossley, J. G.; Knight, J. G.; Lightfoot, P.; Martin, A.; Muldowney, M. P.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2367.
(44) Siebert, H.; Handrich, M. *Z. Anorg. Allg. Chem.* **1976**, *426*, 173.
(45) Ehrlich, B. S.; Kaplan, M. *J. Chem. Phys.* **1971**, *54*, 612.
(46) Gao, Y.; Jiao, X.; Fan, W.; Shen, J.-K.; Shi, Q.; Basolo, F. *J. Coord. Chem.* **1993**, *29*, 349.
(47) Stang, P. J.; Zhdankin, V. V.; Zefirov, N. S. *Mendeleev Commun.* **1992**, 159.
(48) Zefirov, N. S.; Zhdankin, V. V.; Safronov, S. O.; Kaznacheev, A. A. *Zh. Org. Khim.* **1989**, *25*, 1807.
(49) Zhdankin, V. V.; Tykwinski, R; Williamson, B. L.; Stang, P. J.; Zefirov, N. S. *Tetrahedron Lett.* **1991**, *32*, 733.
(50) Magnus, P.; Hulme, C.; Weber, W. *J. Am. Chem. Soc.* **1994**, *116*, 4501.
(51) Magnus, P.; Lacour, J.; Weber, W. *J. Am. Chem. Soc.* **1993**, *115*, 9347.
(52) Magnus, P.; Lacour, J. *J. Am. Chem. Soc.* **1992**, *114*, 3993.
(53) Magnus, P.; Lacour, J. *J. Am. Chem. Soc.* **1992**, *114*, 767.
(54) Arimoto, M.; Yamaguchi, H.; Fujita, E.; Ochiai, M.; Nagao, Y. *Tetrahedron Lett.* **1987**, *28*, 6289.
(55) Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Hopkins, T. E. *Tetrahedron* **1988**, *44*, 1603.
(56) Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Tuncay, A. *Tetrahedron Lett.* **1989**, *30*, 3019.
(57) Gately, D. A.; Luther, T. A.; Norton, J. R.; Miller, M. M.; Anderson, O. P. *J. Org. Chem.* **1992**, *57*, 6496.
(58) Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 3228.
(59) Zhdankin, V. V.; Crittell, C. M.; Stang, P. J.; Zefirov, N. S. *Tetrahedron Lett.* **1990**, *31*, 4821.
(60) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1990**, *112*, 6437.
(61) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4571.
(62) Stang, P. J.; Williamson, B. L.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 5870.
(63) Stang, P. J.; Tykwinski, R.; Zhdankin, V. V. *J. Org. Chem.* **1992**, *57*, 1861.
(64) Williamson, B. L.; Tykwinski, R. R.; Stang, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 93.
(65) Tykwinski, R. R.; Stang, P. J. *Tetrahedron* **1993**, *49*, 3043.
(66) Williamson, B. L.; Stang, P. J.; Arif, A. M. *J. Am. Chem. Soc.* **1993**, *115*, 2590.
(67) Stang, P. J.; Ullmann, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1469.
(68) Stang, P. J.; Ullmann, J. *Synthesis* **1991**, 1073.
(69) Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Org. Chem.* **1987**, *52*, 3650.
(70) Kitamura, T.; Furuki, R.; Nagata, K.; Zheng, L.; Taniguchi, H. *Synlett* **1993**, 193.
(71) Kitamura, T.; Furuki, R.; Nagata, K.; Taniguchi, H.; Stang, P. J. *J. Org. Chem.* **1992**, *57*, 6810. Kitamura, T.; Furuki, R.; Taniguchi, H.; Stang, P. J. *Tetrahedron Lett.* **1990**, *31*, 703.
(72) Kitamura, T.; Furuki, R.; Taniguchi, H.; Stang, P. J. *Tetrahedron* **1992**, *48*, 7149.

