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# Polyvalent Iodine in Organic Chemistry: Recent Developments, 2002–2005

E. D. Matveeva, M. V. Proskurnina, and N. S. Zefirov

*Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, Moscow, 119992, Russia*

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ABSTRACT: *In the last three years, great strides were achieved in the field of organic chemistry of polyvalent iodine compounds. This paper includes the published works on this field from 2002–2005 (Zhdankin, V. V.; Stang, P. J Chem Rev 2002, 102, 2523–2584; Stang, P. J. J Org Chem 2003, 68, 2997–3008; Wirth, T.; Hirt, U. H. Synthesis 1999, 1271–1287; Morales-Rojas, H.; Moss, R. A. Chem Rev 2002, 102, 2497–2521). It focuses on eight areas: (1) hypervalent iodine reagents as mild oxidants, (2) the addition of hypervalent iodine compounds to alkenes, (3) fluorination of organic compounds by hypervalent iodine compounds, (4) some new reactions of nucleophilic substitution of hypervalent iodine moiety, (5) iodine(III) compounds as a source of nitrene and carbene moiety, (6) novel and new iodine(III) compounds and methods of their preparation, (7) polyvalent iodine compounds in synthesis of natural compounds, and (8) miscellaneous. The published works focus on some hypervalent iodine reagents that have received a widespread practical application in organic chemistry.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:595–617, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20273

*Correspondence to:* E. D. Matveeva; e-mail: matveeva@org.chem.msu.ru.

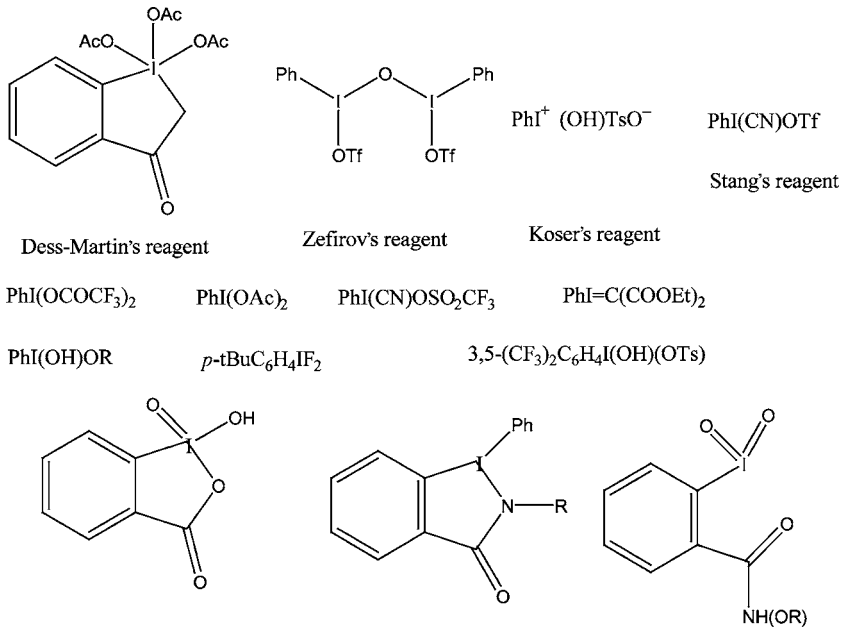

## *HYPERVALENT IODINE REAGENTS AS MILD OXIDANTS*

Because of their functional group tolerance and ease of use, hypervalent iodine reagents have been widely used in organic synthesis as versatile selective oxidizing agents [1–8] (Scheme 1). For example, the unique oxidizing properties of Dess–Martin reagent allow the rapid and selective construction of complex polycycles, including natural product analogues, diverse drugs and lead-like molecules, aminosugars, and unsaturated carbonyl compounds [9–12]. Various hypervalent iodine reagents (for example, *p*-Me(m-$CF_3$)$C_6H_4IO$, $C_6H_5I(OAc)_2$, and *p*-Me(m-$CF_3$)$C_6H_4I(OAc)_2$) were used in oxidative α-tosylozylation of phenols, alcohols in good to moderate yields (see Scheme 2) [13] and in the allylic oxidation of alkenes to enones (as reoxidant perfluoro-octylselenic acid) in good yield (see Schemes 3 and 4) [14].

The method [15] was successfully applied to the direct preparation of thiazoles, imidazoles, and imidazo[1,2-α]pyridines by subsequent treatment of alcohols with iodosylbenzene and *p*-toluenesulfonic acid and thioamides, benzamidine, and 2-aminopyridine, respectively (Scheme 5).

Ligand-exchange solid-state reaction by grinding $PhI(OAc)_2$ and ROH presents a new reagent PhI(OH)OR, where R = *p*-Ts, *p*-Ms [15,16], for example, for mild oxidation α,β-diketones, alkenes (Scheme 6).

During the investigation of asymmetric Diels–Alder reaction, $PhI(OAc)_2$ was used for oxidation of




**SCHEME 1**

hydroquinone to benzoquinone. This reaction is effective in acetone (Scheme 7) [17].

Hypervalent iodine oxidation of emodin (1,3,8-trihydroxy-6-methylanthraquinone) with various (diacetoxyiodo)arenes in the presence of potassium hydroxide also provides quinones-3-aryloxy-1,8-dihydroxy-2-iodoantraquinones in moderate yields [18].

Oxidation of 6-hydroxyflavone and 6-hydroxyflavanones with $PhI(OAc)_2$ in acetic acid leads to regioselective acetoxylation, thereby providing a novel and convenient route for the synthesis of 5-acetoxylated products (Scheme 8) [19].

Modified $Ph(OAc)_2$ is an excellent oxidant of oximes of ketones (Scheme 9) [20].

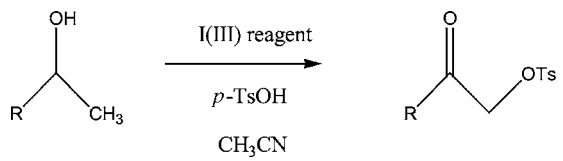
Hypervalent iodine reagents have great popularity as a mild oxidant for the conversion of aldehydes or ketones [20,21]. Some of the best-known reagents of these types for alcohol oxidation are *o*-iodobenzoic acid, as a synthetic precursor to the popular Dess–Martin reagent, *o*-iodoxybenzoic acid, and their derivatives. One perceived limitation for *o*-iodobenzoic acid has been the need to use DMSO as a reaction solvent in order to dissolve it [23]. But it was developed as the practical protocol for the use of *o*-iodobenzoic acid in ethylacetate as a solvent [24]. The reaction converts a range of primary and secondary alcohols to aldehydes and ketones. *o*-Iodoxybenzoic acid can be used for dehydrogenation of carbonyl compounds [25], in particular complexation of it with 4-methoxypyridine-*N*-oxide results in the new reagent, which is sufficiently reactive to effect dehydrogenation of carbonyl compounds at room temperature (Scheme 10) [26,27].

*o*-Iodoxybenzoic acid can also be used for benzylic and allylic oxidation [28], in the presence of alkenes, N-heterocycles, and amides. Aldehydes does not interfere (Scheme 11).

The best recent example is the oxidation of alcohols (primary and secondary alcohols, 1,2-diols, ketoalcohols) by iodoxybenzoic acid in ionic liquids (the best results in 1-butyl-3-methylimidazolium chloride) [29] (Scheme 12).

A series of alcohols were oxidized with *o*-iodoxybenzoic acid or modified *o*-iodoxybenzoic acid [30,31] and catalyzed by β-cyclodextrin in a water–acetone mixture at room temperature with excellent yields. No overoxidation to acids was observed; the reaction in such conditions is highly selective for vicinal dioles in oxidizing only the secondary hydroxyl group [29, 32–36] (Scheme 13).

No overoxidation to acids was observed in the case of aldehyde products; various functionalities such as methoxy and nitro groups, chlorine, all the double bonds and a furan ring can tolerate the

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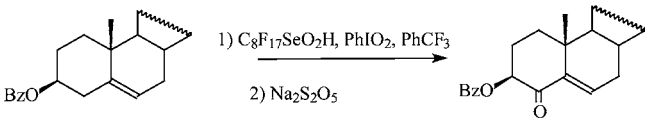


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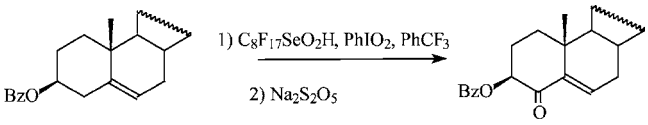


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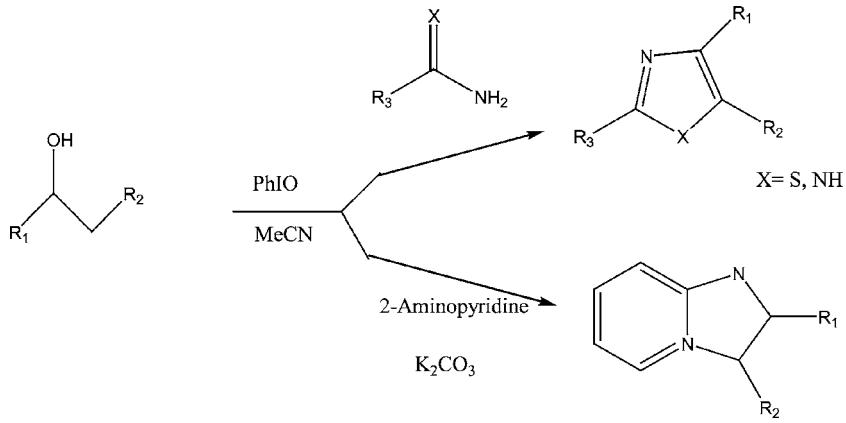


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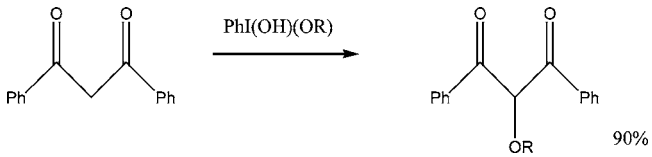


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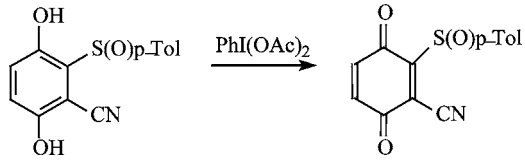


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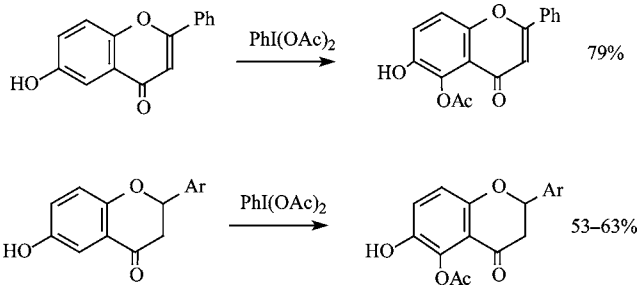
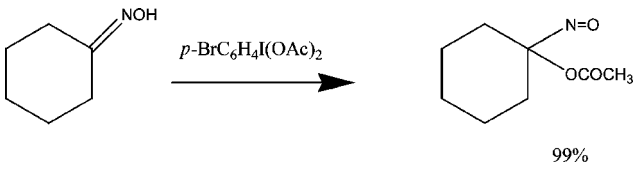



SCHEME 8

oxidation. 1,2-Diols are oxidized to α-dicarbonyls or α-ketols without cleavage of 1,2-diols bond. Recently, the synthesis of novel 2-iodoxybenzoic acid-amides and esters was reported. They are stable and soluble reagents having oxidizing properties similar to iodoxybenzoic acid [37]. 2-Iodoxybenzenesulfamides show different aspects of reactivity similar to previously reported amides of iodoxybenzoic acid [35,38–40]. The polymer-supported iodoxybenzoic acid esters and amides oxidize benzyl alcohol to benzaldehyde [41,42]. 2-Iodoxybenzoic acid and its derivatives are also an efficient oxidizing agent for polycyclic aromatic hydrocarbons [43]. Resulting quinones of benzo[α]pyrene and benz[α]anthracenes serve as starting compounds for the synthesis of the active metabolites of these hydrocarbons thought to be involved in their mechanism of carcinogenesis.

