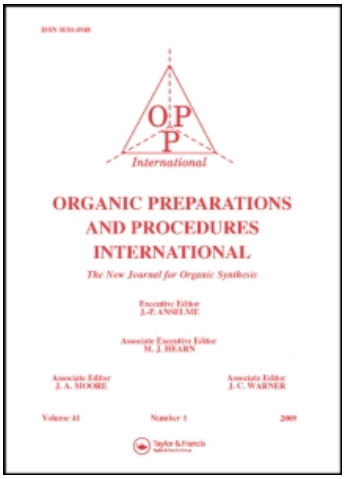

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RECENT PROGRESS IN THE USE OF HYPERVALENT IODINE REAGENTS IN ORGANIC SYNTHESIS. A REVIEW

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RECENT PROGRESS IN THE USE OF HYPERVALENT IODINE REAGENTS IN ORGANIC SYNTHESIS. A REVIEW

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INTRODUCTION

There has been considerable attention on hypervalent iodine compounds in organic synthesis. This paper mostly surveys recent progress in the use of hypervalent iodine reagents in organic synthesis since 1993. From 1980 to 1992 many reviews and a monograph on this subject have been published and discussed.[1-14] Also in 1994-1996 several reviews on the related subject have been reported.[15-21]

Hypervalent iodine reagents are generally used as mild oxidizing agents and show electrophilic character, which resemble Hg(II), Tl(III), and Pb(IV) in chemical properties. Furthermore, hypervalent iodine compounds undergo ligand exchange and ligand-ligand coupling reactions at iodine(III) atom, in analogy with transition metals. The high nucleofugality of the phenyliodonio group (-I^+Ph) is an especially valuable property for the use of hypervalent iodine compounds, which is widely applied to organic synthesis. This review will focus mainly on the iodine(III)-promoted reactions, *i. e.* oxidation, addition, and substitution, and the reactions using iodonium salts such as fluoroalkyl, alkenyl, alkynyl and aryliodonium salts and emphasizes the synthetic utility.

I. HYPERVALENT IODINE REAGENTS

Many types of hypervalent iodine reagents have been used to organic synthesis.[1-21] Among those hypervalent iodine reagents, the types of IX_3 and $ArIX_2$ have been available for synthetic purpose. The hypervalent iodine reagents and the typical applications are listed in Table 1. Also the new iodine(III) reagents recently appeared are given in Table 2.

TABLE 1. Selected Iodine(III) Reagents Prepared before 1990 and Typical Applications

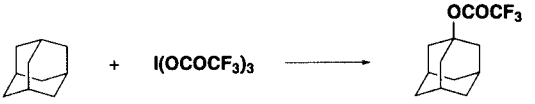
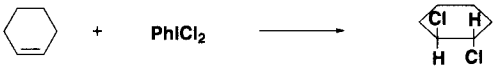
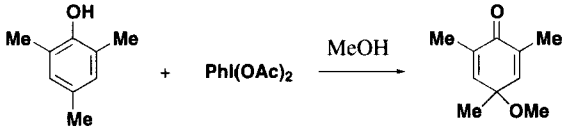
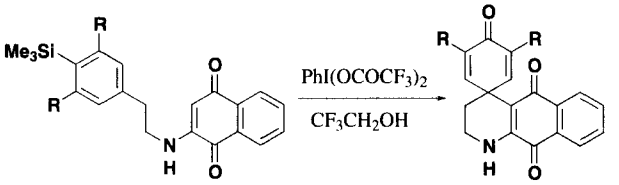
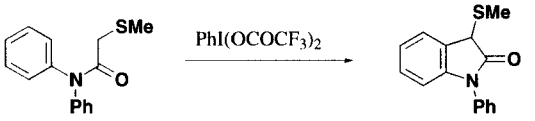
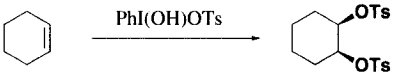
Iodine(III) Reagents	Synthetic Applications	
$I(OCOCF_3)_3$		(1)[22,23]
	$2ArH + I(OCOCF_3)_3 \longrightarrow Ar_2I^+OCOCF_3$	(2)[24,25]
TfOI=O	$2\,RC{\equiv}CSiMe_3 + TfOI{=}O \longrightarrow (RC{\equiv}C)_2I^+OTf^-$	(3)[26]
	$2\,ArSiMe_3 + TfOI{=}O \longrightarrow Ar_2I^+OTf^-$	(4)[27]
PhIO	$PhCH(OH)CH(OH)Ph + PhIO \longrightarrow 2\,PhCHO$	(5)[28]
	$ArCOCH_3 + PhIO \longrightarrow ArC(OMe)_2CH_2OH$	(6)[29]
$PhICl_2$		(7)[30-32]
$ArIF_2$	$Ph_2C{=}CH_2 + ArIF_2 \xrightarrow{H^+} PhCF_2CH_2Ph$	(8)[33,34]
$PhI(OAc)_2$	$PhCOCH_2R + PhI(OAc)_2 \longrightarrow PhC(OMe)_2CH(R)OAc$	(9)[35]
		(10)[36]
$PhI(OCOCF_3)_2$		(11)[37]
		(12)[38]
	$R\text{-}CONH_2 + PhI(OCOCF_3)_2 \xrightarrow{H_2O} R\text{-}NH_3^+CF_3CO_2^-$	(13)[39]
PhI(OH)OTs		(14)[40]