(73) Zefirov, N. S.; Sorokin, V. D.; Zhdankin, V. V.; Koz'min, A. A. *Zh. Org. Khim.* **1986**, *22*, 450.
(74) Lyalin, V. V.; Orda, V. V.; Alekseeva, L. A.; Yagupolskii, L. M. *Zh. Org. Khim.* **1970**, *6*, 329.
(75) Personal communication of Dr. V. D. Sorokin, University of Texas at Arlington.
(76) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563.
(77) Takaya, T.; Enyo, H.; Imoto, E. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1032.
(78) Moriarty, R. M.; Vaid, R. K.; Duncan, M. P.; Ochiai, M.; Inenaga, M.; Nagao, Y. *Tetrahedron Lett.* **1988**, *29*, 6913.
(79) Ochiai, M.; Inenaga, M.; Nagao, Y.; Moriarty, R. M.; Vaid, R. K.; Duncan, M. P. *Tetrahedron Lett.* **1988**, *29*, 6917.
(80) Graven, A.; Jorgensen, K. A.; Dahl, S.; Stanczak, A. *J. Org. Chem.* **1994**, *59*, 3543.
(81) Sohmiya, H.; Kimura, T.; Bauchat, P.; Fujita, M.; Ando, T. *Chem. Lett.* **1991**, 1391.
(82) Sohmiya, H.; Kimura, T.; Fujita, M.; Ando, T. *Chem. Lett.* **1992**, 891.
(83) Suzuki, H.; Ikegami, T.; Matano, Y. *Tetrahedron Lett.* **1994**, *35*, 8197.
(84) Takata, T.; Tajima, R.; Ando, W. *J. Org. Chem.* **1983**, *48*, 4764.
(85) Moriarty, R. M.; Hu, H.; Gupta, S. C. *Tetrahedron Lett.* **1981**, *22*, 1283. Moriarty, R. M.; Hou, K. C. *Tetrahedron Lett.* **1984**, *25*, 691.
(86) Prakash, O.; Tanwar, M. P.; Goyal, S.; Pahuja, S. *Tetrahedron Lett.* **1992**, *33*, 6519.
(87) Prakash, O.; Kumar, D.; Saini, R. K.; Singh, S. P. *Synth. Commun.* **1994**, *24*, 2167.
(88) Prakash, O.; Mendiratta, S. *Synth. Commun.* **1992**, *22*, 327.
(89) Moriarty, R. M.; Gupta S. C.; Hu, H.; Berenschot, D. R.; White, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 686.
(90) Zefirov, N. S.; Kozhushkov, S. I.; Zhdankin, V. V.; Safronov, S. O. *Zh. Org. Khim.* **1989**, *25*, 1109.
(91) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Sorokin, V. D.; Semerikov, V. N.; Koz'min, A. A.; Caple, R.; Berglund, B. *Tetrahedron Lett.* **1986**, *27*, 3971.
(92) Zefirov, N. S.; Zhdankin, V. V.; Caple, R.; Palyulin, V. A.; Berglund, B.; Tykwinski, R.; Koz'min, A. S. *Izv. AN SSSR, Ser. Khim.* **1988**, 1452.
(93) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, Y.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095.
(94) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 869.
(95) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *J. Chem. Soc., Chem. Commun.* **1985**, 697.
(96) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Tetrahedron Lett.* **1983**, *24*, 777.
(97) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Chem. Pharm. Bull.* **1985**, *33*, 41.
(98) Lee, K.; Kim, D. Y.; Oh, Y. *Tetrahedron Lett.* **1988**, *29*, 667.
(99) Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1319.
(100) Ochiai, M.; Ito, T.; Masaki, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 15.
(101) Moriarty, R. M.; Prakash, O.; Duncan, M. P. *J. Chem. Soc., Perkin Trans. 1* **1987**, 559.
(102) Moriarty, R. M.; Duncan, M. P.; Prakash, O. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1781.
(103) Moriarty, R. M.; Prakash, O.; Duncan, M. P. *Synth. Commun.* **1986**, *16*, 1239.
(104) Kim, D. Y.; Mang, J. Y.; Oh, D. Y. *Synth. Commun.* **1994**, *24*, 629.
(105) Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *Tetrahedron Lett.* **1989**, *30*, 667.
(106) Zhdankin, V. V.; Tykwinski, R.; Caple, R.; Berglund, B.; Koz'min, A. S.; Zefirov, N. S. *Tetrahedron Lett.* **1988**, *29*, 3703.
(107) Zhdankin, V. V.; Tykwinski, R.; Mullikin, M.; Berglund, B.; Caple, R.; Zefirov, N. S.; Koz'min, A. S. *J. Org. Chem.* **1989**, *54*, 2605.
(108) McMurry, T. J.; Groves, J. T. In *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum Press: New York, 1986; pp 1−28.
(109) Blake, R.; Coon, M. J. *J. Biol. Chem.* **1989**, *264*, 3694.
(110) Viski, P.; Groves, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 8537.
(111) Leanord, D. R.; Lindsay Smith, J. R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1917. Leanord, D. R.; Lindsay Smith, J. R. *J. Chem. Soc., Perkin Trans. 2* **1991**, 25.
(112) Baciocchi, E.; Lanzalunga, O. *Tetrahedron* **1993**, *33*, 7267.
(113) Baciocchi, E.; d'Acunzo, F.; Galli, C.; Ioele, M. *J. Chem. Soc., Chem. Commun.* **1995**, 429.
(114) Baciocchi, E.; Ioele, M. *J. Org. Chem.* **1995**, *60*, 5504.
(115) Kinneary, J. F.; Albert, J. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 6124.
(116) Upadhyay, M. J.; Bhattacharya, P. K.; Ganeshpure, P. A.; Satish, S. *J. Mol. Catal.* **1992**, *77*, 277.
(117) Khan, M. M. T.; Chatterjee, D.; Khan, N. H.; Kureshi, R. I.; Bhatt, K. N. *J. Mol. Catal.* **1992**, *77*, 153.
(118) Souvignet, E.; Pautet, F.; Daudon, M. *J. Mol. Catal.* **1994**, *88*, 7.
(119) Bressan, M.; Forti, L.; Morvillo, A. *Inorg. Chim. Acta* **1993**, *211*, 217.
(120) Hill, C. L.; Zhang, X. *Nature* **1995**, *373*, 324.
(121) Moriarty, R. M.; Penmasta, R.; Prakash, I. *Tetrahedron Lett.* **1985**, *26*, 4699.
(122) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 4977.
(123) Yang, Y.; Diederich, F.; Valentine, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7195.
(124) Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 1779.
(125) Mylonas, V. E.; Sigalas, M. P.; Katsoulos, G. A.; Tsipis, C. A.; Varvoglis, A. G. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1691.
(126) Protasiewicz, J. D. *J. Chem. Soc., Chem. Commun.* **1995**, 1115.
(127) Carpenter, W. *J. Org. Chem.* **1966**, *31*, 2688.
(128) Fuchigami, T.; Fujita, T. *J. Org. Chem.* **1994**, *59*, 7190.
(129) Tsushima, T.; Kawada, K.; Tsuji, T. *Tetrahedron Lett.* **1982**, *23*, 1165.
(130) Zupan, M.; Pollak, A. *J. Fluorine Chem.* **1976**, *7*, 445. Patrick, T. B.; Scheibel, J. J.; Hall, W. E.; Lee, Y. H. *J. Org. Chem.* **1980**, *45*, 4492.
(131) Motherwell, W. B.; Wilkinson, J. A. *Synlett* **1991**, 191.
(132) Edmunds, J. J.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1989**, 881.
(133) Caddick, S.; Motherwell, W. B.; Wilkinson, J. A. *J. Chem. Soc., Chem. Commun.* **1991**, 674.
(134) Edmunds, J. J.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1348.
(135) Koen, M. J.; Le Guyader, F.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1995**, 1241.
(136) Koser, G. F.; Chen, K.; Huang, Y.; Summers, C. A. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1375.
(137) Zefirov, N. S.; Koz'min, A. S.; Kasumov, T.; Potekhin, K. A.; Sorokin, V. D.; Brel, V. K.; Abramkin, E. V.; Struchkov, Yu. T.; Zhdankin, V. V.; Stang, P. J. *J. Org. Chem.* **1992**, *57*, 2433.
(138) Zefirov, N. S.; Samsoniya, N. Sh.; Kutateladze, T. G.; Zhdankin, V. V. *Zh. Org. Khim.* **1991**, *27*, 220.
(139) Lucas, H. J.; Kennedy, E. R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 482.
(140) Moskovkina, T. V.; Vysotskii, V. I. *Zh. Org. Khim.* **1991**, *27*, 833.
(141) Mikolajczyk, M.; Midura, W. H.; Grzejszczak, S.; Montanari, F.; Cinquini, M.; Wieczorek, M. W.; Wojciechowska, J. K. *Tetrahedron* **1994**, *50*, 8053.
(142) Masson, S.; Thuillier, A. *Bull. Soc. Chim. Fr.* **1969**, 4368.
(143) Andreev, V. A.; Anfilogova, S. N.; Pekh, T. I.; Belikova, N. A. *Zh. Org. Khim.* **1993**, *29*, 142. Anfilogova, S. N.; Belikova, N. A. *Neftekhimiya* **1993**, *33*, 156; *Chem. Abstr.* **1994**, *120*, 106440e.
(144) Marchand, A. P.; Sorokin, V. D.; Rajagopal, D.; Bott, S. G. *Tetrahedron* **1994**, *50*, 9933.
(145) Poli, R.; Kelland, M. A. *J. Organomet. Chem.* **1991**, *419*, 127. Poli, R.; Gordon, J. C.; Desai, J. U.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1518. Gordon, J. C.; Lee, V. T.; Poli, R. *Inorg. Chem.* **1993**, *32*, 4460.
(146) Crispini, A.; Ghedini, M.; Neve, F. *Inorg. Chim. Acta* **1993**, *209*, 235.
(147) Burford, N.; Clyburne, J. A. C.; Gates, D. P.; Schriver, M. J.; Richardson, J. F. *J. Chem. Soc., Dalton Trans.* **1994**, 997.
(148) Radhakrishna, A. S.; Sivaprakash, K.; Singh, B. B. *Synth. Commun.* **1991**, *21*, 1625.
(149) Radhakrishna, A. S.; Augustine, B.; Sivaprakash, K.; Singh, B. B. *Synth. Commun.* **1991**, *21*, 1473.
(150) Sharefkin, J. G.; Saltzman, H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 660.
(151) Zhdankin, V. V.; Scheuller, M. C.; Stang, P. J. *Tetrahedron Lett.* **1993**, *34*, 6853.
(152) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1993**, *115*, 9808.
(153) Gallop, P. M.; Paz, M. A.; Stang, P. J.; Zhdankin, V. V.; Tykwinski, R. *J. Am. Chem. Soc.* **1993**, *115*, 11702.
(154) McKillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299.
(155) Ochiai, M.; Oshima, K.; Ito, T.; Masaki, Y.; Shiro, M. *Tetrahedron Lett.* **1991**, *32*, 1327.
(156) Ochiai, M.; Takaoka, Y.; Masaki, Y.; Nagao, Y.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 5677.
(157) Ray, D. G., III; Koser, G. F. *J. Org. Chem.* **1992**, *57*, 1607.
(158) Lee, C. K.; Mak, T. C. W.; Li, W. K.; Kirner, J. F. *Acta Crystallogr.* **1977**, *B33*, 1620. Bardan, M.; Birchall, T.; Frampton, C. S.; Kapoor, P. *Can. J. Chem.* **1989**, *67*, 1878. Frohn, H. J.; Helber, J.; Richter, A. *Chem. Ztg.* **1983**, *107*, 169.
(159) Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 889.
(160) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenz, B. A. *J. Org. Chem.* **1976**, *41*, 3609.
(161) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Koz'min, A. A. *Zh. Org. Chem.* **1984**, *20*, 446.
(162) Zhdankin, V. V.; Tykwinski, R.; Caple, R.; Berglund, B.; Koz'min, A. S.; Zefirov, N. S. *Tetrahedron Lett.* **1988**, *29*, 3717.
(163) Zhdankin, V. V.; Tykwinski, R.; Mullikin, M.; Berglund, B.; Caple, R.; Zefirov, N. S.; Koz'min, A. S. *J. Org. Chem.* **1989**, *54*, 2609.
(164) Kitamura, T.; Matsuyuki, J.; Taniguchi, H. *Synthesis* **1994**, 147.
(165) Kita, Y.; Okunaka, R.; Kondo, M.; Tohma, H.; Inagaki, M.; Hatanaka, K. *J. Chem. Soc., Chem. Commun.* **1992**, 429.