The oxidative action of $PhI(OCOCF_3)_2$ was developed for the construction of a series of N,O,S-containing heterocycle-fused quinolinone derivatives, [44,45] (by generation of electrophilic *N*-acylnitrenium ions in the key cyclization step)—for example, see Scheme 14.

An intermolecular formation of new C—N linkages realizes in the reaction of *N*-methoxy- and *N*-para-methoxyphenylacetamides with $PhI(OCOCF_3)_2$: *N*-acylnitrenium intermediates

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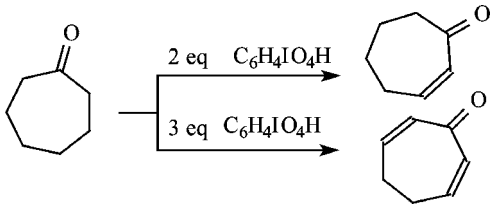
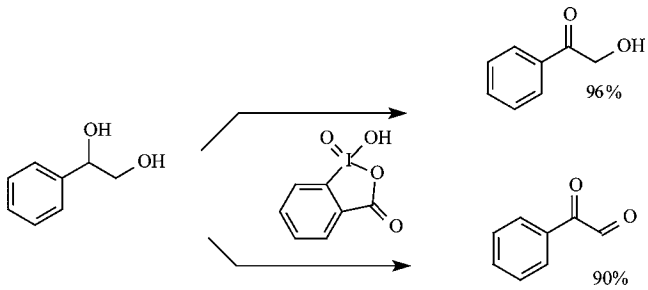



SCHEME 10


SCHEME 11

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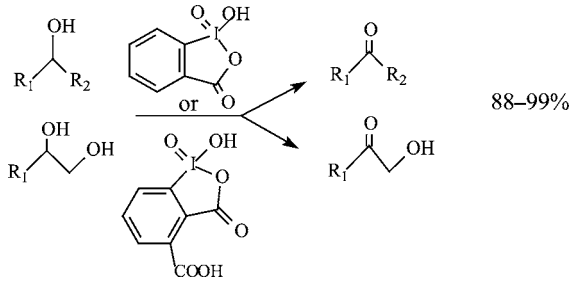



SCHEME 13

generated by the action on properly substituted amides exerts a selective control to afford either quinolin-2-ones or pyrrolidin-2-ones in good yields and complete selectivity [46,47]. The cyclization process can take two different pathways depending on the nature of the amide N-substituent to afford either quinoline or pyrrolidine skeletons (Scheme 15).

The oxidation can proceed involving the generation of aromatic cation radical with direct aromatic carbon–oxygen bond formation reaction—a simple yet novel method for chroman derivatives [48] (Scheme 16).

The same type of intramolecular cyclization is realized with the formation of C—C bond [49,50] (Scheme 17).

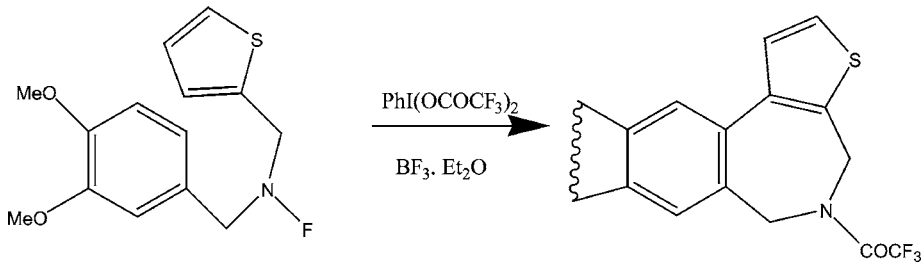
The oxidation of phenols with hypervalent iodine reagents generates *o*-quinones [51] and 6-alkyl-6-alkoxycyclohexa-2,4-dienones as a part of a useful strategy in the regio- and stereo-selective construction of highly substituted bicyclic and polycyclic ring system [52].

The Mn(salen) catalyzed epoxidation of olefins by PhIO, $C_6H_5IO$, and $Bu_4NIO_4$ afford predominantly the Mn(V) (oxo)species, leading to extensive loss of stereospecificity [53].

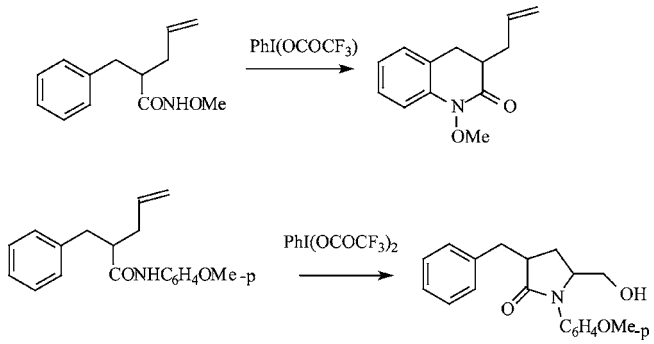
Inorganic compounds of iodine(V), the complexes of iodine(V) oxide $I_2O_5$ and its acid $HIO_3$ with DMSO (1:1), are the efficient oxidants and can be used for dehydrogenation of aldehydes and ketones [54]. Alcohols are inert to these reagents, so carbonyl dehydrogenation may be performed in their presence (Schemes 18 and 19).

## *THE ADDITION OF HYPERVALENT IODINE COMPOUNDS TO ALKENES*

The simple addition of electrophilic reagents to double bonds is one of the conceptually important and synthetically useful processes in organic chemistry. The addition reactions with iodine electrophiles followed by either an intermolecular or intramolecular attack of nucleophile can be found in a great variety of syntheses as a very reliable method for the functionalization of double bonds. There are numerous ways to efficiently perform iodination of alkenes or iodocyclizations. Hypervalent iodine(III) compounds can also be used as efficient electrophiles, although these are more commonly used as metal-free, mild, and selective oxidants. Simple and easily accessible iodine(III) reagents like diacetoxy iodobenzene, bis(trifluoroacetoxy)iodobenzene or hydroxyl(tosyloxy)iodobenzene, and others have been employed as electrophiles. The iodosylbenzene used with sulfur trioxide gas to prepare cyclic sulfates with alkenes was first reported by Zefirov and coworkers [55]. A simple one-pot version of the Zefirov's reaction is the reaction of iodosylbenzene




**SCHEME 14**



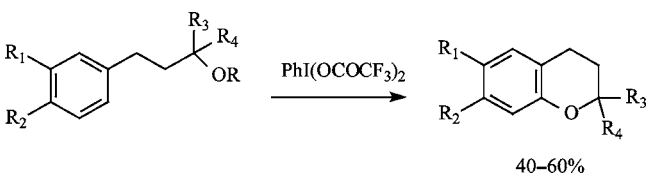

**SCHEME 15**

with $SO_3$ DMF–complex at 0°C forming an active sulfating reagent, which results in the direct formation of cyclic sulfates after subsequent addition of alkenes [56] (yields 40–75%) (Scheme 20):

Recent recyclable hypervalent iodine reagents for vicinal halomethoxylation of unsaturated compounds are 4,4′-bis(dichloroiodo)biphenyl and 3-(dichloroiodo)benzoic acid [57]. Sometimes such reactions are accompanied by oxidizing rearrangements [58] (Schemes 21 and 22).

The reagent for oxidative conversion of alkenes to amino acid esters can be prepared easily from $PhI(OAc)_2$ and N-protected natural amino acids [59] (Scheme 23).

The intermediates in these reactions are only speculated upon and might involve cyclic and positively charged ones, which undergo further reactions because of the extremely good leaving group ability of the hypervalent iodine moiety.




**SCHEME 16**

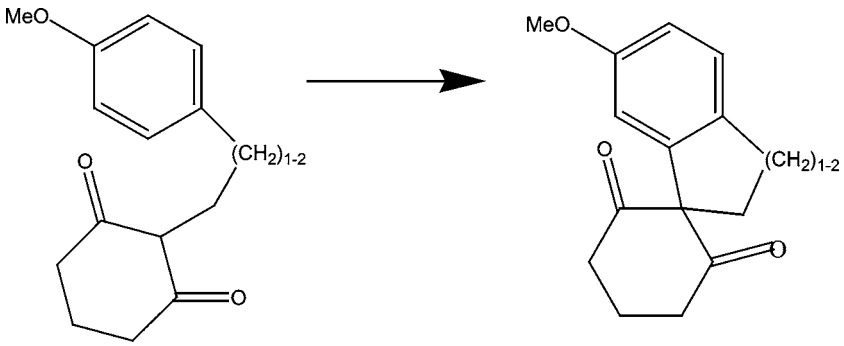
Despite their potential, hypervalent iodine reagents have rarely been used as chiral reagents in stereoselective reactions. For example, they were employed for stereoselective electrophilic functionalization of alkene [60] (Schemes 24 and 25).

A novel lactonization of double bond with aryl-$\lambda^3$-iodan was performed, but this type of reagent gave only very small enantioselectivities [61] (Scheme 26).

The reaction of unusual cycloaddition of phenyliodonium-bis(sulfonyl)methylides with alkenes provides the multiply trisubstituted indanes with good yields [62,63]. The present stereoselective and regioselective cycloaddition provides a convenient preparatory route to trans, trans-configured 1,2,3-trisubstituted indanes, in which the benzene ring is derived from the arenesulfonyl functionality of bis(sulfonyl)ylide (Scheme 27).

The reaction of the same ylides with a variety of norbornene derivatives provides functionalized indanes with good yields. This diastereoselective cycloaddition provides a convenient preparatory route of multicyclic structures with well-defined stereochemical configuration [64,65]. Cycloaddition of iodonium ylides with thiophene gave 2,5-disubstituted thiophene [66].

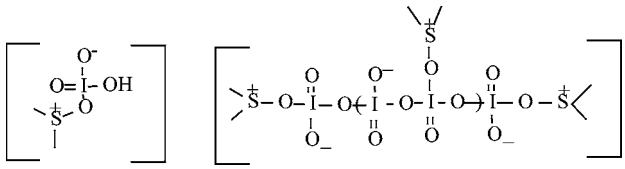
This termal reaction with cyclic alkenes results in exclusively 1,2,3-trisubstituted cis(1,2)/cis(2,3)-configured benzocyclopentenes by electrophilic




SCHEME 17

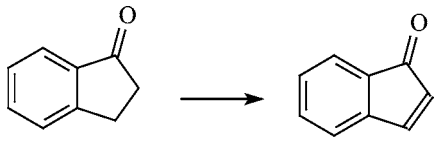
attack of the ylide on the olefinic double bond. This unusual transformation provides a convenient and direct method for the diastereoselective synthesis of functionalized bicycle[3.3.0.]octanes, when cyclopentenes are used as a cycloalkene partner [67,68].