TABLE 1. Continued

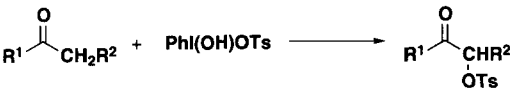
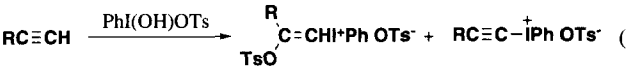
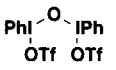
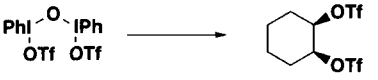
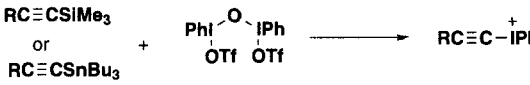
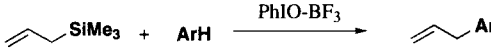
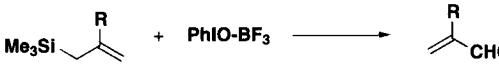
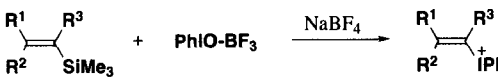
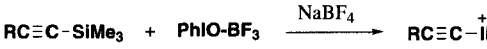
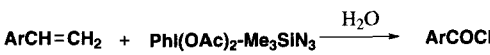
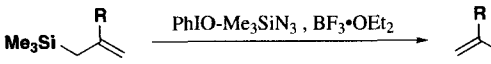
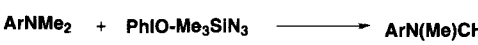
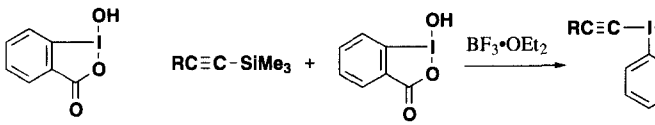
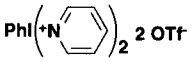
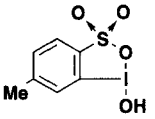
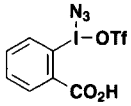
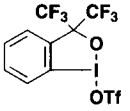
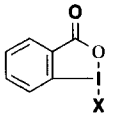
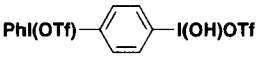
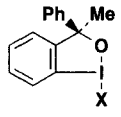
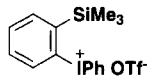
Iodine(III) Reagents	Synthetic Applications	
		(15)[41]
		(16)[42]
		(17)[43,44]
		(18)[45-47]
		(19)[48]
PhIO-BF_3		(20)[49]
		(21)[50]
		(22)[51]
		(23)[52]
$PhI(OAc)_2$-Me_3SiN_3		(24)[53]
PhIO-Me_3SiN_3		(25)[54]
		(26)[55]
		(27)[56]

TABLE 2. Recent Iodine(III) Reagents Applied to Organic Synthesis

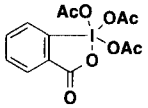
Iodine(III) Reagents	Synthetic Applications
	oxidation[57]
	preparation of alkynyliodonium salts[68]
	azido transfer[61]
$PhI(SC_6F_5)_2$	arylsulfanylation[75]
$PhI(OH)OPO(OPh)_2$	oxyphosphorylation[77]
$PhI(SCN)_2$	thiocyanation[79]
	preparation of alkynyliodonium salts[65]
	X = $OPO(OPh)_2$: ligand exchange[58] OO^tBu: oxidation[59,60] N_3: azido transfer[61-63] OTf: preparation of alkynyliodonium salts[64,65] NHR: amidation[66] CN: cyanation[63,67]
$R_f I(OH)OSO_2R$	preparation of fluoroalkyliodonium salts[69-72]
ArI(CN)X X = OTf, OTs	preparation of alkyny,[73] aryl,[73] and alkenyliodonium salts[74]
$(NC)_2IOTf$	preparation of diaryl and dialkynyliodonium salts[76]
$O{=}IOSO_2F$	preparation of diaryliodonium salts[78]
	preparation of bisiodonium salts[80,81]
	X = Cl, N_3 asymmetric functionalization[82]
	efficient benzyne precursor[83,84]

II. IODINE(III)-PROMOTED REACTIONS

The iodine(III)-promoted reactions are introduced and discussed as the following types of the reactions: (1) oxidation, (2) addition, and (3) substitution.

1. OXIDATION

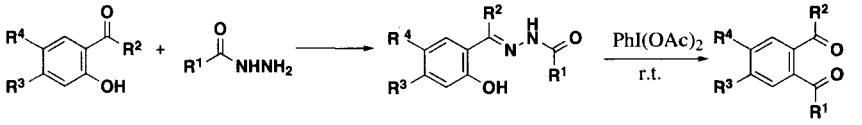
Oxidation by hypervalent iodine reagents is a well-known method.[85-89] Inorganic compounds involve commercially available periodic acid and its salts. The known organic reagents[85] are $I(OAc)_3$, $I(OCOCF_3)_3$, $PhICl_2$, PhIO, $PhI(OAc)_2$, $PhI(OCOCF_3)_2$, $PhIO_2$, *o*-iodosylbenzoic acid, and Dess-Martin periodinane **1**.