(166) Moriarty, R. M.; Berglund, B. A.; Penmasta, R. *Tetrahedron Lett.* **1992**, *33*, 6065.
(167) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Samoshin, V. V.; Koz'min, A. A. *Zh. Org. Chem.* **1984**, *20*, 444.
(168) Merkushev, E. B.; Karpitskaya, L. G.; Novosel'tseva, G. I. *Dokl. Akad. Nauk SSSR* **1979**, *245*, 607.
(169) Vasil'eva, V. P.; Khalfina, I. L.; Karpitskaya, L. G.; Merkushev, E. B. *Zh. Org. Khim.* **1987**, *23*, 2225.
(170) Karpitskaya, L. G.; Vasil'eva, V. P.; Merkushev, E. B. *Zh. Org. Khim.* **1991**, *27*, 1961.
(171) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Prakash, I. *J. Org. Chem.* **1988**, *53*, 6124.
(172) Moriarty, R. M.; Hopkins, T. E.; Vaid, R. K.; Vaid, B. K.; Levy, S. G. *Synthesis* **1992**, 847.
(173) Pelter, A.; Elgendy, S. M. A. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1891.
(174) McKillop, A.; McLaren, L.; Taylor, R. J. K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2047.
(175) Fleck, A. E.; Hobart, J. A.; Morrow, G. W. *Synth. Commun.* **1992**, *22*, 179.
(176) Dhanalekshmi, S.; Balasubramanian, K. K.; Ventakatachalam, C. S. *Tetrahedron* **1994**, *50*, 6387.
(177) Mitchell, A. S.; Russell, R. A. *Tetrahedron Lett.* **1993**, *34*, 545.
(178) Karam, O.; Jacquesy, J.-C.; Jouannetaud, M.-P. *Tetrahedron Lett.* **1994**, *35*, 2541.
(179) Wipf, P.; Kim, Y.; Fritch, P. C. *J. Org. Chem.* **1993**, *58*, 7195.
(180) Kita, Y.; Tohma, H.; Kikuchi, K.; Inagaki, M.; Yakura, T. *J. Org. Chem.* **1991**, *56*, 435.
(181) Kaçan, M.; Koyuncu, D.; McKillop, A. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1771.
(182) Murakata, M.; Yamada, K.; Hoshino, O. *J. Chem. Soc., Chem. Commun.* **1994**, 443.
(183) Hara, H.; Inoue, T.; Nakamura, H.; Endoh, M.; Hoshino, O. *Tetrahedron Lett.* **1992**, *43*, 6491.
(184) Pelter, A.; Ward, R. S.; Abd-El-Ghani, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2249.
(185) Pelter, A.; Elgendy, S. M. A. *Tetrahedron: Asymmetry* **1994**, *5*, 329.
(186) Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura, T. *J. Am. Chem. Soc.* **1992**, *114*, 2175.
(187) Gates, B. D.; Dalidowicz, P.; Tebben, A.; Wang, S.; Swenton, J. S. *J. Org. Chem.* **1992**, *57*, 2135.
(188) Deady, L. W.; Quazi, N. H. *Aust. J. Chem.* **1993**, *46*, 411.
(189) Moriarty, R. M.; Berglund, B. A.; Rao, M. S. C. *Synthesis* **1993**, 318.
(190) Zeng, H.; Chen, Z.-C. *Synth. Commun.* **1993**, *23*, 2497.
(191) Barton, D. H. R.; Jaszberenyi, J. C.; Shinada, T. *Tetrahedron Lett.* **1993**, *45*, 7191.
(192) Chen, D. W.; Chen, Z. C. *Synthesis* **1994**, 773.
(193) Yang, R.-Y.; Dai, L.-X. *J. Org. Chem.* **1993**, *58*, 3381.
(194) Chen, D.-W.; Chen, Z.-C. *Synth. Commun.* **1995**, *25*, 1617.
(195) Moriarty, R. M.; Chany, C. J., II; Vaid, R. K.; Prakash, O.; Tuladhar, S. M. *J. Org. Chem.* **1993**, *58*, 2478.
(196) Cardellini, L.; Greci, L.; Maurelly, E.; Orena, M.; Stipa, P.; Tosi, G. *Heterocycles* **1992**, *34*, 1917.
(197) Reddy, G. C. *Tetrahedron Lett.* **1995**, *36*, 1001.
(198) Matsuura, I.; Ueda, T.; Murakami, N.; Nagai, S.; Sakakibara, J. *Chem. Pharm. Bull.* **1993**, *41*, 608.
(199) Kumar, D.; Prakash, O.; Singh, S. P. *J. Chem. Research (S)* **1993**, 244.
(200) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 287.
(201) Rychnovsky, S. D.; Griesgraber, G.; Kim, J. *J. Am. Chem. Soc.* **1994**, *116*, 2621.
(202) Poli, G.; Belvisi, L.; Manzoni, L.; Scolastico, C. *J. Org. Chem.* **1993**, *58*, 3165.
(203) Chen, D.-W.; Chen, Z.-C. *Tetrahedron Lett.* **1994**, *35*, 7637.
(204) Chen, D.-W.; Chen, Z.-C. *Synth. Commun.* **1995**, *25*, 1605.
(205) Liu, Z.-D.; Chen, Z.-C. *Heteroatom Chem.* **1992**, *3*, 559.
(206) D'Auria, M.; Mauriello, G. *Tetrahedron Lett.* **1995**, *36*, 4883.
(207) Boyle, R. W.; Johnson, C. K.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1995**, 527.
(208) Yamamoto, Y.; Ohno, M.; Eguchi, S. *Tetrahedron Lett.* **1995**, *36*, 5539.
(209) Georgiev, G.; Kamenska, E.; Christov, L.; Sideridou-Karayannidou, I.; Karayannidis, G.; Varvoglis, A. *Eur. Polym. J.* **1992**, *28*, 207.
(210) Togo, H.; Aoki, M.; Yokoyama, M. *Tetrahedron Lett.* **1991**, *32*, 6559.
(211) Togo, H.; Aoki, M.; Yokoyama, M. *Chem. Lett.* **1991**, 1691.
(212) Togo, H.; Aoki, M.; Kuramochi, T.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2417.
(213) Vismara, E.; Torri, G.; Pastori, N.; Marchiandi, M. *Tetrahedron Lett.* **1992**, *33*, 7575.
(214) Togo, H.; Aoki, M.; Yokoyama, M. *Chem. Lett.* **1992**, 2169.
(215) Togo, H.; Aoki, M.; Yokoyama, M. *Tetrahedron* **1993**, *36*, 8241.
(216) Togo, H.; Muraki, T.; Yokoyama, M. *Synthesis* **1995**, 155.
(217) Arencibia, M. T.; Freire, R.; Perales, A.; Rodriguez, M. S.; Suàrez, E. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3349.
(218) Boto, A.; Betancor, C.; Prangè, T.; Suàrez, E. *Tetrahedron Lett.* **1992**, *33*, 6687.
(219) Boto, A.; Betancor, C.; Prangè, T.; Suàrez, E. *J. Org. Chem.* **1994**, *59*, 4393.
(220) Boto, A.; Betancor, C.; Suàrez, E. *Tetrahedron Lett.* **1994**, *35*, 5509.
(221) Boto, A.; Betancor, C.; Suàrez, E. *Tetrahedron Lett.* **1994**, *35*, 6933.
(222) Boto, A.; Betancor, C.; Hernàndez, R.; Rodriguez, M. S.; Suàrez, E. *Tetrahedron Lett.* **1993**, *34*, 4865.
(223) Galatsis, P.; Millan, S. D. *Tetrahedron Lett.* **1991**, *32*, 7493.
(224) Mowbray, C. E.; Pattenden, G. *Tetrahedron Lett.* **1993**, *34*, 127.
(225) de Armas, P.; Francisco, C. G.; Suàrez, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 772.
(226) Inanaga, J.; Sugimoto, Y.; Yokoyama, Y.; Hanamoto, T. *Tetrahedron Lett.* **1992**, *33*, 8109.
(227) De Mico, A.; Margarita, R.; Piancatelly, G. *Tetrahedron Lett.* **1995**, *36*, 3553.
(228) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476.
(229) Schmeisser, M.; Lehmann, E.; Naumann, D. *Chem. Ber.* **1977**, *110*, 2665.
(230) Dasent, W. E.; Waddington, T. C. *J. Chem. Soc.* **1960**, 3350.
(231) Bushnell, G. W.; Fischer, A.; Ibrahim, P. N. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1281.
(232) Gallos, J.; Varvoglis, A.; Alcock, N. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 757. Kokkou, S. C.; Cheer, C. J. *Acta Crystallogr.* **1986**, *C42*, 1159. Kokkou, S. C.; Cheer, C. J. *Acta Crystallogr.* **1986**, *C42*, 1748.
(233) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 1542.
(234) Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, *45*, 1543.
(235) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324.
(236) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462.
(237) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
(238) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Semerikov, V. N.; Koz'min, A. S. *Dokl. AN SSSR* **1986**, *288*, 385.
(239) Shah, M.; Taschner, M. J.; Koser, G. F. *Tetrahedron Lett.* **1986**, *27*, 4557. Shah, M.; Taschner, M. J.; Koser, G. F.; Rach, N. L.; Jenkins, T. E.; Cyr, P.; Powers, D. *Tetrahedron Lett.* **1986**, *27*, 5437.
(240) Kim, H.; Schlecht, M. F. *Tetrahedron Lett.* **1987**, *28*, 5229.
(241) Schaumann, E.; Kirschning, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1481.
(242) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Koz'min, A. S.; Chizhov, O. S. *Zh. Org. Khim.* **1985**, *21*, 2461.
(243) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700.
(244) Margida, A. J.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4703.
(245) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1990**, *55*, 1513.
(246) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452.
(247) Stang, P. J.; Surber, B. W.; Chen, Z-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228.
(248) Carman, C. S.; Koser, G. F. *J. Org. Chem.* **1983**, *48*, 2534.
(249) Margida, A. J.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 3643.
(250) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem.* **1989**, *54*, 1101.
(251) Tuncay, A.; Dustman, J. A.; Fisher, G.; Tuncay, C. I. *Tetrahedron Lett.* **1992**, *33*, 7647.
(252) Prakash, O.; Saini, N. *Synth. Commun.* **1993**, *23*, 1455.
(253) Prakash, O.; Tanwar, M. P. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1168. Mohan, J.; Singh, V.; Kataria, S. *J. Chin. Chem. Soc.* **1994**, *41*, 617. Litkei, G.; Gulácsi, K.; Antus, S.; Blaskó, G. *Liebigs Ann.* **1995**, 1711. Andrews, I. P.; Lewis, N. J.; McKillop, A.; Wells, A. S. *Heterocycles* **1994**, *38*, 713. Prakash, O.; Saini, R. K.; Kumar, D.; Singh, S. P. *Synth. Commun.* **1995**, *25*, 3363.
(254) Kirschning, A.; Dräger, G.; Harders, J. *Synlett* **1993**, 289.
(255) Kirschning, A. *J. Org. Chem.* **1995**, *60*, 1228.
(256) Zefirov, N. S.; Zhdankin, V. V.; Makhon'kova, G. V.; Dan'kov, Yu. V.; Koz'min, A. S. *J. Org. Chem.* **1985**, *50*, 1872.
(257) MacDonald, T. L.; Narasimhan, N. *J. Org. Chem.* **1985**, *50*, 5000.
(258) Moriarty, R. M.; Khosrowshahi, J. S.; Penmasta, R. *Tetrahedron Lett.* **1989**, *30*, 791. Moriarty, R. M.; Khosrowshahi, J. S. *Synthesis* **1989**, 855. Moriarty, R. M.; Khosrowshahi, J. S. *Synth. Commun.* **1989**, *19*, 1395.
(259) Lazbin, I. M.; Koser, G. F. *J. Org. Chem.* **1986**, *51*, 2669.
(260) Vasudevan, A.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 5158.
(261) Lazbin, I. M.; Koser, G. F. *J. Org. Chem.* **1987**, *52*, 476.
(262) Moriarty, R. M.; Khosrowshahi, J. S.; Awasthi, A. K.; Penmasta, R. *Synth. Commun.* **1988**, *18*, 1179.
(263) Bovonsombat, P.; Angara, G. J.; McNelis, E. *Synlett* **1992**, 131.
(264) Bovonsombat, P.; McNelis, E. *Synthesis* **1993**, 237.
(265) Bovonsombat, P.; Djuardi, E.; McNelis, E. *Tetrahedron Lett.* **1994**, *35*, 2841.
(266) Angara, G. J.; McNelis, E. *Tetrahedron Lett.* **1991**, *32*, 2099.
(267) Bovonsombat, P.; Angara, G. J.; McNelis, E. *Tetrahedron Lett.* **1994**, *37*, 6787.
(268) Angara, G. J.; Bovonsombat, P.; McNelis, E. *Tetrahedron Lett.* **1992**, *33*, 2285.
(269) Bovonsombat, P.; McNelis, E. *Tetrahedron Lett.* **1992**, *33*, 7705.
(270) Bovonsombat, P.; McNelis, E. *Tetrahedron* **1993**, *49*, 1525.
(271) Bovonsombat, P.; McNelis, E. *Tetrahedron Lett.* **1994**, *35*, 6431.