An efficient 1,2-dehydrocarborane precursor, phenyl[*o*-(trimethylsilyl)-carboranyl] iodonium acetate was readily prepared by the reaction of [*o*-(trimethysilyl)carboranyl]lithium and $PhI(OAc)_2$. The facile 2+4 cycloaddition of [*o*-(-(trimethysilyl)carboranyl]iodonium acetate with dienes as anthracene, naphthalene, norborna-2,5-diene, and 2,5-dimethylfuran gives high yields of 1,2-dehydrocarborane adducts in the presence of desilylating agent. The reaction of [*o*-(-(trimethysilyl)carboranyl]iodonium acetate with a cyclic alkene and strained cycloalkynes afforded the adducts formed by the ene reaction and a 2+2 cycloaddition reaction. The structures of trapping products with anthracene and norborna-2,5-diene were confirmed by the single crystal X-ray [69].



SCHEME 18

As alkynyliodonium salts are good 1,3-dipolarophiles, various [3+2] cycloadditions have been investigated. 1,3-Dipolar cycloaddition reaction of inactivated alkynyliodoniumn salts with 2,4,6-trimethylbenzonitrile *N*-oxide gave isoxazolyliodonium salts with good to high yields (43–90%). An attempt of simultaneous elimination of the phenyliodonio and trimethylsilyl groups on treatment with $Bu_4NF$ and trapping didehydroisoxazole intermediate with various dienes was unsuccessful; only isoxazole ring product 2,4,6-trimethylbenzonitrile was obtained [70].

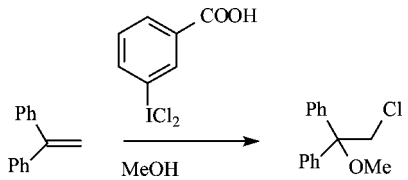


SCHEME 19

## *FLUORINATION OF ORGANIC COMPOUNDS*

The fluorination of organic compounds is a special problem in halogenation. It can be solved in many cases due to the chemistry of hypervalent iodine. The stereo- and/or regio-selective synthesis of fluorine-containing organic compounds employing hypervalent iodine fluorides such as $ArIF_2$, $IF_5$,


SCHEME 20

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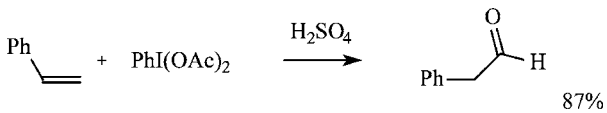


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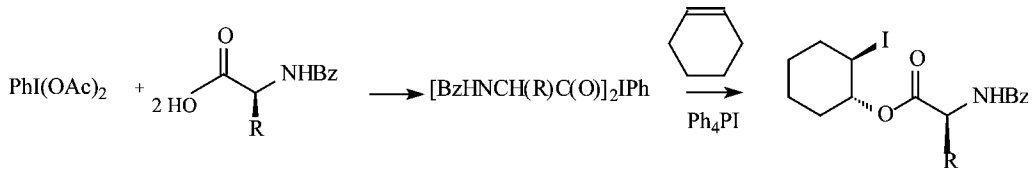

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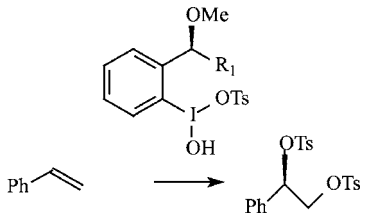

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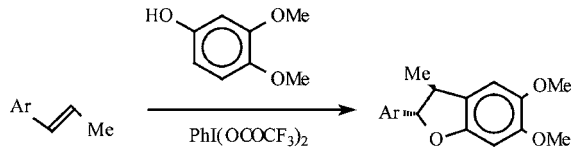

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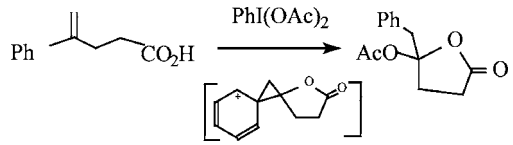


SCHEME 26

and (*E*)-2-fluoro-alk-1-enyl-4-aryl iodonium salts R(F)C=C(H)IF-Ar was realized with preparatory yields [71] (Schemes 28 and 29).

The reaction of aryl group-substituted alkenes with $ArIF_2$ is known to produce *gem*-difluorocompounds with the migration of the aryl group (Schemes 30 and 31). This reagent can be used in situ as a useful fluorination reagent for β-ketoesters (Scheme 32).

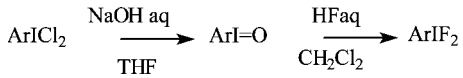
Many different classes of organic compounds can be reacted efficiently with the solution of $I_2/IF_5/Et_3N$-3HF, which is easy to prepare and stable at a low pressure. This reagent can be used for electrochemical fluorination of various organic compounds also involving iodo-compounds [72,73] (Scheme 33). This reagent ($I_2/IF_5/Et_3N$-3HF [74]) can be used for the fluorination of various organic compounds—alcohols, ketones, acids, epoxydes, phenols and so on (Scheme 34).

Nucleophilic sulfur-containing compounds have a particular affinity for electrophilic hypervalent iodine difluorides; for example, sulfides containing an electron-withdrawing group in the α-position are activated by difluoroiodoalkylbenzene, and the reaction is analogous to the classical Pummerer reaction [75] (Scheme 35).

The α-fluorosulfides were formed cleanly and with overall good yields (~60–80%). Introduction of fluorine syn to the bulky phenyl group suggested the Pummerer intermediate adduct being deprotonated by fluoride from the α-face necessitating intermolecular delivery of fluoride from β-face through the highly synchronous transition state [76] (Scheme 36):

3-Fluoro-4,5-dihydro-3-phenylsulfanyl-anti–5-phenyl-2(3*H*)-furanones present a single diastereoisomer in 62% yield. The use of second equivalent of $ArIF_2$ and the subsequent pyrolytic elimination of sulfenic acid present the synthesis of vinyl fluorides [76] (Scheme 37).

A similar polyfluorination reaction takes place on the alkyl chain with migration of the aryl in



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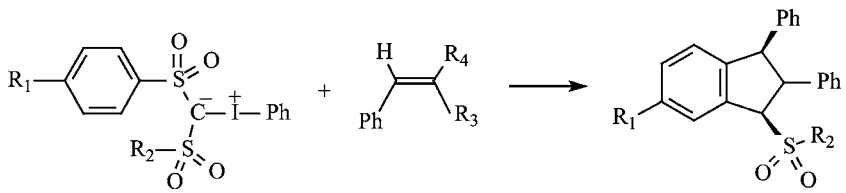
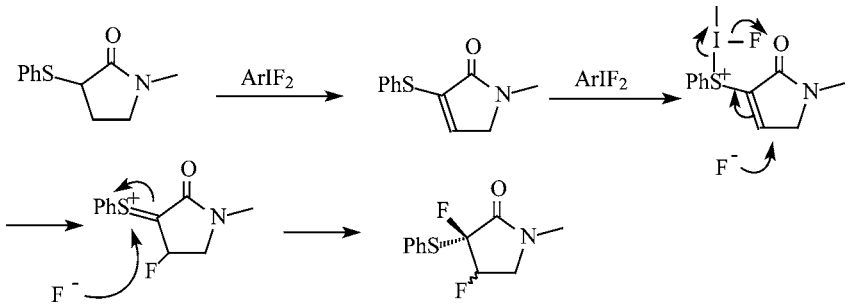
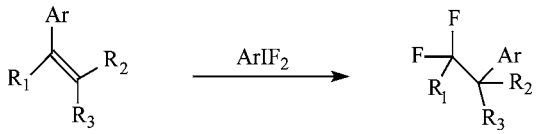


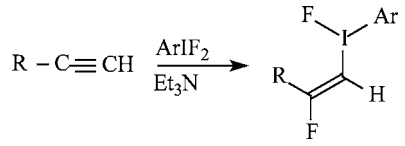
SCHEME 27



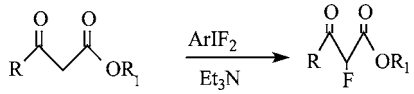
SCHEME 29



SCHEME 30



SCHEME 31

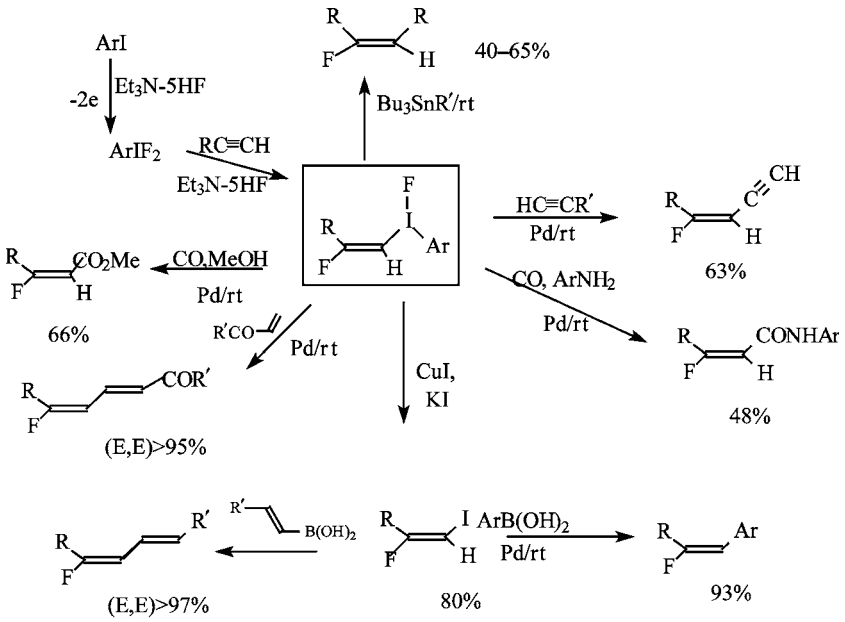


SCHEME 32

the reaction of $IF_5$ with *p*-chlorophenylalkyl sulfides. The fluorine atoms were introduced at only the α- and β-carbons of the sulfur group, whereas γ-carbon remained unfluorinated [76] (Scheme 38).