1

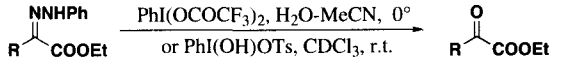
These hypervalent organoiodine reagents have been applied to the oxidation of alcohols to aldehydes or ketones,[90-92] the conversion of aldehydes to acids,[90] the preparation of carbonyl compounds,[93-95] and the oxidation of sulfides[96,97] and selenides.[98]

Recent reports on the oxidation by these hypervalent iodine reagents are the synthesis of 1,2-diacetylbenzenes from *o*-hydroxyacylketone acylhydrazones using $PhI(OAc)_2$ (Eq. 28)[99] and

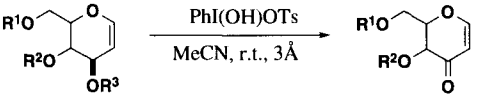


R^1 = Me, Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 2-furyl, 2-thienyl
R^2 = H, Me, Et; R^3 = H, OMe; R^4 = H, Me

the regeneration of α-keto esters from the phenylhydrazones by using $PhI(OCOCF_3)_2$ or PhI(OH)OTs (Eq. 29).[100] These reactions proceed *via* azo intermediates generated by oxidation of the hydrazone moiety.

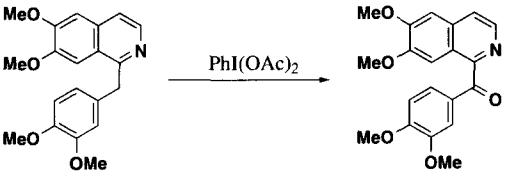


Selective oxidation of protected glycals proceeds with PhI(OH)OTs (Eq. 30).[101,102] The selective oxidation of the allylic position in the glycals is probably initiated by addition of



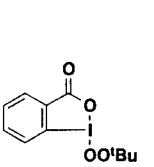
R^1 = Bu, Ac; R^2 = Bu, H, CH_2OCH_3, $SiMe_2Bu^t$, $SnBu_3$

PhI(OH)OTs on the enol ether moiety, followed by elimination of tosylate ion, PhI, and water, leading to the ketones. The benzylic position of paraverine (**2**) is also oxidized by $PhI(OAc)_2$ (Eq. 31).[103]



A hypervalent iodine peroxide, 1-(*tert*-butylperoxy)-1,2-benziodoxol-3(*1H*)-one (**3**), oxidizes benzyl, allyl, and propargyl ethers to the corresponding esters (Eqs. 32-34).[60]

o-Iodoxybenzoic acid is used for the mild oxidation of alcohols (Eq. 35) and 1,2-diols (Eq. 36).[104,105] *o*-Iodoxybenzoic acid is insoluble in most organic solvents, such as sulfolane, DMF, MeCN, $CHCl_3$, CH_2Cl_2, acetone, and THF, but dissolves readily in DMSO (up to 1.5M). Similar oxidations of alcohols and hydroxyketones can be conducted by using hypervalent iodine(V) reagents **4** and **5**.[107,108]



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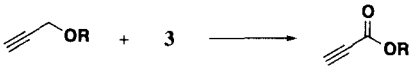
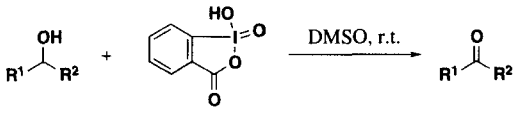
(32)

(33)



(34)



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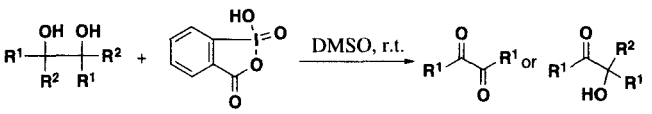
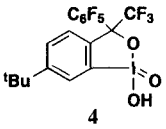


(36)

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



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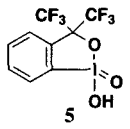
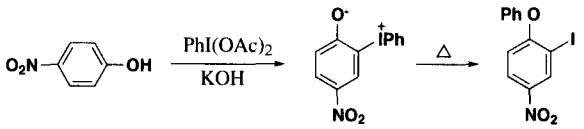


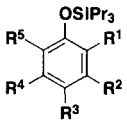
5

The oxidation of phenol gives usually resinous products[109] but in the case of phenols bearing electron-withdrawing groups such as NO_2, iodonium ylides are formed.[110-112] The iodonium ylides are shown to undergo migration of phenyl group yielding *ortho*-iodophenyl phenyl ethers (Eq. 37).



(37)

The mild procedure using hypervalent iodine reagents is applied to the preparation of cyclohexadienones (Eq. 38). The oxidation of phenols with $PhI(OAc)_2$ in methanol gives methoxycyclohexadienones[113,114] at room temperature. The oxidation using $PhI(OCOCF_3)_2$ proceeds under milder conditions at 0°. The oxidation with $PhI(OCOCF_3)_2$ in aqueous acetonitrile yields *p*-quinols and the higher yields are obtained when trispropylsilylated phenols (**6**) are oxidized.[115] The oxidation of phenol derivatives is applied to synthesis of antibiotic aranorosin (Eq. 39).[116]



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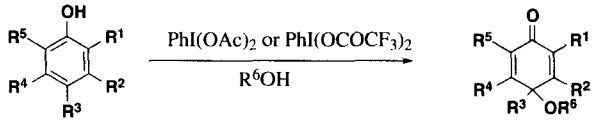

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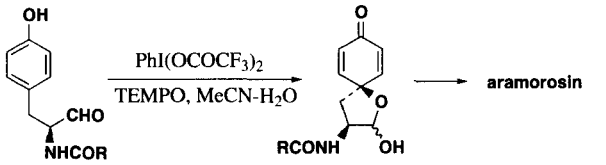
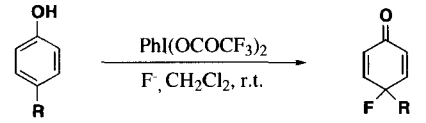


(39)