(272) Bovonsombat, P.; McNelis, E. *Tetrahedron Lett.* **1993**, *34*, 4277. Djuardi, E.; Bovonsombat, P.; McNelis, E. *Tetrahedron* **1994**, *50*, 11793.

(273) Bovonsombat, P.; McNelis, E. *Synth. Commun.* **1995**, *25*, 1223.

(274) Marchand, A. P.; Rajagopal, D.; Bott, S. G.; Watson, W. H.; Sun, D. *Book of Abstracts*, 209th American Chemical Society National Meeting, Anaheim, CA, Spring, 1995; American Chemical Society: Washington, DC, 1984; ORGN 361.

(275) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210.

(276) Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. *J. Org. Chem.* **1990**, *55*, 315.

(277) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 4988.

(278) Koser, G. F.; Kokil, P. B.; Shah, M. *Tetrahedron Lett.* **1987**, *28*, 5431.

(279) Kikugawa, Y.; Kawase, M. *Chem. Lett.* **1990**, 581.

(280) Ray, D. G., III; Koser, G. F. *J. Am. Chem. Soc.* **1990**, *112*, 5672.

(281) Moriarty, R. M.; Penmasta, R.; Prakash, I. *Tetrahedron Lett.* **1987**, *28*, 877.

(282) Koser, G. F.; Lodaya, J. S.; Ray, D. G., III; Kokil, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 2987.

(283) Koser, G. F.; Chen, X.; Chen, K.; Sun, G. *Tetrahedron Lett.* **1993**, *34*, 779.

(284) Stang, P. J.; Kitamura, T.; Boehshar, M.; Wingert, H. *J. Am. Chem. Soc.* **1989**, *111*, 2225.

(285) Alcock, N. W.; Waddington, T. C. *J. Chem. Soc.* **1963**, 4103.

(286) Zefirov, N. S.; Koz'min, A. S.; Zhdankin, V. V. *Izv. AN SSSR, Ser. Khim.* **1983**, 1682.

(287) Potekhin, K. A.; Yanovskiy, A. I.; Struchkov, Yu. T.; Sorokin, V. D.; Koz'min, A. S.; Zhdankin, V. V.; Zefirov, N. S. *Dokl. AN SSSR* **1988**, *301*, 119.

(288) van Look, G. *Chem. Eng. News* **1989**, *67* (30), 2.

(289) Balthazar, T. M.; Godaz, D. E.; Stults, B. R. *J. Org. Chem.* **1979**, *44*, 1447. Naae, D. G.; Gougoutas, J. Z. *J. Org. Chem.* **1975**, *40*, 2129. Prout, K.; Stevens, N. M.; Coda, A.; Tazzoli, V.; Shaw, R. A.; Demir, T. *Z. Naturforsch.* **1976**, *31b*, 687.

(290) Jaffe, H.; Leffler, J. E. *J. Org. Chem.* **1975**, *40*, 797.

(291) Koser, G. F.; Sun, G.; Porter, C. W.; Youngs, W. J. *J. Org. Chem.* **1993**, *58*, 7310.

(292) Balthazar, T. M.; Miles, J. A.; Stults, B. R. *J. Org. Chem.* **1978**, *43*, 4538.

(293) Leffler, J. E.; Jaffe, H. *J. Org. Chem.* **1973**, *38*, 2719.

(294) (a) Shefter, E.; Wolf, W. *J. Pharm. Sci.* **1965**, *54*, 104. (b) Etter, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5326, 5331. Gougoutas, J. Z.; Clardy, J. C. *J. Solid State Chem.* **1972**, *4*, 226. Gougoutas, J. Z.; Clardy, J. C. *J. Solid State Chem.* **1972**, *4*, 230. Gougoutas, J. Z.; Lessinger, L. *J. Solid State Chem.* **1974**, *9*, 155. Batchelor, R. J.; Birchall, T.; Sawyer, J. F. *Inorg. Chem.* **1986,** *25*, 1415.

(295) Ochiai, M.; Masaki, Y.; Shiro, M. *J. Org. Chem.* **1991**, *56*, 5511.

(296) Ochiai, M.; Ito, T.; Masaki, Y.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 6269.

(297) Ochiai, M.; Ito, T.; Shiro, M. *J. Chem. Soc., Chem. Commun.* **1993**, 218.

(298) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T. Unpublished results.

(299) Panetta, C. A.; Garlick, S. M.; Durst, H. D.; Longo, F. R.; Ward, J. R. *J. Org. Chem.* **1990**, *55*, 5202.

(300) Baker, G. P.; Mann, F. G.; Sheppard, N.; Tetlow, A. J. *J. Chem. Soc.* **1965**, 3721. Gavina, F.; Luis, S. V.; Costero, A. M.; Gil, P. *Tetrahedron* **1986**, *42*, 155.

(301) Moss, R. A.; Alwis, K. W.; Bizzigotti, G. O. *J. Am. Chem. Soc.* **1983**, *105*, 681. Ramesh, V.; Labes, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 738. Katritzky, A. R.; Duell, B. L.; Durst, H. D.; Knier, B. L. *J. Org. Chem.* **1988**, *53*, 3972. Moss, R. A.; Alwis, K. W.; Shin, J.-S. *J. Am. Chem. Soc.* **1984**, *106*, 2651. Moss, R. A.; Wilk, B.; Krogh-Jespersen, K.; Blair, J.; Westbrook, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 250. Moss, R. A.; Zhang, H. *Tetrahedron Lett.* **1993**, *34*, 6225. Moss, R. A.; Swarup, S.; Ganguli, S. *J. Chem. Soc., Chem. Commun.* **1987**, 860. Moss, R. A.; Chatterjee, S.; Wilk, B. *J. Org. Chem.* **1986**, *51*, 4303.

(302) Moss, R. A.; Scrimin, P.; Rosen, R. T. *Tetrahedron Lett.* **1987**, *28*, 251. Moss, R. A.; Kim, K. Y.; Swarup, S. *J. Am. Chem. Soc.* **1986**, *108*, 788.

(303) Moss, R. A.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 4471.

(304) Zhdankin, V. V.; Kuehl, C. J.; Bolz, J. T.; Formaneck, M. S.; Simonsen, A. J. *Tetrahedron Lett.* **1994**, *35*, 7323.

(305) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Formaneck, M. S.; Bolz, J. T. *Tetrahedron Lett.* **1994**, *35*, 9677.

(306) Hadjiarapoglou, L.; Spyroudis, S.; Varvoglis, A. *Synthesis* **1983**, 207.

(307) Papadopoulou, M.; Varvoglis, A. *J. Chem. Res. (S)* **1983**, 66. Papadopoulou, M.; Varvoglis, A. *J. Chem. Res. (S)* **1984**, 166.

(308) Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361.

(309) Mishra, A. K.; Olmstead, M. M.; Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 3210.

(310) Abramovitch, R. A.; Bailey, T. D.; Takaya, T.; Uma, V. *J. Org. Chem.* **1974**, *39*, 340.

(311) Mansuy, D.; Mahy, J. P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161.

(312) Cicero, R. L.; Zhao, D.; Protasiewicz, J. D. *Inorg. Chem.* **1996**, *35*, 275.

(313) Evans, D. A.; Faul, M. M.; Bilodeau, M. *J. Org. Chem.* **1991**, *56*, 6744.