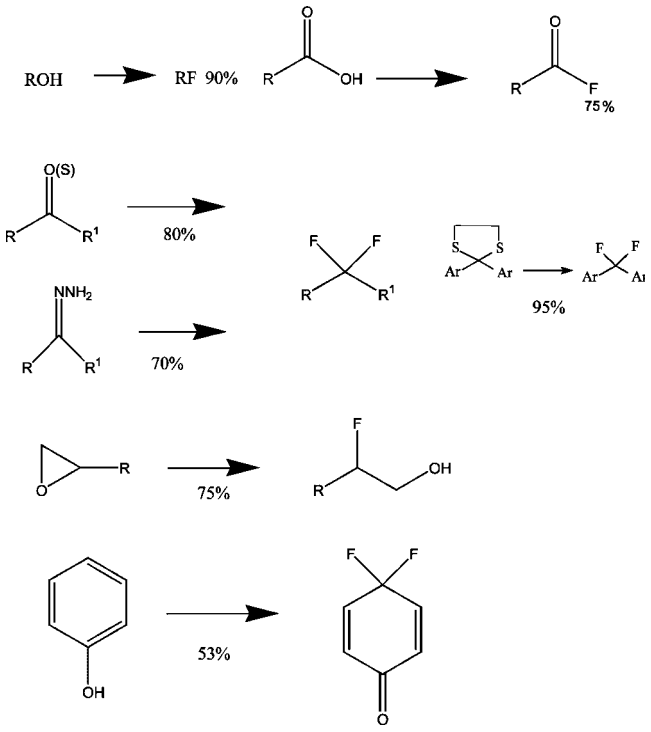
## *SOME NEW REACTIONS OF NUCLEOPHILIC SUBSTITUTION OF HYPERVALENT IODINE MOIETY*

The hypervalent iodine(III) reagents induced mild and efficient direct nucleophilic substitution of different aromatic compounds by various nucleophiles such as –SCN, –SAr, –OAc, $–N_3$, –CN, β-dicarbonyl compounds, and many others [1–6]. The phenyliodonio group is evaluated to be $10^6$ times as effective a nucleophuge as the triflate leaving group or $10^{12}$ times more reactive than the iodo group itself. This value shows that the iodonio group is



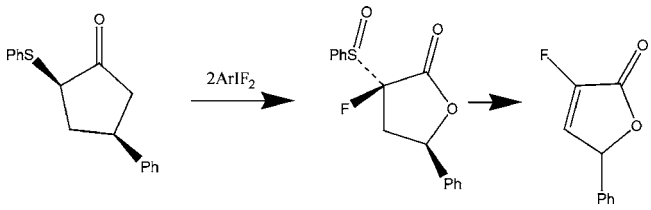
Stereo-and regioselective synrhesis of (*E*)-fluorosubstituted alkenes.

SCHEME 33

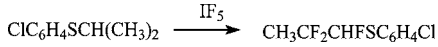



SCHEME 34

the most efficient leaving group ever determined quantitatively [77]. A plausible mechanism of these reactions included the formation of ST complex (single-transfer complex) yielding aromatic cation radicals, which react with nucleophile by one-electron oxidation followed by deprotonation to give the product—for example, see Scheme 39 [78,79].



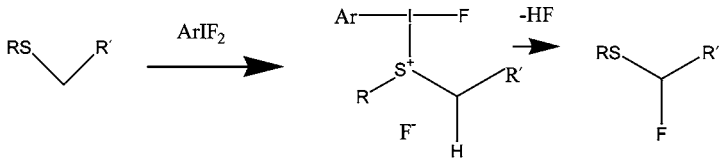

SCHEME 37




SCHEME 38

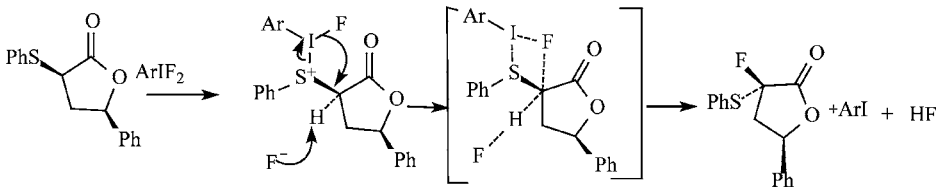
Numerous investigations indicate that hypernucleofugality of the phenyl-$\lambda^3$-iodanyl group is responsible for the unique vinylic $S_N2$-reaction. (*E*)-(β-alkynylvinyl)phenyl-$\lambda^3$-iodanes also smoothly undergo an unusual vinylic $S_N2$ reaction under mild conditions to give (*Z*)-vinylic compounds with exclusive inversion of configuration [80]. In addition, (*Z*)-1-decenyl-λ3-iodane does not undergo vinylic $S_N2$ displacement by the reaction with excess amounts of tetrabutylammonium chloride in dichloromethane at room temperature. Instead the reaction affords 1-decyne quantitatively. Last, (*E*)-vinyl-λ3-iodane affords the inverted (*Z*)-1-chlorodec-1-ene under the conditions in a high yield [80].

Investigation of solvolysis of some vinyl iodonium salts presents new insights into vinyl cation intermediates [81], focusing on whether or not a classical primary vinyl cation can be generated. The

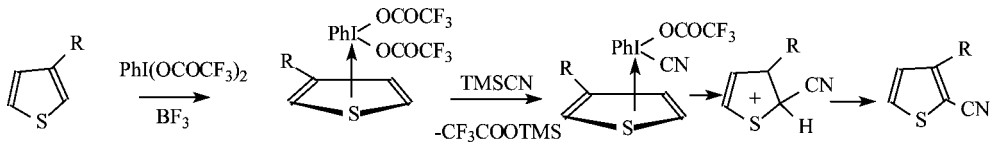



R′ =$CO_2R$, $CONR_2$, COR, CN
RS= sulfide, thioketal, xanthate

SCHEME 35




SCHEME 36

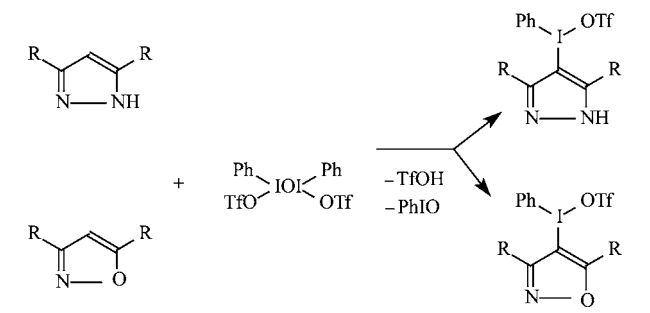


**SCHEME 39**

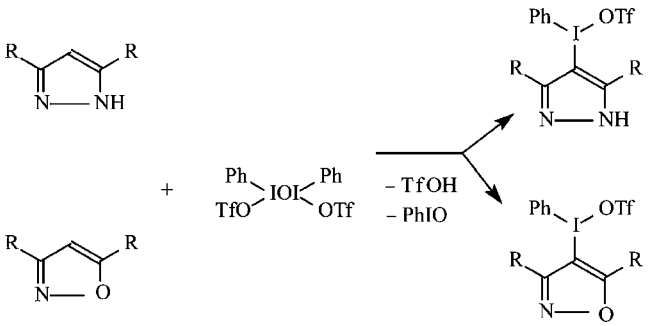
formation of the primary cation is avoided, when possible, by participation of the β-substituent in the heterolysis to form a vinylenebenzenium ion or a secondary vinyl cation. Definitive evidence against a primary vinyl cation is provided from the data about the solvolysis of 4-methylcyclohexylidenemethyl iodonium salt [82].

The reaction of nucleophilic substitution was used for the design of structures in the chemistry of pyrroles, pyrazoles, and isoxazoles [83]. Iodonium salts of pyrazoles and isoxazoles were synthesized using Zefirov's reagent or generating it in situ; the yields are quantitative in both cases (Schemes 40–42).

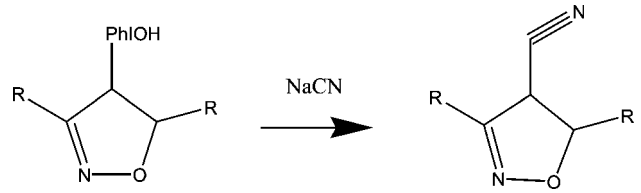
The reactions of nucleophilic substitution of iodine(III) moiety allows the creation of novel C-heteroatom bonds (C—P, C—S, C—Se, and C—Te). Copper-mediated cross-coupling of H-phosphonates with stereochemically pure (*E*)-vinyliodonium salts is a novel and very mild stereoselective preparation of 2-arylphosphonates at room temperature [84] (Schemes 43–45).



**SCHEME 40**



**SCHEME 41**

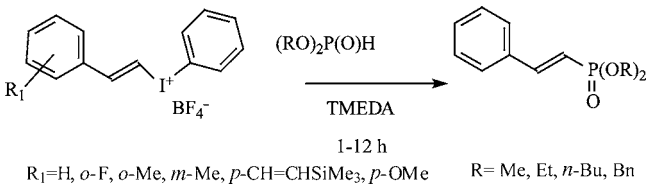


**SCHEME 42**

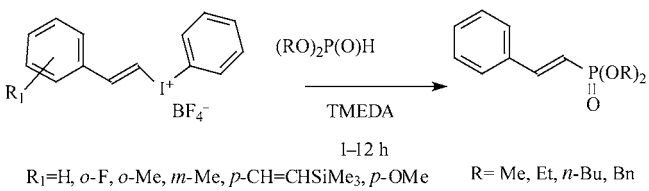
Reactions with nucleophiles are the general methods for the synthesis of 1-alkynyl-(diphenyl)sulfonium, -selenonium and -telluronium salts. This synthesis involves a heteroatom transfer reaction between 1-alkynyl(phenyl)-λ3-iodanes and diphenyl chalcogens under mild conditions. In this reaction, the 1-alkynyl group of the λ3-iodanes was selectively transferred to the chalcogen atom in preference to the phenyl group [85] (Schemes 46–48).

High reactivity of iodonium salts in the reactions with nucleophiles leads to the possibility of forming complexes with molecules donors. Pyridinium complex 1 was identified as a stable compound (mp 210°C) [86] (Scheme 49).

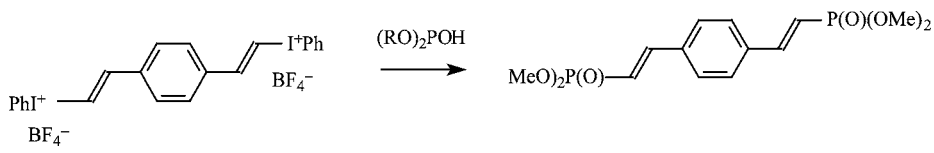
Analogous complexes with 2,6-lutidine, piperidine, morpholine, and quinucliline were thermally lower and in the presence of moist air. They



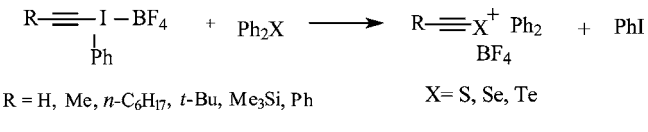
**SCHEME 43**



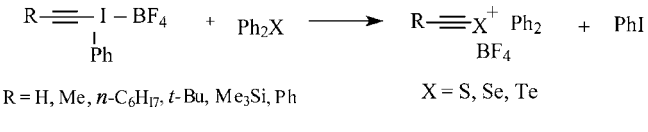
**SCHEME 44**



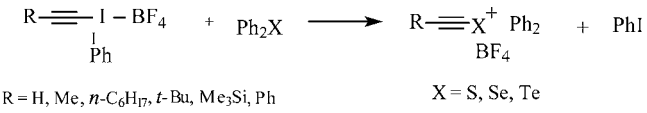

**SCHEME 45**



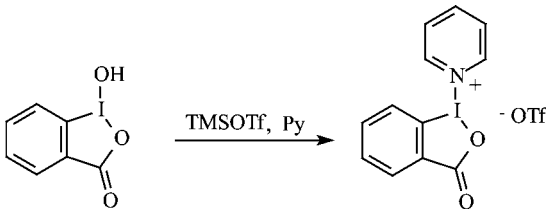

**SCHEME 46**




**SCHEME 47**




**SCHEME 48**




**SCHEME 49**

underwent hydrolysis with the formation of benziodoxole and respective ammonium triflate salts [87].