The *ipso* fluorination of 4-alkylphenols takes place when 4-alkylphenols are treated with $PhI(OCOCF_3)_2$ in the presence of pyridinium polyhydrogen fluoride (Eq. 40).[117] Similarly, *p*-thiocyanation of phenols proceeds by using $PhI(SCN)_2$ prepared *in situ* from $PhICl_2$ and $Pb(SCN)_2$ (Eq. 41).[79]



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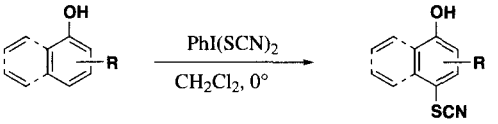
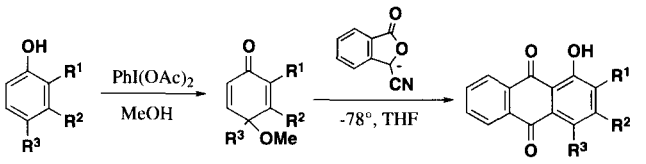


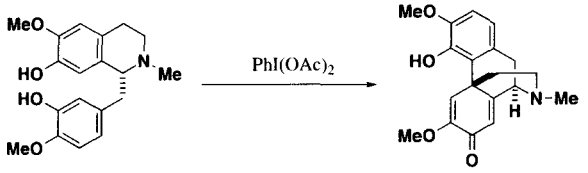
(41)

Cyclohexadienones are applied to synthesis of anthraquinones using the reaction of 3-cyanophthalide (Eq. 42).[114]

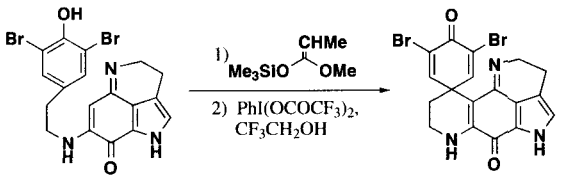


(42)

More useful applications are devoted to the synthesis of heterocyclic compounds and natural products. Previous reviews illustrate some applications.[1,5,9,14,15,118,119] For examples, there are alkaloid syntheses by oxidative aryl-aryl coupling reactions (Eqs. 43[120] and 44[121]).

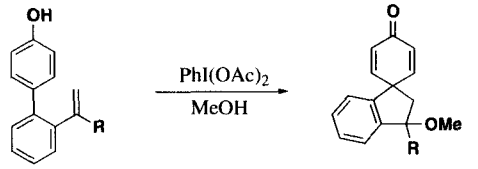


(43)



(44)

Recent reports on the oxidative cyclization involve the formation of 5, 6 and 7-membered spirocyclodienones (Eqs. 45-48).[122-125]



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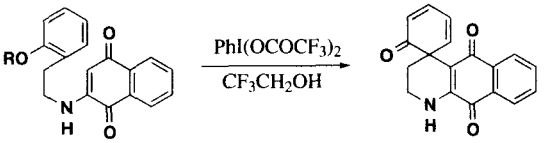
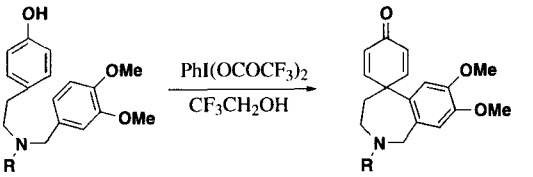
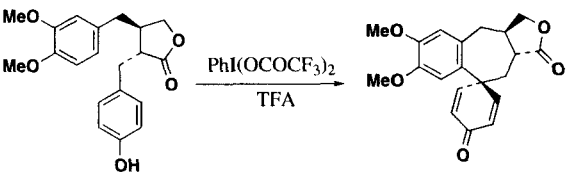


(46)

R = H, TMS, TBDMS

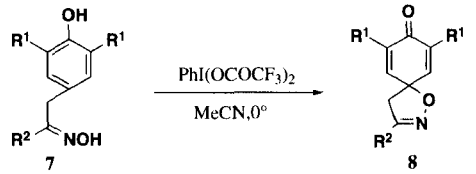


(47)



(48)

The oxidative cyclization of phenolic oximes is readily achieved by using $PhI(OCOCF_3)_2$. Reaction of phenolic oximes **7** with $PhI(OCOCF_3)_2$ in MeCN at 0° gives spirocyclic isoxazolines **8** (Eq. 49).[126] Similar cyclizations of **9** proceed with $PhI(OAc)_2$ in MeCN at 0° to afford spiroxazolines

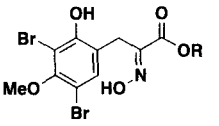


7 8

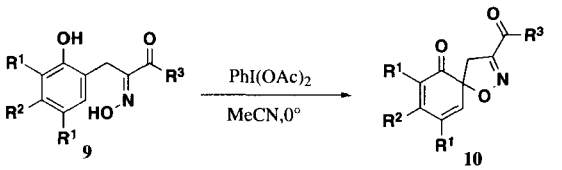
(49)

R^1 = H, Br; R^2 = Me, Et, ^{t}Bu, CO_2Me, Ph, 4-BrC_6H_4

10 (Eq. 50).[127] Interestingly, this method is applied to asymmetric synthesis of **10** from oxime **11**, which provides a 82% diastereoisomeric excess of chiral spiroisoxazolines by using PhIO and (-)-camphorsulfonic acid.