(314) Evans, D. A.; Faul, M. M.; Bilodeau, M. *J. Am. Chem. Soc.* **1994**, *116*, 2742.

(315) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328.

(316) Pérez, P. J.; Brookhart, M.; Templeton, J. L. *Organometallics* **1993**, *12*, 261.

(317) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326.

(318) O'Connor, K. J.; Wey, S.-J.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001.

(319) Noda, K.; Hosoya, N.; Irie, R.; Ito, Y.; Katsuki, T. *Synlett* **1993**, 469.

(320) Nishibayashi, Y.; Chiba, T.; Ohe, K.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1243.

(321) Potekhin, K. A.; Panov, V. N.; Maleev, A. V.; Goncharov, A. V.; Struchkov, Yu. T.; Glynskii, A. G.; Semerikov, V. N.; Berglund, B.; Koz'min, A. S.; Caple, R.; Zhdankin, V. V.; Zefirov, N. S. *Dokl. AN SSSR* **1989**, *305*, 1136.

(322) Potekhin, K. A.; Maleev, A. V.; Struchkov, Yu. T.; Glynskii, A. G.; Semerikov, V. N.; Caple, R.; Koz'min, A. S.; Zhdankin, V. V.; Zefirov, N. S. *Dokl. AN SSSR* **1990**, *311*, 373.

(323) Yang, R.-Y.; Dai, L.-X. *Synthesis* **1993**, 481.

(324) Cech, F.; Zbiral, E. *Tetrahedron* **1975**, *31*, 605.

(325) Zbiral, E.; Ehrenfreund, J. *Tetrahedron* **1971**, *27*, 4125. Zbiral, E.; Nestler, G. *Tetrahedron* **1970**, *26*, 2945. Ehrenfreund, J.; Zbiral, E. *Liebigs Ann. Chem.* **1973**, 290.

(326) Moriarty, R. M.; Khosrowshahi, J. S. *Tetrahedron Lett.* **1986**, *27*, 2809.

(327) Moriarty, R. M.; Khosrowshahi, J. S. *Synth. Commun.* **1987**, *17*, 89.

(328) Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura, T. *Tetrahedron Lett.* **1991**, *32*, 4321.

(329) Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3684.

(330) Kita, Y.; Tohma, H.; Takada, T.; Mitoh, S.; Fujita, S.; Gyoten, M. *Synlett* **1994**, 427.

(331) Fontana, F.; Minisci, F.; Yan, Y. M.; Zhao, L. *Tetrahedron Lett.* **1993**, *34*, 2517.

(332) Tingoli, M.; Tiecco, M.; Chianelli, D.; Balducci, R.; Temperini, A. *J. Org. Chem.* **1991**, *56*, 6809.

(333) Czernecki, S.; Randriamandimby, D. *Tetrahedron Lett.* **1993**, *34*, 7915.

(334) Magnus, P.; Evans, A.; Lacour, J. *Tetrahedron Lett.* **1992**, *33*, 2933.

(335) Magnus, P.; Roe, M. B.; Hulme, C. *J. Chem. Soc., Chem. Commun.* **1995**, 263.

(336) Magnus, P.; Hulme, C. *Tetrahedron Lett.* **1994**, *35*, 8097.

(337) Kirschning, A.; Domann, S.; Dräger, G.; Rose, L. *Synlett* **1995**, 767.

(338) Krasutsky, A. P.; Kuehl, C. J.; Zhdankin, V. V. *Synlett* **1995**, 1081.

(339) Grushin, V. V. *Acc. Chem. Res.* **1992**, *25*, 529.

(340) Kita, Y.; Okuno, T.; Tohma, H.; Akai, S.; Matsumoto, K. *Tetrahedron Lett.* **1994**, *35*, 2717.

(341) (a) Kita, Y.; Takada, T.; Mihara, S.; Tohma, H. *Synlett* **1995**, 211. (b) Greidanus, J. W.; Rebel, W. J.; Sandin, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 1505. (c) Kotali, E.; Varvoglis, A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2759. Kotali, E.; Varvoglis, A. *J. Chem. Res. (S)* **1989**, 142.

(342) Montanari, V.; Resnati, G. *Tetrahedron Lett.* **1994**, *35*, 8015.

(343) Bravo, P.; Montanari, V.; Resnati, G.; DesMarteau, D. D. *J. Org. Chem.* **1994**, *59*, 6093.

(344) Cotter, J. L.; Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 4692.

(345) Moss, R. A.; Wilk, B.; Krogh-Jespersen, K.; Westbrook, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 6730.

(346) Reich, H. J.; Peake, S. L. *J. Am. Chem. Soc.* **1978**, *100*, 4888.

(347) Knapp, S.; Naughton, A. B. J.; Dhar, T. G. M. *Tetrahedron Lett.* **1992**, *33*, 1025.

(348) Kim, S.; Fuchs, P. L. *Tetrahedron Lett.* **1994**, *35*, 7163.

(349) Wiberg, K. B.; Pratt, W. E.; Matturo, M. G. *J. Org. Chem.* **1982**, *47*, 2720.

(350) Della, E. W.; Head, N. J. *J. Org. Chem.* **1992**, *57*, 2850.

(351) Zefirov, N. S.; Zhdankin, V. V.; Koz'min, A. S. *Izv. AN SSSR, Ser. Khim.* **1982**, 1676.

(352) Zefirov, N. S.; Zhdankin, V. V.; Sorokin, V. D.; Dan'kov, Yu. V.; Kirin, V. N.; Koz'min, A. S. *Zh. Org. Khim.* **1982**, *18*, 2608.

(353) Zefirov, N. S.; Zhdankin, V. V.; Koz'min, A. A. *Tetrahedron Lett.* **1986**, *27*, 1845.

(354) Damon, D. B.; Hoover, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 6439.

(355) Morris, D. G.; Shepperd, A. G. *J. Chem. Soc., Chem. Commun.* **1981**, 1250.

(356) Bradley, G. W.; Holloway, J. H.; Koh, H. J.; Morris, D. G.; Watson, P. G. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3001.

(357) Lyalin, V. V.; Orda, V. V.; Alekseeva, L. A.; Yagupolskii, L. M. *J. Org. Chem. USSR* **1972**, *8*, 1027.

(358) Mironova, A. A.; Soloshonok, I. V.; Maletina, I. I.; Orda, V. V.; Yagupolskii, L. M. *Zh. Org. Khim.* **1988**, *24*, 593.

(359) Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3307.

(360) Zhdankin, V. V.; Kuehl, C. J.; Simonsen, A. J. *Tetrahedron Lett.* **1995**, *36*, 2203.

(361) Yagupolskii, L. M.; Maletina, I. I.; Kondratenko, N. V.; Orda, V. V. *Synthesis* **1978**, 835.

(362) Umemoto, T.; Kuriu, Y.; Shuyama, H.; Miyano, O.; Nakayama, S. *J. Fluorine Chem.* **1982**, *20*, 695. Umemoto, T.; Kuriu, Y.; Shuyama, H.; Miyano, O.; Nakayama, S. *J. Fluorine Chem.* **1986**.

(363) Zhdankin, V. V.; Kuehl, C. *Tetrahedron Lett.* **1994**, *35*, 1809.

(364) Zhdankin, V. V.; Kuehl, C. J.; Bolz, J. T.; Zefirov, N. S. *Mendeleev Commun.* **1994**, 165.

(365) Kuehl, C. J.; Bolz, J. T.; Zhdankin, V. V. *Synthesis* **1995**, 312.

(366) Tyrra, W.; Naumann, D. *Can. J. Chem.* **1991**, *69*, 327.

(367) Kuehl, C. J. *M.S. Thesis*, University of Minnesota, Duluth, **1995**.

(368) Umemoto, T. *Tetrahedron Lett.* **1984**, *25*, 81. Umemoto, T.; Kuriu, Y.; Nakayama, S. *Tetrahedron Lett.* **1982**, *23*, 4101. Umemoto, T.; Kuriu, Y.; Nakayama, S. *Tetrahedron Lett.* **1982**, *23*, 1169. Umemoto, T.; Kuriu, Y.; Nakayama, S.; Miyano, O. *Tetrahedron Lett.* **1982**, *23*, 1471. Umemoto, T.; Kuriu, Y.; Shuyama, H. *Chem. Lett.* **1981**, 1663. Umemoto, T.; Kuriu, Y.; Miyano, O. *Tetrahedron Lett.* **1982**, *23*, 3579. Umemoto, T.; Kuriu, Y. *Tetrahedron Lett.* **1981**, *22*, 5197. Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3823. Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2008. Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 439.

(369) Stang, P. J.; Tykwinski, R.; Zhdankin, V. V. *J. Heterocycl. Chem.* **1992**, *29*, 815.

(370) Stang, P. J.; Zhdankin, V. V.; Tykwinski, R.; Zefirov, N. S. *Tetrahedron Lett.* **1992**, *33*, 1419.

(371) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4572.

(372) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Mismash, B.; Woodward, J. K.; Simonsen, A. J. *Tetrahedron Lett.* **1995**, *36*, 7975.

(373) Zhdankin, V. V.; Kuehl, C. J.; Arif, A. M.; Stang, P. J. *Mendeleev Commun.* **1996**, in press.