The first example of a pentavalent iodine complex was prepared the same way [87] (Scheme 50).

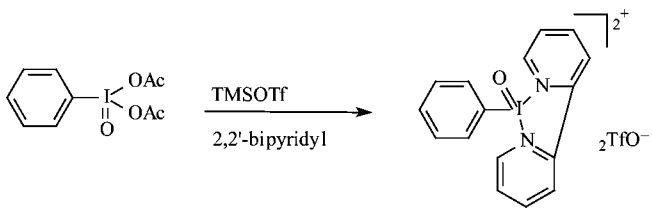
For the first time, the synthesis and characterization of supramolecular complexes between diaryl-$\lambda^3$-iodanes and 18-crown-6 are reported. X-ray crystal 1:1 or 2:1 structures of these complexes indicate that each iodine atom contacts with three adjacent oxygen atoms of 18-crown-6 through two hypervalent secondary bondings and a weak interaction [88]. $^1$H NMR analyses and MS spectra show that in dichloromethane solution, $Ph_2IBF_4$ exclusively forms the 1:1 complex with 18C6 (binding constant $K_a$, $1.02 \times 10^{-3}M^{-1}$). The binding constants decrease with the increased solvent donor ability. Decreased binding magnitude was measured with 15C5, dibenzo-18C6, dibenzo-21C7, and dibenzo-30C10.

## *IODINE(III) COMPOUNDS AS A SOURCE OF NITRENE AND CARBENE MOIETY*

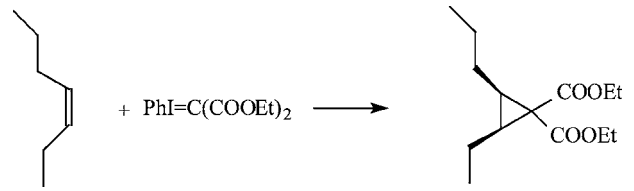
Phenyliodonium ylides, readily available upon treatment of CH-acidic compounds such as 1,2-dicarbonyl derivatives with iodobenzene diacetate, react in the presence of rhodium(II) or copper catalysts to yield products derived from carbenoid pathways [89]. Asymmetric carbene transfer involving diazo decomposition is almost exclusively restricted in the research laboratory, and only a few large-scale processes are known [90]. Heating of phenyliodonium bis(ethoxycarbonyl)methanide in *cis*-hept-3-ene at 100° yielded the *cis*-cyclopropane with some minor product [90] (Scheme 51).

The $[Rh_2(OAc)_4]$-catalyzed cyclopropanation of *cis*- and *trans*-pent-2-ene with Meldrum's ylide was stereospecific and yielded the cyclopropanation two cyclopropanes, respectively, as expected for a carbene mechanism [91,92] (Scheme 52).

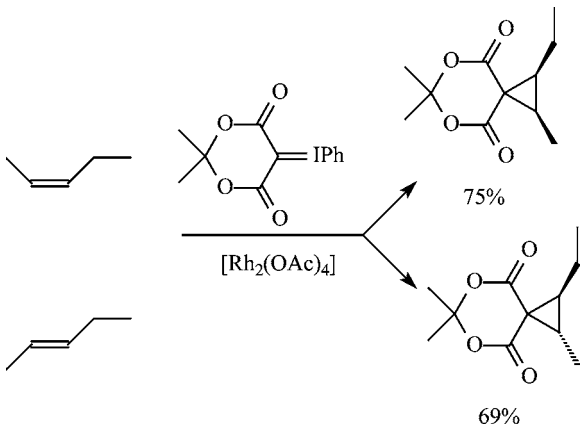
The Rh(II)-catalyzed cyclopropanations of terminal olefins were optimized. This reagent combination uses Meldrum's acid, $PhI(OAc)_2$, $Al_2O_3$, 4A




**SCHEME 50**




**SCHEME 51**

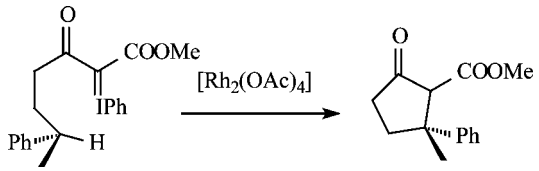



**SCHEME 52**

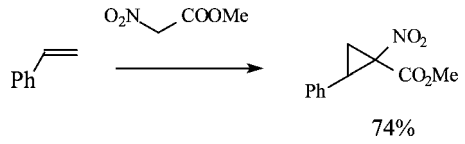
molecular sieves, and $[Rh_2(OAc)_4]$ catalyst (yields of up to 80%) [93]. Ylides can be generated in situ [94,95].

The stereochemical course of the CH insertion was established with optically pure iodoylide, having a chiral tertiary center (Scheme 53). It cyclized with achiral catalyst—>98% retention of configuration [94].

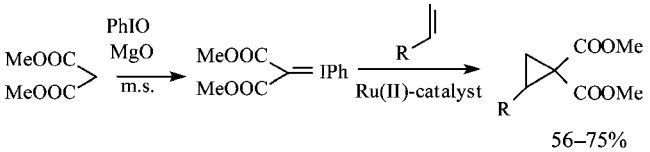
In situ generated iodonium ylides, which are prepared from α-nitro esters or ketones with $PhI(OAc)_2$ in the presence of $[Rh_2(OPiv)_4]$ (OPiv = pivalate), allow for efficient preparations of substitutes 1-nitro-1-carbonylcyclopropans [95–97] (Schemes 54 and 55).




**SCHEME 53**




**SCHEME 54**




**SCHEME 55**

Carbomethoxy iodonium ylides are also exploited in the synthesis of cyclopropanes, cyclopropenes, 2-tetralones, and various heterocycles [98] (Scheme 56).

Aryliodonium ylides of 2-hydroxy-1,4-naphthoquinone react with amines to afford good yields of indanedione 2-carboxamides [99] (Scheme 57).

The reaction proceeds through expulsion of iodobenzene, carbene formation, and the Wolff rearrangement of the latter to α,α-dioxoketene, a reaction pathway that has been proposed for the ring contraction of analogous ylides to cyclopentene derivatives [100].

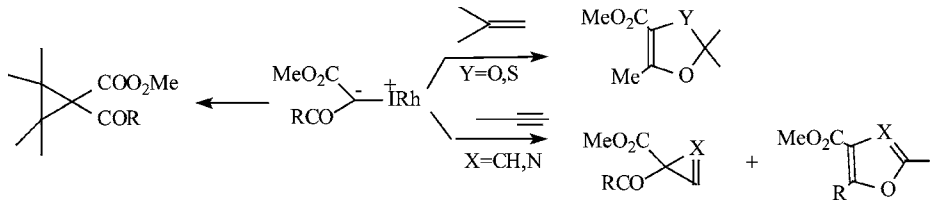
Alkynyliodonium salts and their alkylidenecarbenes provide valuable opportunities for C—C formation by carbene insertion into inactivated C—H bonds. For example, such methodology using Stang's reagent was effective for creation of tricyclic core of (±)-halichlorine [101].

The reagent PhINTs is commonly employed in aziridination is a two-electron oxidant (Scheme 58), using simple copper catalysts [102–104]. $LCu^{II}$/PhINTs and $LCu^{I}$/PhINTs systems, where L is [2.1.1]-(2,6)-pyridinophane, readily lose PhI to produce a ligand-centered radical, $LCu^{III}(NTs)^{2+}$ with most of its spin density localized on a nitrene nitrogen. This radical should be able to attack C=C bond [102]. The olefin aziridination with TsNIPh [105] with this new copper catalyst shows a very fast reaction (2–10 min at 0–20°C) with excellent yields of aziridine (87–98%) using starting mono-, di-, tri-, and tetra-substituted olefins, including those with electron-withdrawing groups [106] (Scheme 59).

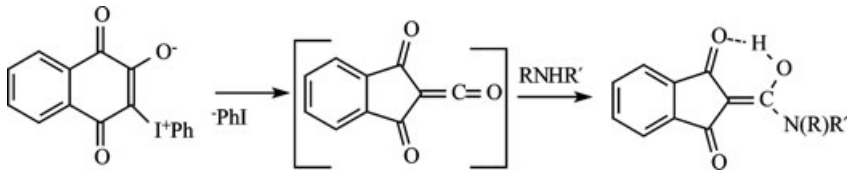
Using this source of nitrene, a new methodology is developed for the preparation of 1-aminopyridinium ylides, important synthetic blocs for the synthesis of indolizines as intermediates for the synthesis of alkaloids, and 1(*H*),2-diazepine derivatives [104] (Scheme 60):

Transition metal-catalyzed nitrene insertion into C—H bonds is increasingly attractive as a C—N bond formation strategy [107]. It was shown that copper(I) homoscorpionate complexes can affect benzene amidation by PhI=NTs in moderate yields. It was described as amidation of C($sp^2$)-H bonds of heteroarenes such as furan, pyrrole, and thiophene using ruthenium(II) porphyrin—{$[Ru^{II}(TTP)(CO)$; $H_2(TTP)$-*meso*-tetrakis(tolyl)porphyrin}—as a catalyst by the same reagent [108] (Scheme 61).

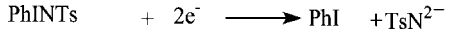
Further, the thermal-catalyzed or photochemical reaction of iodonium ylides with pyrroles provides exclusively α-substituted pyrroles with good yields. The involvement of carbenes (or carbenoids) in these reactions has been questioned (Scheme 62).



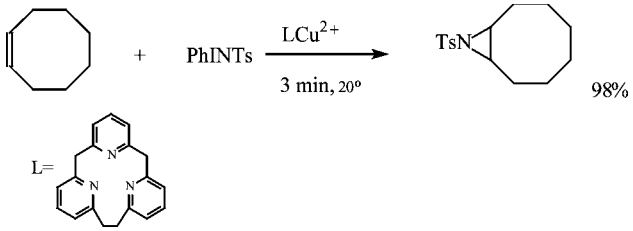
SCHEME 56



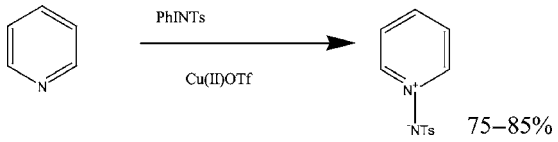
SCHEME 57



SCHEME 58



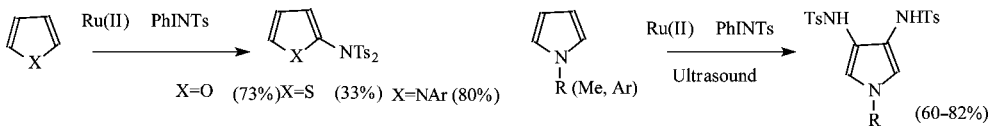
SCHEME 59



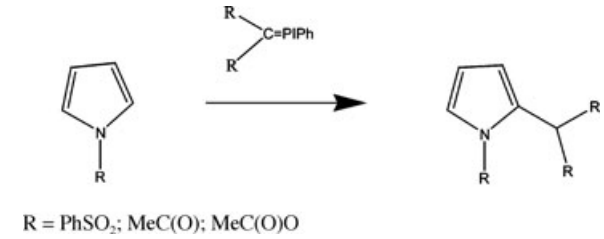
SCHEME 60

This methodology can be utilized as short syntheszies of various anti-inflammatory and analgesic agents of considerable potency, prepared previously via multistep synthesis.