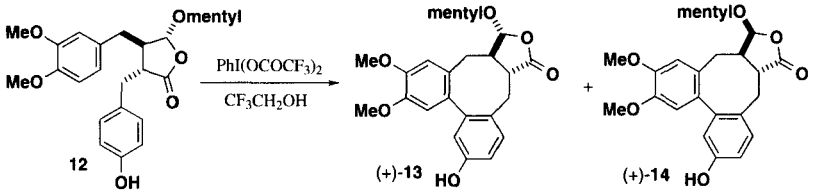
11: R = (-)-8-phenylmenthyl



(50)

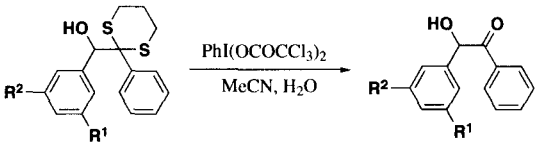
R^1 = H, Br; R^2 = H, OMe; R^3 = OMe, OBu^t, $NH(CH_2)_3OMe$

Another example of asymmetric synthesis using hypervalent iodine reagents is the oxidation of a homochiral 2,3-dibenzylbutyrolactone **12** by $PhI(OCOCF_3)_2$, which provides two asymmetric syntheses of the isostegane derivatives (+)-**13** and (+)-**14** (Eq. 51).[128]



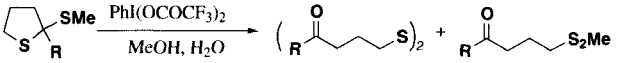
(51)

Deprotection of dithioacetals by $PhI(OCOCl_3)_2$ gives the corresponding carbonyl compounds (Eq. 52).[129] Dethioacetalization of semicyclic dithioacetals by $PhI(OCOCF_3)_2$ affords the



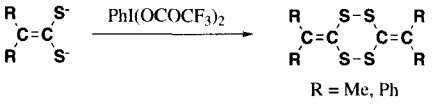
(52)

corresponding ring-opened carbonyl compounds (Eq. 53).[130] Introduction of ethylene glycol unit into a disaccharide thioglycoside is also achieved by using $PhIO\text{-}SnClO_4\text{-}AgClO_4$.[131]



(53)

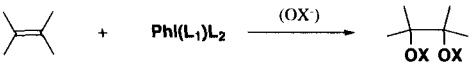
Oxidative coupling of the dianions of alkandithioic acids with $PhI(OCOCF_3)_2$ gives the corresponding 1,2,4,5-tetrathianes (Eq. 54).[132]



(54)

2. ADDITION

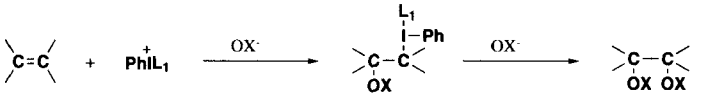
Reactions of alkenes and ketones with hypervalent iodine reagents exhibit interesting features in that functional groups are introduced into the double bond and the α position of the ketones.[1,4,5,9,10,119] For examples, vicinal functionalized alkanes are readily obtained by the reaction of alkenes with $PhI(OAc)_2$, PhI(OH)OTs, PhI(OTf)OI(OTf)Ph and the related hypervalent iodine reagents (Eq. 55).[41,43,45-47,133-135] These additions to alkenes are believed to proceed with anti addition



(55)

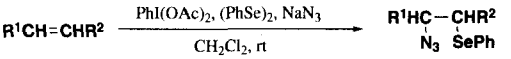
L_1, L_2 = OAc, OH, OTs, OTf, OMs, $OCOCF_3$, OI(OTf)Ph
OX = OAc, OTs, OMs, $OClO_3$, $OCOCF_3$, OTf

of hypervalent iodine reagents followed by S_N2 type displacement with nucleophiles (Scheme 1). Therefore, the stereochemistry of the adducts from cyclohexene is cis.



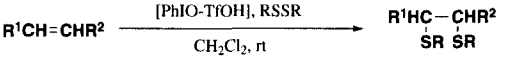
Scheme 1

As demonstrated above, a variety of nucleophilic agents can be introduced by using hypervalent iodine reagents. Recently, azido-phenylselenenylation of alkenes has been reported (Eq. 56).[136,137] However, on the basis of the regioselectivity and the cyclization from 1,6-heptadiene, this azido-phenylselenenylation reaction is suggested to proceed with a radical mechanism.



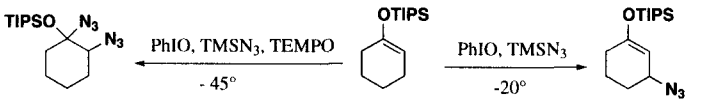
(56)

Addition of diphenyl and dimethyl disulfides to alkenes successfully proceeds with [PhIO-TfOH] to give high yields of 1,2-*bis*(phenylsulfanyl)alkanes and 1,2-*bis*(methylsulfanyl)alkanes, respectively (Eq. 57).[138]

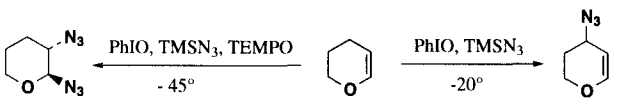


(57)

Vicinal double azidonation of enol ethers are achieved by using $PhIO/TMSN_3$ together with catalytic amounts of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) (Schemes 2[139] and 3[140]). Interestingly, the same reaction in the absence of TEMPO yields the allylic azidonation products.