(374) Beringer, F. M.; Galton, S. A. *J. Org. Chem.* **1965**, *30*, 1930.

(375) Kitamura, T.; Stang, P. J. *J. Org. Chem.***1988**, *53*, 4105.

(376) Stang, P. J.; Kitamura, T. *Org. Syn.* **1992**, *70*, 118.

(377) Bachi, M. D.; Bar-Ner, N.; Crittell, C. M.; Stang, P. J.; Williamson, B. L. *J. Org. Chem.* **1991**, *56*, 3912.

(378) Stang, P. J.; Arif, A. M.; Crittell. C. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 287.

(379) Ochiai, M.; Kunishima, M; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 4501.

(380) Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 118.

(381) Omai, I. *Organotin Chemistry*; Elsevier: New York, 1989.

(382) Williamson, B. L.; Stang, P. J. *Synlett* **1992**, 199.

(383) Kitamura, T.; Furuki, R.; Zheng, L.; Fujimoto, T.; Taniguchi, H. *Chem. Lett.* **1992**, 2241.

(384) Stang, P. J.; Zhdankin, V. V.; Arif, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 8997.

(385) Ochiai, M.; Kunishima, M.; Fuji, K.; Nagao, Y.; Shiro, M. *Chem. Pharm. Bull.* **1989**, *37*, 1948.

(386) Mironova, A. A.; Maletina, I. I.; Iksanova, S. V.; Orda, V. V.; Yagupolskii, L. M. *Zh. Org. Khim.* **1989**, *25*, 306.

(387) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348.

(388) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

(389) Bachi, M. D.; Bar-Ner, N.; Stang, P. J.; Williamson, B. L. *J. Org. Chem.* **1993**, *58*, 7923.

(390) Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Shiro, M.; Fujita, E. *J. Am. Chem. Soc.* **1986**, *108*, 8281.

(391) Tykwinski, R.; Stang, P. J.; Persky, N. E. *Tetrahedron Lett.* **1994**, *35*, 23.

(392) Stang, P. J.; Kitamura, T. *J. Am. Chem. Soc.* **1987**, *109*, 7561.

(393) Kitamura, T.; Tanaka, T.; Taniguchi, H.; Stang, P. J. *J. Chem. Soc. Perkin Trans. 1* **1991**, 2892.

(394) Kitamura, T.; Lee, C. H.; Taniguchi, H.; Matsumoto, M.; Sano, Y. *J. Org. Chem.* **1994**, *59*, 8053.

(395) Kitamura, T.; Mihara, I.; Taniguchi, H.; Stang, P. J. *J. Chem. Soc., Chem. Commun.* **1990**, 614.

(396) Murch, P.; Williamson, B. L.; Stang, P. J. *Synthesis* **1994**, 1255.

(397) Ochiai, M.; Kunishima, M.; Fuji, K.; Nagao, Y. *J. Org. Chem.* **1988**, *53*, 6144.

(398) Kitamura, T.; Stang, P. J. *Tetrahedron Lett.* **1988**, *29*, 1887.

(399) Stang, P. J.; Crittell, C. M. *J. Org. Chem.* **1992**, *57*, 4305.

(400) Laali, K. K.; Regitz, M.; Birkel, M.; Stang, P. J.; Crittell, C. M. *J. Org. Chem.* **1993**, *58*, 4105.

(401) Schmidpeter, A.; Mayer, P.; Stocker, J.; Roberts, K. A.; Stang, P. J. *Heteroat. Chem.* **1991**, *2*, 569.

(402) Stang, P. J. *Acc. Chem. Res.* **1991**, *24*, 304.

(403) Kitamura, T.; Zheng, L.; Taniguchi, H.; Sakurai, M.; Tanaka, R. *Tetrahedron Lett.* **1993**, *34*, 4055.

(404) Stang, P. J.; Boehshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832.

(405) Allen, A. D.; Roberts, K. A.; Kitamura, T.; Stang, P. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1988**, *110*, 622.

(406) Segal, D.; Shalitin, Y.; Wingert, H.; Kitamura, T.; Stang, P. J. *FEBS Lett.* **1989**, *247*, 217.

(407) Banson, J. A.; Kuo, J. M.; Miles, B.; Fischer, D. R.; Stang, P. J.; Raushel, F. M. *Biochemistry* **1995** *34*, 743.

(408) Banzon, J. A.; Kuo, J.-M.; Fischer, D. R.; Stang, P. J.; Raushel, F. M. *Biochemistry* **1995**, *34*, 750.

(409) Blenkenship, J. N.; Abu-Soud, H.; Francisco, W. A., Raushel, F. M.; Fischer, D. R.; Stang, P. J. *J. Am. Chem. Soc.* **1991** *113*, 8560.

(410) Liu, Z. D.; Chen, Z. C. *J. Org. Chem.* **1993**, *58*, 1924.

(411) Williamson, B. L.; Murch, P.; Fischer, D. R.; Stang, P. J. *Synlett* **1993**, 858.

(412) Stang, P. J.; Murch, P. Unpublished observations.

(413) Tykwinski, R. R.; Williamson, B. L.; Fischer, D. R.; Stang, P. J.; Arif, A. M. *J. Org. Chem.* **1993**, *58*, 5235.

(414) Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3135.

(415) Casalnuovo, J. A.; Shore, N. E. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH Publishers: Weinheim, 1995; Chapter 5, pp 139−172.

(416) Shore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Felming, I., Eds.; Pergamon: New York, 1991; Vol. 5, pp 1037−1064.

(417) Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

(418) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5655.

(419) Denmark, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5, pp 751−784.

(420) Santelli-Roovier, C.; Santelli, M. *Synthesis* **1983**, 429.

(421) Schildknegt, K.; Bohstedt, A. C.; Feldman, K. S.; Sambandam, A. *J. Am. Chem. Soc.* **1995**, *117*, 7544.

(422) Ochiai, M.; Uemura, K.; Oshima, K.; Masaki, Y.; Kunishima, M.; Tani, S. *Tetrahedron Lett.* **1991**, *32*, 4753.

(423) Ochiai, M.; Uemura, K.; Masaki, Y. *J. Am. Chem. Soc.* **1993**, *115*, 2528.

(424) Stang, P. J.; Crittell, C. M. *Organometallics* **1990**, *9*, 3191.

(425) Tykwinski, R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203.

(426) Kanis, D.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(427) Hirsch, A.; Hanack, M. In *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*; Bredas, J. L., Chance, R. R., Eds.; Kluwer: New York, 1990.

(428) Stang, P. J.; Crittell, C. M.; Arif, A. M. *Organometallics* **1993**, *12*, 4799.

(429) Stang, P. J.; Blume, T.; Zhdankin, V. V. *Synthesis* **1993**, 35.

(430) Stang, P. J.; Schwartz, A.; Blume, T.; Zhdankin, V. V. *Tetrahedron Lett.* **1992**, *33*, 6759.

(431) Kotali, E.; Varvoglis, A.; Bozopoulos, A. *J. Chem. Soc., Perkin Trans. 1* **1989**, 827.

(432) Maas, G.; Regitz, M.; Moll, U.; Rahm, R.; Krebs, F.; Hector, R.; Stang, P. J.; Crittell, C. M.; Williamson, B. L. *Tetrahedron* **1992**, *48*, 3527.

(433) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351.

(434) Hinkle, R. J.; Poulter, G. T.; Stang, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 11626.

(435) Hinkle, R. J.; Stang, P. J. *Synthesis* **1994**, 313.

(436) Ochiai, M.; Oshima, K.; Masaki, Y. *Tetrahedron Lett.* **1991**, *32*, 7711.

(437) Stang, P. J.; Wingert, H.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 7235.

(438) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059.

(439) Ochiai, M.; Oshima, K.; Masaki, Y.; Kunishima, M.; Tani, S. *Tetrahedron Lett.* **1993**, *34*, 4829.

(440) Ochiai, M.; Kitagawa, Y.; Toyonari, M.; Uemura, K. *Tetrahedron Lett.* **1994**, *35*, 9407.

(441) Ochiai, M.; Oshima, K.; Masaki, Y. *Chem. Lett.* **1994**, *113*, 871.

(442) Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315.

(443) Kurihara, Y.; Sodeoka, M.; Shibasaki, M. *Chem. Pharm. Bull.* **1994**, *42*, 2357.

(444) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565.

(445) (a) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360. (b) Ochiai, M.; Sueda, T.; Uemura, K.; Masaki, Y. *J. Org. Chem.* **1995**, *60*, 2624.

(446) Kitamura, T.; Matsuyuki, J.; Nagata, K.; Furuki, R.; Taniguchi, H. *Synthesis* **1992**, 945.

(447) Kasumov, T. M.; Brel, V. K.; Koz'min, A. S.; Zefirov, N. S. *Synthesis* **1995**, 775.

(448) Kitamura, T.; Nagata, K.; Nakamura, T.; Furuki, R.; Taniguchi, H. *Tetrahedron* **1995**, *51*, 6229.

(449) Krówczynski, A.; Skulski, L. *Polish J. Chem.* **1993**, *67*, 67.

(450) Stang, P. J.; Zhdankin, V. V.; Tykwinski, R.; Zefirov, N. S. *Tetrahedron Lett.* **1991**, *32*, 7497.