In some cases, the system PhITs-$Ru^{II}$(TTP)(CO) can be efficiently changed (yield 97%) to $NH_2Ts$+PhI$(OAc)_2$-$Ru^{II}$(TTP)(CO) [108–110].



SCHEME 61

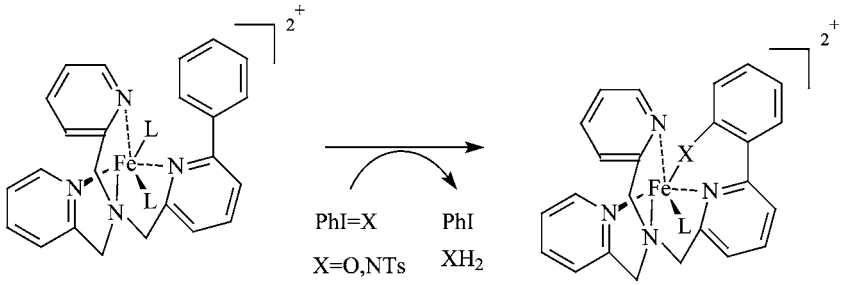


SCHEME 62

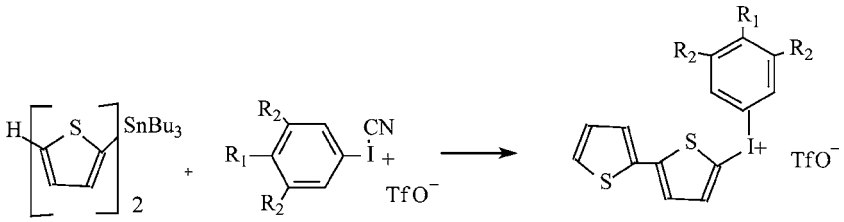
Much attention has been focused on a metal-catalyzed atom and group transfers to organic molecules as a strategy for carbon heteroatom bond formation. The reactivity of [(6-PhTRA)$Fe^{II}$$(NCCH_3)2](ClO_4)_2$ (where TRA is tris(2-pyridylmethyl)amine) was investigated with PhIO (as oxene) and with PhINTs (as nitrene) precursors [1]—it is an efficient and selective method for ortho-aromatic hydroxylation and aromatic amination of $\alpha$-aromatic substituent [110] (Scheme 63).

## *NOVEL AND SOME NEW IODINE(III) COMPOUNDS*

Diaryl(heteroaryl)iodonium and aryl(heteroaryl)-iodonium salts are numerous and widely utilized class of iodine(III) compounds because of their rich




**SCHEME 63**




$R_1 = CF_3, H; R_2 = H, CF_3$

**SCHEME 64**

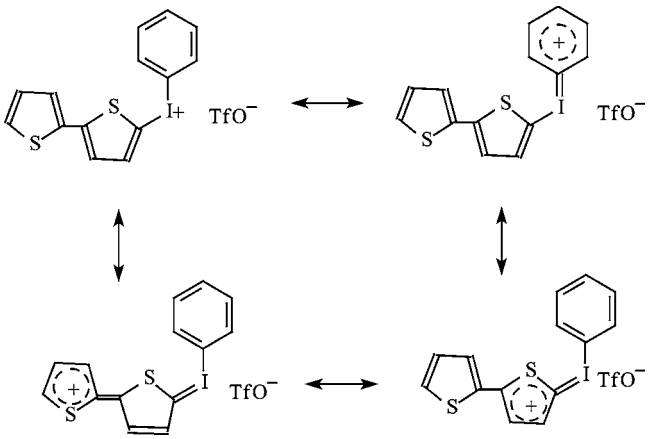
chemistry and practical applications. There are continued efforts to synthesize new structural examples of such compounds. During the last years, a series of bithienyl(aryl)iodonium triflates with increasingly electron-withdrawing substituents on the aryl moiety have been synthesized with good yields [111] (Scheme 64).

Their X-ray crystallographic analysis demonstrates that the solid-state shows highly organized two- or three-dimensional structure, and these salts incorporate extensive networks of secondary bonding interaction between the cationic iodonium centers and the triflate counter ions (Scheme 65). The UV–Vis spectroscopic analysis shows that the electronic interactions between pendent aryl and heteroaryl groups across the iodonium center can be dictated by substitution. Furthermore, the energy of HOMO–LUMO gap decreases substantially in weakly or noncoordinating solvents.

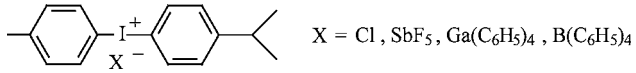
Several new iodonium salts containing weakly coordinating groups [85] were synthesized using the standard method [112] (Scheme 66).

Over the last years, there has been considerable interest and research activity focused on the chemistry of iodine(III) heterocycles, especially derivatives of benziodazoles [1,6]. The preparation of a new class of N-functionalized benzoiodazoles results from 2-iodobenzamides derived from α-amino acids and isolated in the form of stable, white microcrystalline solids with excellent solubility in nonpolar solvents. [113] (Scheme 67).

The cascade of the reactions leads to and allows the preparation of a new structural type of $\lambda^3$-iodane with two carbon ligands and one nitrogen ligand attached to the iodine atom. The benziodoxole ring system is essentially planar and has a relatively long I–N bond of 2.445 Å, which is indicative of substantial ionic character of the I–N interaction (Scheme 68).




**SCHEME 65**

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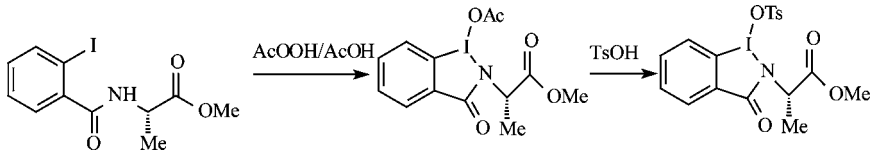

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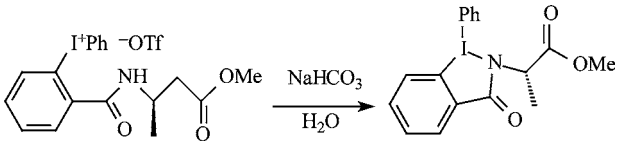

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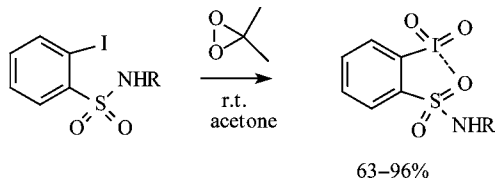


SCHEME 69

The new oxidants are 2-iodoxybenzenesulfamides [31], which display a relatively low solubility in nonpolar organic solvents such as chloroform and methylene chloride (Scheme 69). ESI–MS data indicate the oligomeric or polymeric structure of these compounds.

Hypervalent iodine reagents based on analogous heterocyclic system of benziodoxole have recently emerged as a reagent of choice for various synthetically useful oxidative transformations. Heterocyclic λ5-iodane-1-hydroxy-1,2-benziodoxol-3(1*H*)-one-1-oxide (IBX), in particular, has received a widespread application in organic synthesis as a highly efficient and mild oxidant that can be used for selective oxidation of primary and secondary alcohols and for a variety of other important oxidations. However, application of IBX is restricted because of its potentially explosive nature and extremely low solubility. Several research groups have tried to improve IBX by structurally modifying it [87,88] or by developing the polymer-supported analogs [89,24]. The problem of insolubility can also be solved by using an elevated reaction temperature [90], adding a suitable catalyst [23], performing the reaction in an ionic liquid and water [21], using derivatives of IBX amides [22] and esters [91,92]. IBX amides and esters are stable and soluble reagents having oxidizing properties similar to IBX. These reagents have the pseudobenziodoxole structure because of the intramolecular nonbonding iodine–oxygen interaction (Scheme 70).

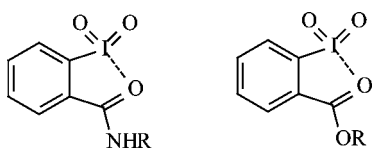
Preparative chemistry of hypervalent iodine compounds has progressed much during the last few years. For example, the old famous reagents—Kozer's reagents—and others can be prepared on a millimolar scale by grinding the two reaction partners for several minutes and by evaporating the acetic acid liberated in the ligand exchange reaction (yields 77–78%) [94] (Scheme 71).

Iodonium ylides belong to one of the fundamental classes of chemistry of hypervalent iodine [114]. Publications on this subject are numerous. The number of new iodonium ylides was prepared by the reaction of corresponding 1,3-dicarbonyl compounds with iodobenzene diacetate according to Koser's method yielding 80–90% [115].

Recently the reaction of iodonium ylides with organoboranes was shown in which unstabilized monocarbonyl iodonium ylides smoothly undergo a 1,2-shift of an alkyl or an aryl group from boron to ylide carbons. This reaction has allowed us to obtain unsymmetrical ketenes [50] (Scheme 72).

New examples of iodonium-phosphonium ylides were reported [116], but their chemistry was not discussed extensively (Scheme 73).

Later, it was established that the structure of this mixed iodonium-phosphonium ylide was not correct [117]. It was shown by NMR and X-ray that α-hypervalent iodine can stabilize the negatively charged α-carbon atom and double C=C bonding takes place (Scheme 74). Dynamic equilibrium between Z-and E-isomers was observed [117–119].



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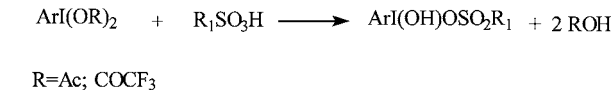

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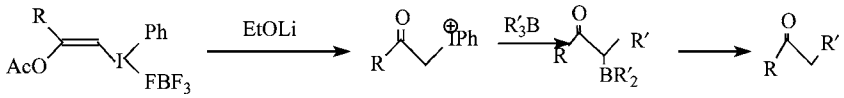

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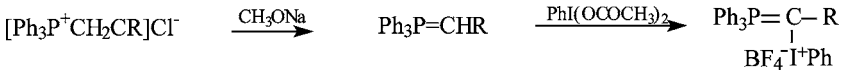
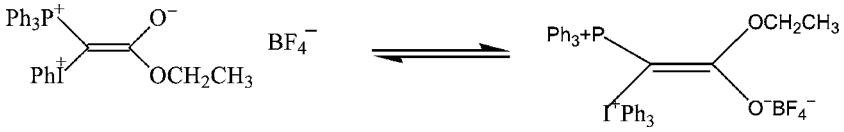


SCHEME 73



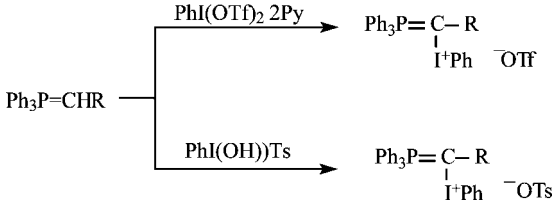
SCHEME 74

It was found that the triflate iodonium derivatives of these novel ylides can be prepared with good yields by the reaction of phosphonium ylides with the pyridinium complex of iododbenzene ditriflate [104,105] (Scheme 75).