Scheme 2

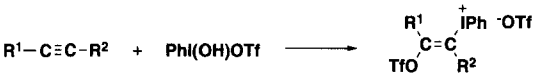


Scheme 3

The difference between these reactions is considered to be that the double azidonation is an azide radical addition process and the allylic azidonation involves ionic dehydrogenation followed by attack of azide ion.[139]

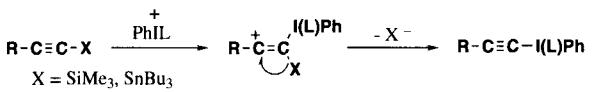
Reaction of alkynes with hypervalent iodine reagents results in the formation of alkenyliodonium salts because of the relatively strong C(sp^2)-I(III) bond, in some cases the alkenyliodonium salts undergo displacement by nucleophiles to give substituted alkenes as demonstrated in Section III. 2b. Reaction of alkynes with PhI(OH)OTs gives a mixture of (E) and (Z) alkenyliodonium tosylates (Eq. 58),[43] while a stereoselective *trans* addition takes place when alkynes are treated with a hypervalent iodine reagent [PhI(OH)OTf] prepared from PhIO and TfOH (Eq. 59).[141] Most of alkynyliodonium salts are synthesized by a similar addition reaction with

(58)



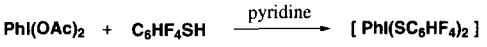
(59)

alkynes bearing silyl or stannyl groups which are easily replaced by hypervalent iodine reagents (Scheme 4).[6,8,11,16,17]

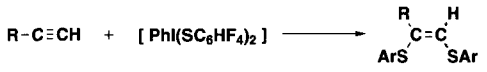


Scheme 4

Addition of arylsulfanyl group to terminal alkynes takes place by using a hypervalent iodine reagent prepared from $PhI(OAc)_2$ and 2,3,5,6-tetrafluorothiophenol in pyridine (Eqs. 60 and 61).[75] The mechanism of this reaction is viewed as proceeding *via* alkynyliodonium or vinyliodonium salts. Unfortunately, phenylsulfanyl group in place of tetrafluorothiophenol leads to dimerization to diphenyl disulfide.



(60)



(61)

3. SUBSTITUTION

Substitution reactions promoted by hypervalent iodine reagents have been observed in the reactions of aromatic compounds, alkenes, alkynes, allyl, and propargylic compounds, ketones, amines, and amides.[1-21] These reactions are initiated by electrophilic addition of hypervalent iodine reagents and the intermediate iodine(III) species undergo displacement by nucleophilic agents leading the final products.

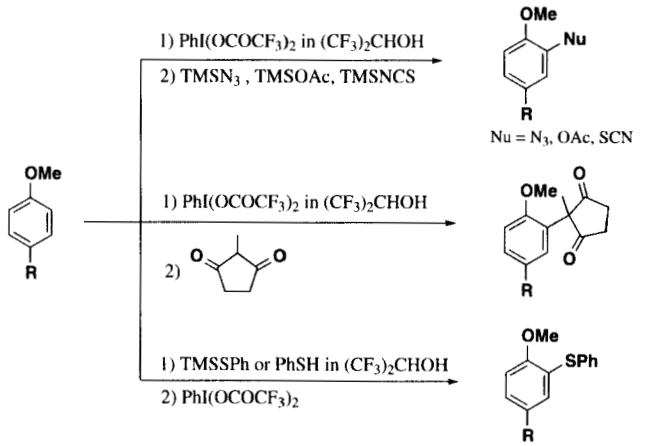
a) Aromatic compounds

The reaction of hypervalent iodine reagents with aromatic substrates has been investigated since early times.[1,3,12,142-145] The most well-known reaction is the electrophilic substitution of aromatic substrates with hypervalent iodine reagents giving diaryliodonium salts. Hydrogen, silyl, and stannyl groups are replaced by the iodine(III) atom (Eq. 62). This reaction is the most popular synthetic method for diaryliodonium salts.

(62)

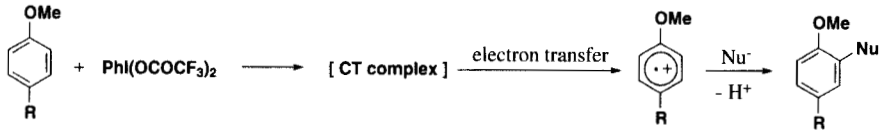
X = H, Me_3Si, Bu_3Sn

Most diaryliodonium salts are sufficiently stable to be isolated and do not undergo substitution reactions even in the presence of nucleophiles unless the nucleophile is a strong one. However, aromatic substitutions promoted iodine(III) reagents take place when the aromatic substrates are activated by electron-donating groups such as methoxy group. *p*-Substituted phenol ethers react with nucleophiles in the presence of $PhI(OCOCF_3)_2$ to give *o,p*-substituted phenol ethers (Scheme 5). Various nucleophiles such as azide,[146-148] acetate[146] β,β-dicarbonyl compounds,[146] thiophenolate,[149,150] and thiocyanate ion[150] are introduced at the *ortho* positions of the *p*-substituted phenol



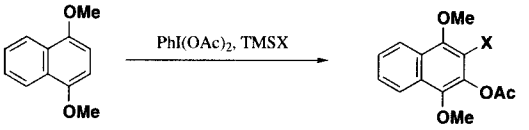
Scheme 5

ethers. These reactions proceed with formation of a charge-transfer complex of phenol ethers with $PhI(OCOCF_3)_2$ followed by single-electron transfer leading radical cations, which are subject to attack of nucleophiles (Scheme 6). The UV and ESR studies support the presence of the CT complexes and the radical cations.[146]