(451) Zefirov, N. S.; Kasumov, T. M.; Koz'min, A. S.; Sorokin, V. D.; Stang, P. J.; Zhdankin, V. V. *Synthesis* **1993**, 1209.

(452) Tyrra, W.; Butler, H.; Naumann, D. *J. Fluorine Chem.* **1993**, *60*, 79.

(453) Beringer, F. M.; Nathan, R. *J. Org. Chem.* **1969**, *34*, 685. Beringer, F. M.; Nathan, R. *J. Org. Chem.* **1970**, *35*, 2095.
(454) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. Stang, P. J.; Chen, K.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 8793.
(455) Wright, W. B.; Meyers, E. A. *Cryst. Struct. Commun.* **1972**, *1*, 95. Petrov, V. N.; Tindeman, C. V.; Struchkov, Yu. T.; Chungtai, F. A.; Budylin, V. A.; Bundel, Yu. G. *Dokl. Akad. Nauk SSSR* **1983**, *269*, 614. Page, S. W.; Mazzola, E. P.; Mighell, A. D.; Himes, V. L.; Hubbard, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 5858. Hubbard, C. R.; Himes, V. L.; Mighell, A. D. *Acta Crystallogr.* **1987**, *B36*, 2819. Moriarty, R. M.; Prakash, O.; Freeman, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6082. Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1977**, 217. Khotsyanova, T. L.; Babushkina, T. A.; Saatsazov, V. V.; Tolstaya, T. P.; Lisichkina, I. N.; Semin, G. K. *Koord. Khim.* **1976**, *2*, 1567. Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1987**, 193. Bozopoulos, A. P.; Rentzeperis, P. J. *Acta Crystallogr.* **1987**, *C43*, 914.
(456) Chen, Z.-C.; Jin, Y.-Y.; Stang, P. J. *J. Org. Chem.* **1987**, *52*, 4117.
(457) Chen, D.-W.; Zhang, Y.-D.; Chen, Z.-C. *Synth. Commun.* **1995**, *25*, 1627.
(458) You, J.-Z.; Chen, Z.-C. *Synthesis* **1992**, 521.
(459) Liu, D.-D.; Chen, D.-W.; Chen, Z.-C. *Synth. Commun.* **1992**, *22*, 2903.
(460) Liu, D.-D.; Chen, Z.-C. *Synthesis* **1993**, 373.
(461) You, J.-Z.; Chen, Z.-C. *Synth. Commun.* **1992**, *22*, 1441.
(462) Liu, Z.-D.; Zeng, H.; Chen, Z.-C. *Synth. Commun.* **1994**, *24*, 475.
(463) You, J.-Z.; Chen, Z.-C. *Synthesis* **1992**, 633.
(464) Chen, Z.-C.; Jin, Y.-Y.; Stang, P. J. *J. Org. Chem.* **1987**, *52*, 4115.
(465) Chen, K.; Koser, G. F. *J. Org. Chem.* **1991**, *56*, 5764.
(466) Kitamura, T.; Yamane, M. *J. Chem. Soc., Chem. Commun.* **1995**, 983.
(467) Grushin, V. V.; Demkina, I. I.; Tolstaya, T. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 505.
(468) Bumagin, N. A.; Sukhomlinova, L. I.; Banchikov, A. N.; Tolstaya, T. P.; Beletskaya, I. P. *Russ. Chem. Bull.* **1992**, *41*, 2130.
(469) Bumagin, N. A.; Sukhomlinova, L. I.; Igushkina, S. O.; Banchikov, A. N.; Tolstaya, T. P.; Beletskaya, I. P. *Russ. Chem. Bull.* **1992**, *41*, 2128.
(470) Bumagin, N. A.; Luzikova, E. V.; Sukhomlinova, L. I.; Tolstaya, T. P.; Beletskaya, I. P. *Russ. Chem. Bull.* **1995**, *44*, 385.
(471) Luzikova, E. V.; Sukhomlinova, L. I.; Tolstaya, T. P.; Bumagin, N. A.; Beletskaya, I. P. *Russ. Chem. Bull.* **1995**, *44*, 556.
(472) Bi, Y.; Neckers, D. C. *Tetrahedron Lett.* **1992**, *33*, 1139. Haack, V.; Klemm, E. *Polym. Bull.* **1994**, *33*, 289. Timpe, H.-J.; Kronfeld, K.-P.; Mahlow, R. *Eur. Polym. J.* **1991**, *27*, 69.
(473) Olah, G. A. *Halonium Ions*; Wiley: New York, 1975.
(474) Lyalin, V. V.; Orda, V. V.; Alekseyeva, L. A.; Yagupolskii, L. M. *J. Org. Chem. USSR* **1971**, *7*, 1524.
(475) Manfredi, A.; Montanari, V.; Quici, S.; Resnati, G. Abstracts of 12th Winter Fluorine Conference, FL, 1995, P62.
(476) Gudrinietse, E.; Neiland, O.; Vanag, G. *Zh. Obsch. Khim.* **1957**, *27*, 2737.
(477) Zhu, S.; Chen, Q. *J. Chem. Soc., Chem. Commun.* **1990**, 1459.
(478) Zhu, S.; Chen, Q.; Kuang, W. *J. Fluorine Chem.* **1993**, *60*, 39.
(479) Zhu, S. *Heteroat. Chem.* **1994**, *5*, 9.
(480) Hackenberg, J.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1991**, 470.
(481) Hadjiarapoglou, L.; Spyroudis, S.; Varvoglis, A. *J. Am. Chem. Soc.* **1985**, *107*, 7178.
(482) Hadjiarapoglou, L.; Varvoglis, A.; Alcock, N. W.; Pike, G. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2839.
(483) Yang, R.-Y.; Dai, L.-X.; Chen, C.-G. *J. Chem. Soc., Chem. Commun.* **1992**, 1487.
(484) Müller, P.; Fernandez, D. *Helv. Chim. Acta* **1995**, *78*, 947.
(485) Fairfax, D. J.; Austin, D. J.; Xu, S. L.; Padwa, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2837.
(486) Moriarty, R. M.; Kim, J.; Guo, L. *Tetrahedron Lett.* **1993**, *34*, 4129.
(487) Neiland, O. Ya.; Adamsone, B. Ya. *Chem. Heterocycl. Comd.* **1991**, *27*, 670.
(488) Kokkinidis, G.; Sazpu, D.; Hatzigrigoriou, E.; Varvoglis, A. *Electrochim. Acta* **1990**, *35*, 455.
(489) Akiyama, F. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2016.
(490) Saito, T.; Gon, S.; Kikuchi, H.; Motoki, S. *J. Chem. Res. (S)* **1994**, 2.
(491) Spyroudis, S.; Tarantili, P. *J. Org. Chem.* **1993**, *58*, 4885.
(492) Saito, T.; Kikuchi, H.; Kondo, A. *Synthesis* **1995**, 87.
(493) Potekhin, K. A.; Struchkov, Yu. T.; Zhdankin, V. V.; Sorokin, V. D.; Koz'min, A. S.; Zefirov, N. S. *Dokl. AN SSSR* **1986**, *288*, 1374.
(494) Zefirov, N. S.; Zhdankin, V. V.; Koz'min, A. S.; Agaev, A. T.; Magerramov, A. M. *Izv. AN SSSR, Ser. Khim.* **1987**, 2873.
(495) Semerikov, V. N.; Sorokin, V. D.; Koz'min, A. S.; Zhdankin, V. V.; Zefirov, N. S. *Zh. Org. Khim.* **1988**, *24*, 888.
(496) Zefirov, N. S.; Kozhushkov, S. I.; Zhdankin, V. V. *Zh. Org. Khim.* **1988**, *24*, 1560.
(497) Yang, R.-Y.; Dai, L.-X.; Ma, R.-J. *Heteroat. Chem.* **1992**, *3*, 585.
(498) Prakash, O.; Kumar, D.; Saini, R. K.; Singh, S. P. *Tetrahedron Lett.* **1994**, *35*, 4211.
(499) Georgantji, A.; Spyroudis, S. *Tetrahedron Lett.* **1995**, *36*, 443.
(500) Papoutsis, I.; Spyroudis, S.; Varvoglis, A. *Tetrahedron Lett.* **1994**, *35*, 8449.
(501) Wittig, G.; Rieber, M. *Ann. Chem.* **1949**, *562*, 187.
(502) Clauss, K. *Ber. Dtsch. Chem. Ges.* **1955**, *88*, 268. Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1971**, *36*, 4055. Reich, H. J.; Cooperman, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 5077.
(503) Barton, D. H. R.; Jaszberenyi, J. Cs.; Lessmann, K.; Timár, T. *Tetrahedron* **1992**, *48*, 8881.
(504) Willgerodt, C.; Howells, V. A. *Chem. Ber.* **1900**, *33*, 841.
(505) Katritzky, A. R.; Savage, J. P.; Gallos, J. K.; Durst, H. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1515.
(506) Katritzky, A. R.; Savage, J. P.; Gallos, J. K.; Durst, H. D. *Org. Prep. Proc. Int.* **1989**, *21*, 157.
(507) Weclas-Henderson, L.; Nguyen, T. T.; Hayes, R. A.; Martin, J. C. *J. Org. Chem.* **1991**, *56*, 6565.
(508) Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.
(509) Evans, D. A.; Kaldor, S. W.; Jones, T. K.; Clardy, J.; Stout, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7001.
(510) Bailey, S. W.; Chandrasekaran, R. Y.; Ayling, J. E. *J. Org. Chem.* **1992**, *57*, 4470.
(511) Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019.
(512) Batchelor, M. J.; Gillespie, R. J.; Golec, J. M. C.; Hedgecock, C. J. R. *Tetrahedron Lett.* **1993**, *34*, 167.
(513) Deruyttere, X.; Dumortier, L.; Van der Eycken, J.; Vandewalle, M. *Synlett* **1992**, 51.
(514) Yamashita, D. S.; Rocco, V. P.; Danishefsky, S. *Tetrahedron Lett.* **1991**, *32*, 6667.
(515) Plumb, J. B.; Harper, D. J. *Chem. Eng. News* **1990**, *68*, 3.
(516) Robins, M. J.; Samano, V.; Johnson, M. D. *J. Org. Chem.* **1990**, *55*, 410.
(517) Linderman, R. J.; Graves, D. M. *J. Org. Chem.* **1989**, *54*, 661.
(518) Burkhart, J. P.; Peet, N. P.; Bey, P. *Tetrahedron Lett.* **1988**, *29*, 3433.
(519) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.
(520) Barton, D. H. R.; Godfrey, C. R. A.; Morzycki, J. W.; Motherwell, W. B.; Stobie, A. *Tetrahedron Lett.* **1982**, *23*, 957.
(521) de Armas, P.; Concepción, J. I.; Francisco, C. G.; Hernández, R.; Salazar, J. A.; Suárez, E. *J. Chem. Soc., Perkin Trans. 1* **1990**, 405.
(522) Barret, R.; Daudon, M. *Synth. Commun.* **1990**, *20*, 1543.
(523) Bayraktaroglu, T. O.; Gooding, M. A.; Khatib, S. F.; Lee, H.; Kourouma, M.; Landolt, R. G. *J. Org. Chem.* **1993**, *58*, 1264.
(524) Grushin, V. V.; Alper, H. *J. Org. Chem.* **1993**, *58*, 4794.
(525) Muzart, J. *Synthesis* **1993**, 11.
(526) Meyer, S. D.; Schreiber, S. I. *J. Org. Chem.* **1994**, *59*, 7549.
(527) Grieco, P. A.; Collins, J. L.; Moher, E. D.; Fleck, T. J.; Gross, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 6078.
(528) (a) Doub, L. U.S. patent 3,422,152; *Chem. Abstr.* **1969**, *70*, 57407n. (b) Jezic, C. U.S. Patent 3,622,586; *Chem. Abstr.* **1972**, *76*, 59460x. (c) Jezic, Z. U.S. Psatent 3,712,920; *Chem. Abstr.* **1973**, *79*, 5254b. (d) Jezic, Z. U.S. Patent, 3,734,928; *Chem. Abstr.* **1973,** *79*, 42151m. (e) Jezic, Z. U.S. Patent 3,759,989; *Chem. Abstr.***1973**, *79*, 126065z. (f) Jezic, Z. U.S. Patent 3,896,-140; *Chem. Abstr.* **1976**, *84*, 4936s. (g) Moyle, C. L. U.S. Patent 3,944,498; *Chem. Abstr.* **1976**, *84*, 181912b. (h) Relenyi, A. G.; Koser, G. F.; Walter, R. W., Jr.; Kruper, W. J.; Shankar, R. B.; Zelinko, A. P. U.S. Patent 5,106,407; *Chem. Abstr.* **1992**, *117*, 247132f.
(529) Horton, G. M. G. *Can. J. Anim. Sci.* **1980**, *60*, 169.
(530) Chalupa, W.; Pastterson, J. A.; Parish, R. C.; Chow, A. W. *J. Anim. Sci.* **1983**, *57*, 186, 195, 201.
(531) Horton, G. M. G. *Can. J. Anim. Sci.* **1980**, *50*, 1160.
(532) Broderick, G. A.; Baltrop, J. E. *J. Anim. Sci.* **1979**, *49*, 1101.
(533) Review: Hayes, D. J. Experimentally induced defects in mitochondrial function. In *Mitochondria: DNA, Proteins and Disease*; Darley-Usmar, V., Schapira, A. V. H., Eds.; Portland Press, Ltd., London, 1994; pp 157−178.
(534) Holland, P. C.; Clark, M. G.; Bloxham, D. P.; Lardy, H. A. *J. Biol. Chem.* **1973**, *248*, 6050.
(535) Gatley, S. J.; Sherratt, H. S. A. *Biochem. J.* **1976**, *158*, 307.
(536) Gatley, S. J.; Al-Bassam, S. S.; Taylor, J. R.; Sherratt, H. S. A. *Biochem. Soc. Trans.* **1975**, *3*, 333.
(537) Holland, P. C.; Sheratt, H. S. A. *Biochem. J.* **1972**, *129*, 39.
(538) Brosnan, M. J.; Hayes, D. J.; Challiss, R. A. I.; Radda, G. K. *Biochem. Soc. Trans.* **1986**, *14*, 1209.
(539) Cooper, J. M.; Petty, R. K. H.; Hayes, D. J.; Challis, R. A. J.; Brosnan, M. J.; Sonbridge, E. A.; Radda, G. K.; Morgan-Hughes, J. A.; Clark, J. B. *J. Neurol. Sci.* **1988**, *83*, 335.
(540) Cooper, J. M.; Petty, R. K. H.; Hayes, D. J.; Morgan-Hughes, J. A.; Clark, J. B. *Biochem. Pharmacol.* **1988**, *37*, 687.
(541) Doussiere, J.; Vignais, P. V. *Biochem. Biophys. Res. Commun.* **1991**, *175*, 143.
(542) Ellis, J. A.; Mayer, S. J.; Jones, O. T. G. *Biochem. J.* **1988**, *251* 887.
(543) Cross, A. R.; Jones, O. T. G. *Biochem. J.* **1986**, *237*, 111.
(544) Cross, A. R. *Biochem. Pharmacol.* **1987**, *36*, 489.
(545) Stuehr, D. J.; Fasehun, O. A.; Kwon, N. S.; Gross, S. S.; Gonzalez, J. A.; Levi, R.; Nathan, C. F. *FASEB J.* **1991**, *5*, 98.
(546) O'Donnell, V. B.; Tew, D. G.; Jones, O. T. G.; England, P. J. *Biochem. J.* **1993**, *290*, 41.