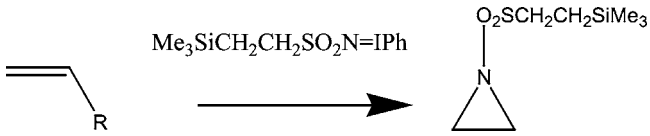
New triphenylphosphorane-derived phenyliodonium triflates and tosylates were investigated by X-ray single crystal. The iodonium-arsonium ylides were synthesized from arsonium ylides [116,120,121].

## *POLYVALENT IODINE COMPOUNDS IN SYNTHESIS OF NATURAL COMPOUNDS*

The criteria of applicability, usefulness, and high selection of reagents in organic chemistry are used in the synthesis of natural compounds. There are many examples of such use of hypervalent compounds of iodine during the 2002–2005 period. The reaction of aziridination is used in the chemistry of steroids. A particularly attractive method for accessing aziridination unsaturated steroid with [*N*-(arylsulfonyl)imino]phenyliodinane has been reported. This was the key study for the synthesis of the endogenous neurosteroid pregnanolone [122] (Schemes 76 and 77).



SCHEME 75

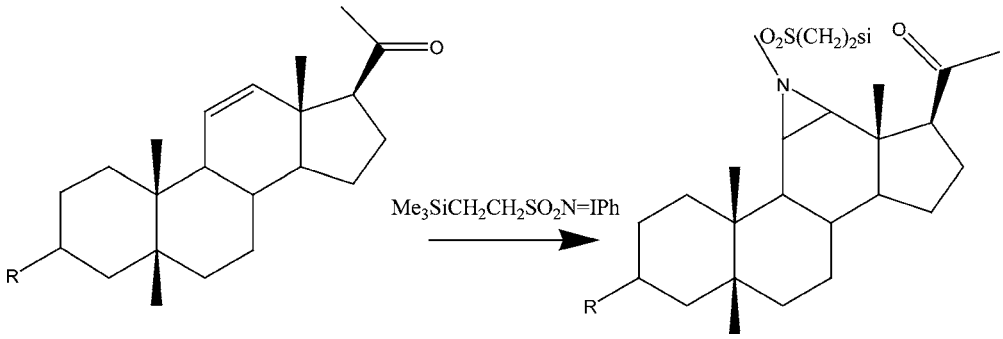


SCHEME 76

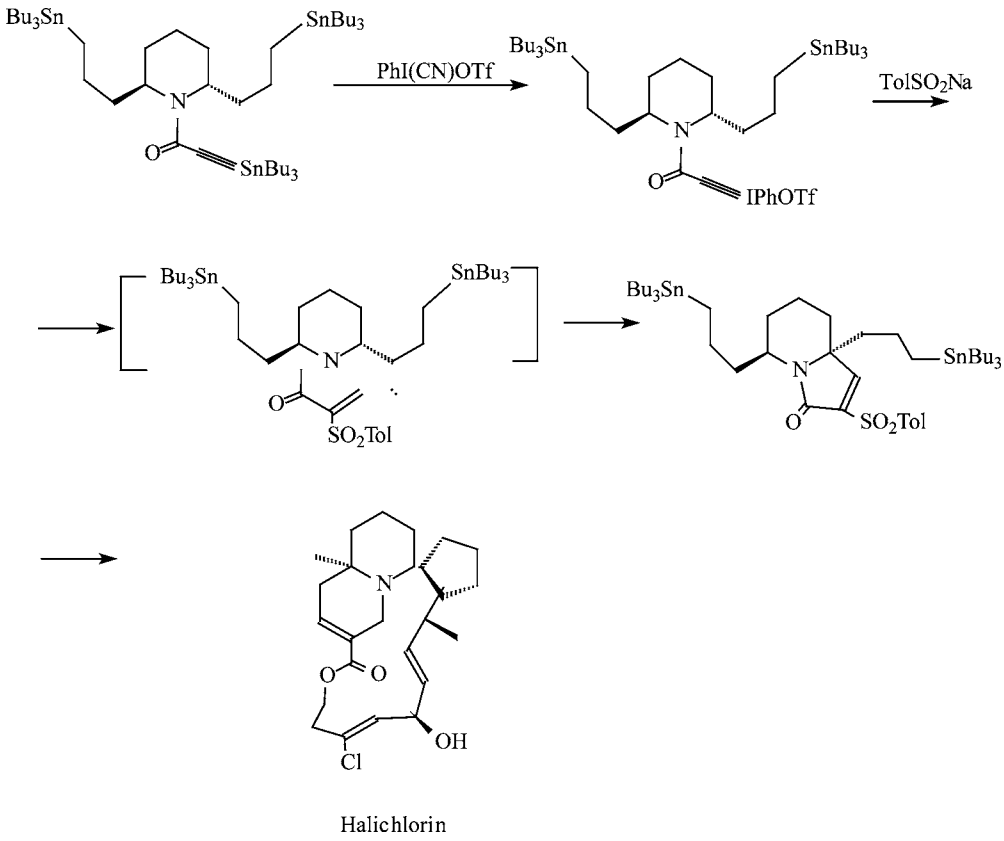
Carbenes derived in situ like nitrenes from iodonium salts—for example, alkylidene-carbenes—provide valuable opportunities for C—C bond formation by an insertion into otherwise inactivated C—H bonds [101]. Alkynyliodonium salt chemistry offers a different perspective on the synthesis of the sponge metabolite halichlorine. Alkynyliodonium salt for this process was obtained by treatment of the corresponding stannane with Stang's reagent PhI (CN)0Tf. This salt can be converted to the bicyclic lactam—the key step in the synthesis of halichlorine [101] (Schemes 78 and 79).

Introduction of azide-group is a key stage of total synthesis. This problem has been successfully solved using iodine(III) compounds. The total synthesis of (±) dibromophakellstatin describes that the molecule is constructed from a key-diazide and formed by hypervalent iodine-mediated diazidation of dihydrodipyrrolopyrazinone ring structure [2]. The haloazidation reaction, using resin-bound hypervalent iodazide, was attempted to obtain a syn-diazide. But resin-bound $I(N_3)_2^-$ provided two products—*syn*-diazides (19%) and *anti*-diazides (24%). Treatment of pyrazinone with solution-phase hypervalent iodine, by in situ formation of $^-I(N_3)_2$, provided *syn*-diazid as a major diastereomer (41%) and *anti*-diazide as a minor diastereomer (7%) [123] (Scheme 80).

The reaction, triggered by an alkoxyl radical generated in situ by the reaction of alcohol with the




**SCHEME 77**



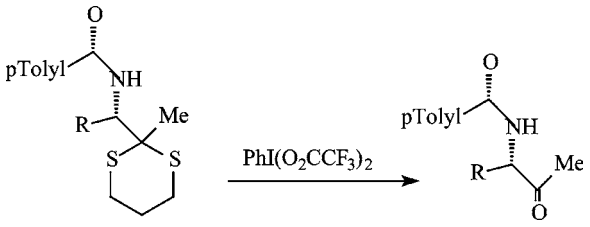

Halichlorin

**SCHEME 78**

iodine reagent in the presence of iodine under mild conditions, can also be extended to β-hydroxy azides belonging to the terpenic and steroid families of natural products [124] (Scheme 81).

The first stereoselective total synthesis of potent antitumor alkaloid, discorhabdin, which is a unique sulfur-containing pyrroloiminoquinone alkaloid, is the next key step in the stereo-controlled total synthesis involving both a diastereoselective oxidative spirocyclization using a hypervalent iodine(III) reagent [125] (Scheme 82).

The 8-oxa-6-azabicyclo[3.2.1]octane ring system forms the characteristic framework of several physiologically active alkaloids of the samandarine, ribasine, and zoanthamine types. For the synthesis of chiral 7-oxa-2-azabicyclo[2.2.1]-heptane and 8-oxa-6-azabicyclo[3.2.1]octane ring systems under neutral conditions, the reaction of phenyl and benzyl amidophosphates and alkyl and benzyl carbamate derivatives of aminoalditols with $PhI(OCOCH_3)_2$ or iodosylbenzene and iodine [126,127] (Scheme 83) was used.



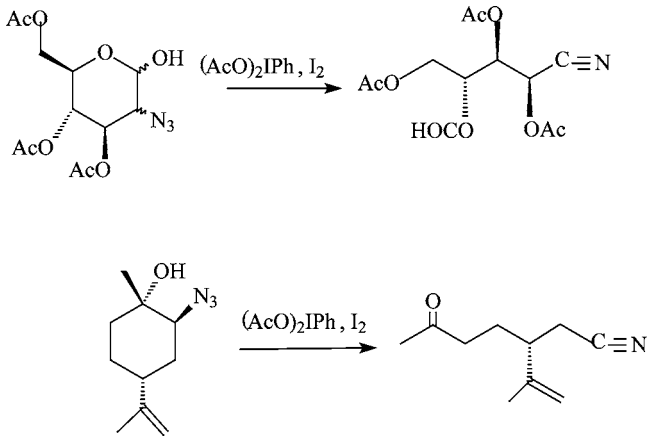

SCHEME 79

This reaction can be considered to be an intermolecular N-glycosidation that goes through an intermolecular 1,5-hydrogen abstraction promoted by an N-amido radical and followed by oxidation of the transient C-radical intermediate to an oxycarbenium ion. This methodology also proved to be useful for the selective oxidation of specific carbons of the carbohydrate skeleton, constituting a good procedure for the synthesis of protected *N*,*O*-uloses.

The key stage of the total synthesis of (–)-CP-263, 114 is the formation of bridgehead double bond via iodo transfer β-scission of a tertiary alkoxyl radical intermediate [127] (Scheme 84).

A range of sulfur-containing amides has been fluorinated with hypervalent iodine- difluoroiodoarene reagents leading to the identification of principal reaction pathways. Cephalosporin esters in the α-position to sulfur undergo fluorination with cleavage of the carbon–sulfur bond to form novel fluorinated β-lactams. Sulfides with electron-withdrawing groups in the α-position undergo α-fluorination in a process analogous to the classical Pummerer reaction. This Fluoro-Pummerer reaction has been exemplified for a range of simple α-phenylsulfanylacetamides. When β-hydrogens are present in a substrate, a different route is followed, with deprotonation by basic fluoride taking place to yield vinyl sulfides, which with an excess fluorinating reagent, can undergo further reaction in a novel tandem Pummerer–Additive–Pummerer process to yield α,β-difluoro sulfides [75] (Scheme 85).

The success of this reaction, which applies to those α-phenylsulfanyl acetamides having β-hydrogens, is caused by the ability of the hypervalent iodine reagent to oxidize sulfur in situ thus allowing sequential Pummerer reactions to take place in one pot. Furthermore, fluoride always acts first as base, and second as a nucleophile, to form the novel α,β-difluorides.