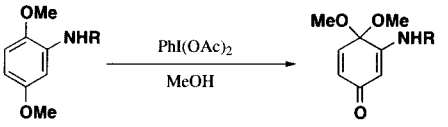


Scheme 6

2,3-Haloacetoxylation of 1,4-dimethoxynaphthalene also takes place when $PhI(OAc)_2$ and a trimethylsilyl halide are used (Eq. 63).[151] However, protected 2,5-dimethoxyanilines are transformed to the quinone monoacetals by using $PhI(OAc)_2$-MeOH (Eq. 64).[152]



(63)

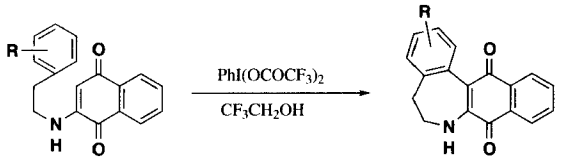


(64)

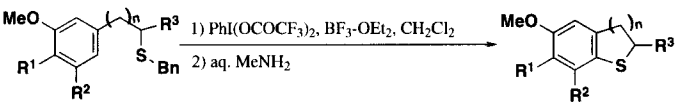
R = Ac, Alloc

Hypervalent iodine reagents oxidize phenols to give cyclohexadienones which incorporate the nucleophiles (Eqs. 38-40), while (dithiocyanatoiodo)benzene, $PhI(SCN)_2$, prepared *in situ* from $PhICl_2$ and $Pb(SCN)_2$ reacts with phenols and naphthols to afford *p*-thiocyanatophenols and 4-thiocyanatonaphthols, respectively (Eq. 41).[79]

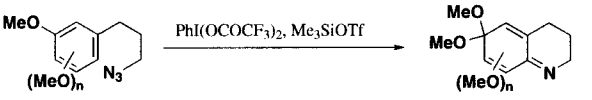
Intramolecular nucleophilic substitution induced by $PhI(OCOCF_3)_2$ gives 2,3-dihydro-1H-azepines,[123] sulfur-containing heterocycles,[153] and quinone imine ketals[154] as shown in Eqs. 65-67.



(65)



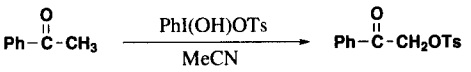
(66)



(67)

b) Ketones

Methyl ketones and aralkyl ketones react with hypervalent iodine reagents to give α-functionalized ketones. A typical example is the conversion of acetophenone with PhI(OH)OTs into α-tosyloxyacetophenone (Eq. 68).[41] This method has been applied to various substituted ketones[41] and β-dicarbonyl compounds.[155] Thus, in addition to tosyloxy group, mesyloxy[156,157] and (+)-10-camphorsulfonyloxy[158] groups are easily introduced at the α position of ketones (Eq. 69). Acetophenone derivatives and a β-diketone also undergo α-acetoxylation with $PhI(OAc)_2$ in acetic acid and acetic anhydride (Eq. 70).[35]

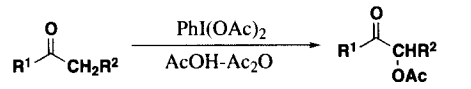


(68)

(69)

R^1 = Me, c-C_3H_5, Ph; R^2 = H, Me, Ph; R^1, R^2 = -$(CH_2)_2$-;

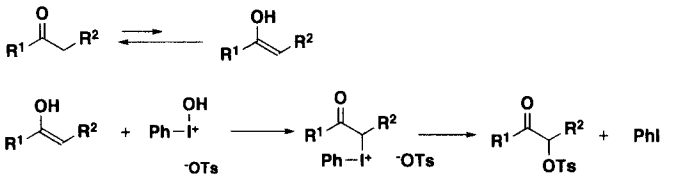
R^3 = *p*-Tol, Me,



(70)

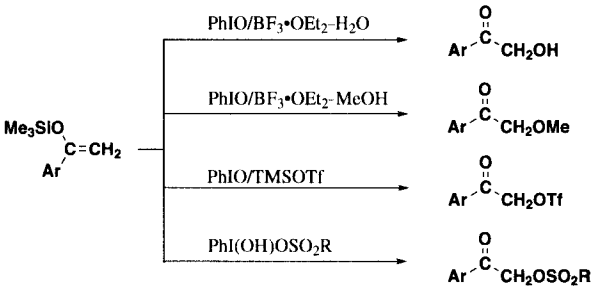
R^1 = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$, R^2 = H; R^1 = CF_3, R^2 = PhCO

α-Functionalization of ketones[41] is initiated by electrophilic addition of a hypervalent iodine reagent to the enol tautomer of the ketone giving the α-phenyliodonioketone (Scheme 7). An S_N 2 type of displacement of phenyliodonio group by tosylate ion yields the corresponding α-tosyloxyketone, for example.



Scheme 7

The use of silyl enol ethers as the enol tautomers of the ketones provides higher yields of α-functionalized ketones under milder reaction conditions than the direct reaction with ketones. A variety of applications are conducted by using silyl enol ethers (Eqs. 71-74).[159-164]



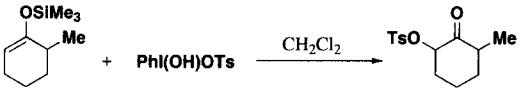
(71)

(72)

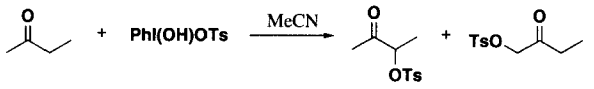
(73)

(74)