(547) Doussiere, J.; Vignais, P. V. *Eur. J. Biochem.* **1992**, *208*, 61.
(548) Hancock, J. T.; White, J. I.; Jones, O. T. G.; Silver, I. A. *Free Radical Bio. Med.* **1991**, *11*, 25.
(549) Pettibone, D. J.; Sweet, C. S.; Risley, E. A.; Kennedy, T. *Eur. J. Pharmacol.* **1985**, *116*, 307.
(550) Gatley, S. J.; Sheratt, H. S. A. *Biochem. Soc. Trans.* **1974**, *2*, 517.
(551) Gennimatta, G. A.; Kotali, E.; Varvoglis, A.; Kyriakidis, D. A.; Tsiftsoglou, A. S. *J. Chemother. Suppl.* **1989**, *4*, 229.
(552) Bretskin, A. P. *Dokl. Akad. Nauk SSSR* **1984**, *275*, 1425.
(553) Tew, D. G. *Biochemistry* **1993**, *32*, 10209.
(554) Pagano, P. J.; Ito, Y.; Tornheim, K.; Gallop, P. M.; Tauber, A. I.; Cohen, R. A. *Am. J. Physiol.* **1995**, *268*, *H*, 2274.
(555) Bishop, A.; Paz, M. A.; Gallop, P. M.; Karnovskyul, M. L. *Free Radical Biol. Med.* **1995**, *18*, 617.
(556) Bishop, A.; Paz, M. A.; Gallop, P. M.; Karnovsky, M. L. *Free Radical Biol. Med.* **1994**, *17*, 311.
(557) Review: *Principles and Applications of Quinoproteins*; Davidson, V. L., Ed.; Marcel Dekker: New York, 1992.
(558) Mah, J.; Paz, M. A.; Flückiger, R.; Gallop, P. M. *FASEB J.* **1993**, *7*, A53.
(559) Salisbury, S. A.; Forrest, H. S.; Cruse, W. B. T.; Kennard, O. *Nature* (London) **1979**, *280*, 8434.
(560) Review: Steinberg, F. M.; Rucker, R. B. In *Modern Nutrition in Health and Disease*; Shils, M. E., Olson, J. A., Shike, M., Eds.; Lea & Febiger: Pennsylvania, 1994; Vol. 1, p 473.
(561) Steinberg, F. M.; Gershwin, M. E.; Rucker, R. B. *J. Nutr.* **1994**, *124*, 744.
(562) Paz, M. A.; Flückiger, R.; Gallop, P. M. The Biomedical Significance of PQQ. In *Principles and Applications of Quinoproteins*; Davidson, V. L., Ed.; Marcel Dekker: New York, 1992; Chapter 17, pp 381−393.
(563) Lehn, J.-M. *Supramolecular Chemistry Concepts and Perspectives*; VCH: Weinheim, 1995.
(564) *Supramolecular Chemistry*; Balzani, V., Decola, L., Eds.; Kluwer Academic Publishers: Dordrecht, 1992.

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