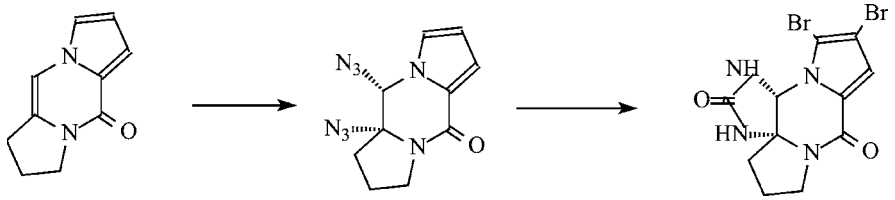



SCHEME 81

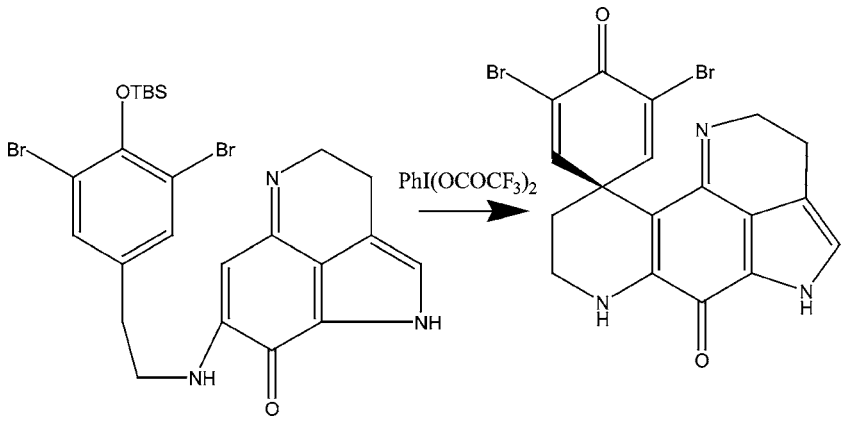
Methodological improvements in many real processes in the chemistry of natural products connect with the chemistry of iodine(III) compounds. A method for the selective hydrolysis of the dithioketal moiety, in the presence of N-sulfinyl group, is required if *N*-sulfinyl α-amino 1,3-dithianes are to be a useful chiral-building block. It is unlikely that the N-sulfinyl group would survive most of traditional methods for thioketal hydrolysis. But bis(trifluoroacetoxy)-iodobenzene was employed in the selective removal of the N-sulfinyl or the thioketal groups. This process was very successful in the asymmetric synthesis of polyoxypeptinamino acid (2*S*,3*R*)-(–)-3-hydroxy-3-methylproline [128].

## *MISCELLANEOUS*

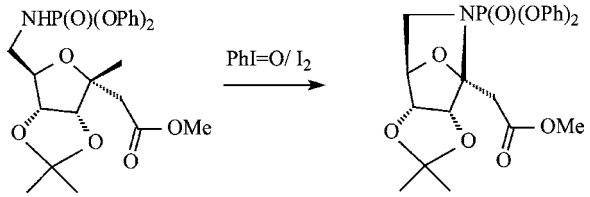
Two reagents–$TMSN_3$ and $PhI(OAc)_2$–promote radical azidation of aldehydes [129], benzal acetals [130], and ethers [131–133] (Schemes 86–88). The mixture of these reagents leads to the formation of $PhI(N_3)_2$, which decomposes to give azide radicals.




SCHEME 80




**SCHEME 82**

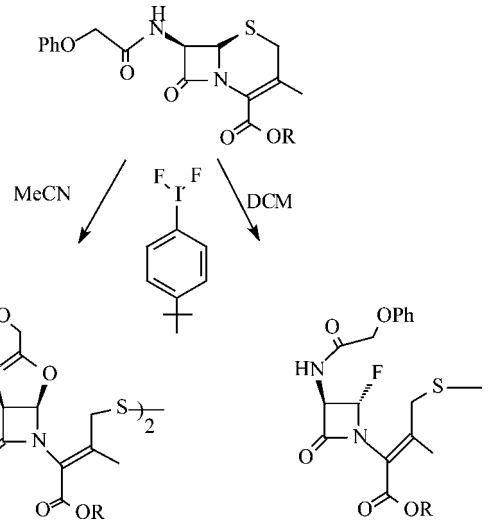



**SCHEME 83**

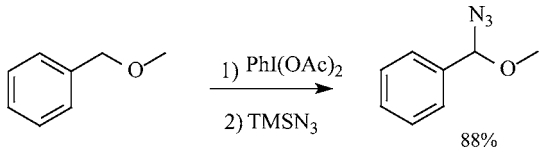
1-tert-Butylperoxy-1,2-benziodoxol-3(1*H*)-one, generating the iodocentralized radical by the action of peroxide, is used as the catalyst in a method for protecting the hydroxy group [134] (Scheme 89).

Little was known about the reduction of unsaturated phenyliodonium salts with 1-alkenyl- and 1-alkynyl-groups, but now a method has been developed for the radical-chain reduction of these compounds by THF. This involves a single-electron transfer from α-tetrahydrofuryl radical to the λ3-iodans in the presence of a catalytic amount of trialkylborane [135] (Scheme 90):

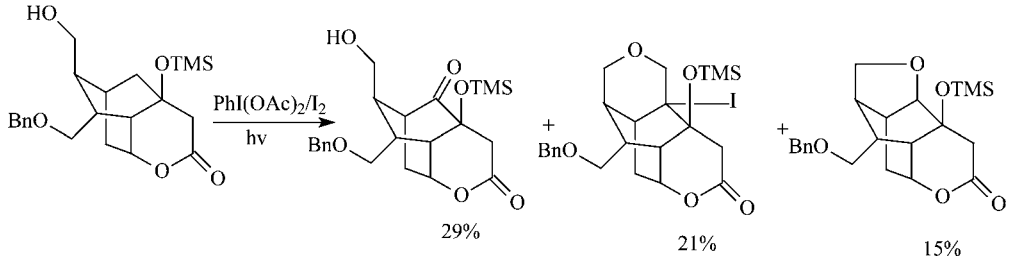
Chemistry of hypervalent iodine presents a new example of generation of bisbenzyne from



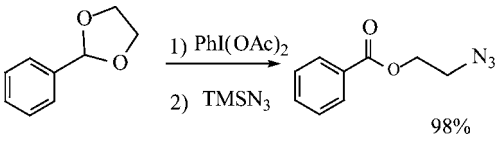

**SCHEME 85**



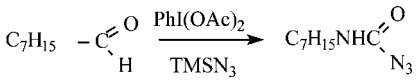

**SCHEME 86**



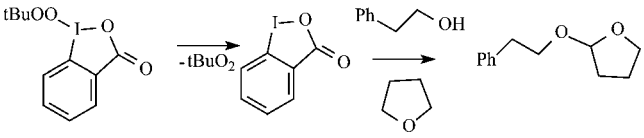

**SCHEME 84**



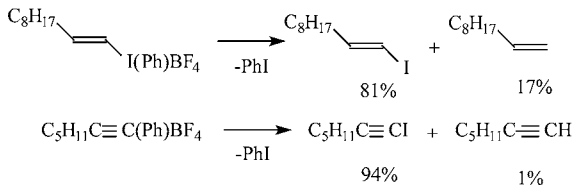

SCHEME 87




SCHEME 88




SCHEME 89

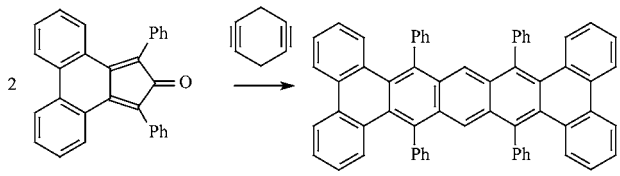



SCHEME 90

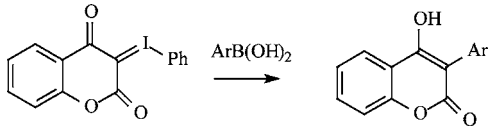
bisiodonium-carboxylate precursor [136]; its biscycloaddition to phenanthrene-derived cyclone permits to synthesize "twistacene" (the yield 1.2%) (Scheme 91).

Palladium-catalyzed coupling reaction of phenyliodonium ylides with aryl boronic acids is a preparative method for the synthesis of 3-arylhydroxycoumarins [137] (Scheme 92).

The interaction of polycyclic epoxide with electrophilic PhI(F)OTf in the presence of $LiClO_4$




SCHEME 91

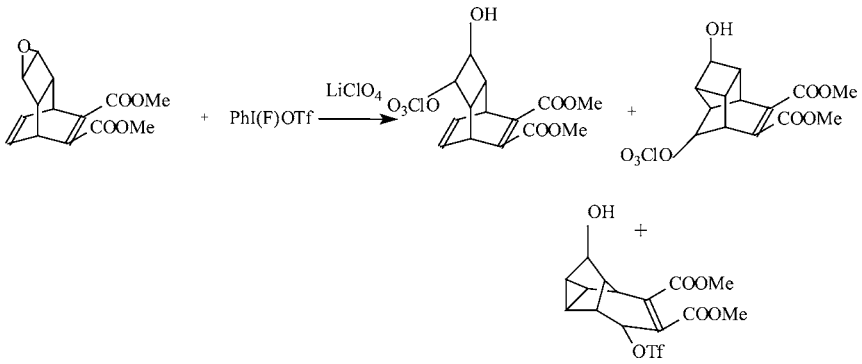



SCHEME 92

gives covalent perchlorates and triflates [138] (Scheme 93).

The rapid development of hyperiodine chemistry has given rise to some publications on the nature of bonds in such type of element organic compounds and their structures. Typically, hypervalent 10-I-3 iodine(III) compounds exhibit a T-shaped geometry with the more electropositive substituent on the iodine in the equatorial position, which is the base of the "T." The two other more electronegative substituents occupy the axial position, which are the wings in the "T." The ab initio molecular orbital calculation suggests that these data and the statistical analysis of the I—O bond lengths in PhI(OR)2, PhI(OAc)2, and PhI(OH)OAc revealed an average of 2.14 Å [139]. According to this method [139], aryl iodine(III) compounds with polar C=O bonds are trimers [140].

The known compound phenyltetrafluoroiodine(V) is shown by X-ray diffraction to have a tetragonal pyramidal structure with an apical phenyl group. This structure is compared to that of $IF(OTeF_5)_4$, where the apical position is occupied




SCHEME 93

by the fluorine atom. $C_6H_5IF_4$ adds $F^-$ forming $C_6H_5IF_5^-$, which has a pentagonal pyramidal structure with an apical phenyl group.

Fluoride abstraction from $C_6H_5IF_4$ by $SbF_5$ results in the formation of the cation $C_6H_5IF_3^+$, which has a pseudotrigonal bipyramidal structure with the phenyl group occupying an equatorial position. Isoelectronic $C_6H_5IOF_2$ has a similar structure, with the phenyl group and oxygen atom both occupying equatorial position [141].

## *CONCLUSIONS*

It is obvious that polyvalent iodine is an effective tool in organic chemistry. The addition reactions with iodine electrophiles followed by either an intermolecular or an intramolecular attack of nucleophile can be found in a great variety of syntheses as a very reliable method for the functionalization of double bonds. Hypervalent iodine(III) compounds can also be used as efficient electrophiles, mild and selective oxidants, and as a source of nitrene and carbene moiety among other findings. This field of chemistry is so significant for synthesis that the next logical step would be the publication of a monograph on preparative chemistry using polyvalent iodine compounds.

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