A further advantage of the use of silyl enol ethers is that the introduction of nucleophiles is achieved regioselectively. For example, the silyl enol ether of 2-methylcyclohexanone gives 2-methyl-6-tosyloxycyclohexanone in the reaction with PhI(OH)OTs (Eq. 75).[164] In contrast, the reaction of 2-butanone with PhI(OH)OTs gives a 1.57:1.00 mixture of 3-and 1-tosyloxy-2-butanones (Eq. 76).[41]

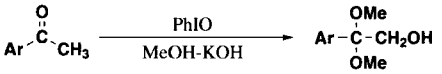


(75)



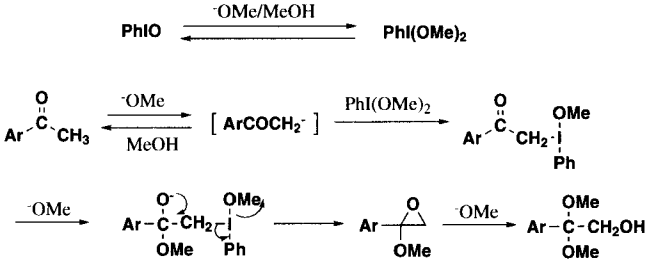
1.57 : 1.00 (76)

α-Functionalization of ketones under basic conditions shows different features from the reactions under the neutral or acidic conditions described above. Treatment of acetophenone derivatives, for example, with PhIO/MeOH-KOH leads to formation of α-hydroxyketone dimethyl acetals in high yields (Eq. 77).[29,165,166]



(77)

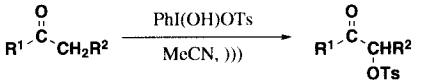
The formation of the α-hydroxyketone dimethyl acetals is explained by the following sequential pathways (Scheme 8);[5] formation of an enolate anion, a ligand-exchange of the *in situ* generated dimethoxyiodobenzene with the enolate anion, attack of methoxide anion, intramolecular cyclization to an epoxide, and finally the ring-opening by attack with methoxide anion.



Scheme 8

Applications of the hypervalent iodine oxidation under the basic conditions to various cyclic systems and heterocyclic compounds have been performed successfully.[5,118,119,167]

Recent advances in the α-functionalization of ketones include the use of an ultrasonic technique and its application to preparation of phosphate esters. The reaction of the ketones with PhI(OH)OTs in MeCN by using ultrasound for 10-30 min provides a rapid and convenient one-pot access to α-tosyloxyketones (Eq. 78).[168]

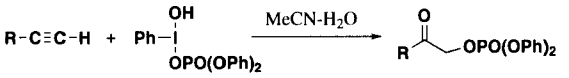


(78)

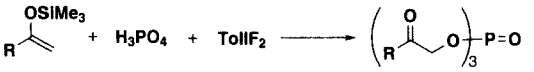
R^1, R^2 = Me, Et, *c*-C_3H_5, Ph, CH_3CO, $(CH_2)_3$, $(CH_2)_4$, $(CH_2)_5$

Terminal alkynes are also candidates for α-functionalization of ketones and undergo regiospecific conversion to α-functionalized ketones. Reaction of terminal alkynes with

PhI(OH)OPO(OPh)$_2$ in MeCN-H_2O gives α-phosphoryloxyketones (Eq. 79).[77] Interestingly, the synthesis of *tris*-ketol phosphates has been achieved by the reaction of silyl enol ethers with phosphoric acid in the presence of *p*-(difluoroiodo)toluene (Eq. 80).[169]



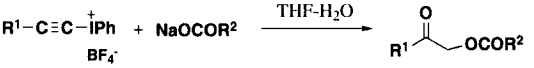
(79)



(80)

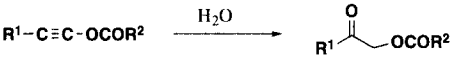
R = Me, Ph, ^{t}Bu, 2-pyridyl, 2-furyl

Reaction of alkynyl(phenyl)iodonium salts with sodium carboxylates in the presence of water affords α-acyloxykotones (Eq. 81).[170] Reaction of alkynyl esters with water under neutral



(81)

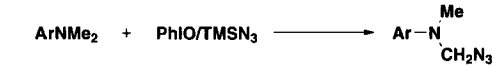
conditions also gives α-acyloxykotones (Eq. 82).[171-174] Accordingly, it is considered that β-ketoesters are formed by either pathways involving vinyliodonium salts[170] and alkynylesters[171,172] through alkynyliodonium salts.



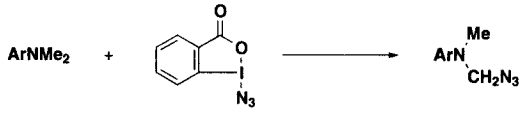
(82)

c) N-Containing Compounds

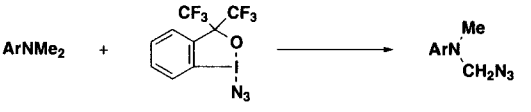
α-Functionalization of N-containing compounds is achieved by using hypervalent iodine reagents. Treatment of N,N-dimethylaniline with a combination of PhIO and $TMSN_3$ gives N-(azidomethy)-N-methylaniline in good yields (Eq. 83).[55] Similar α-azidonation of N,N-dimethylanilines takes place with cyclic azidoiodanes (Eqs. 84, 85).[62] This reaction is applied to α-azidonation of amides, carbamates and ureas (Eq. 86).[175] α-Azido derivatives of substituted piperidines and



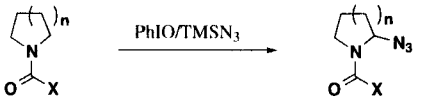
(83)



(84)



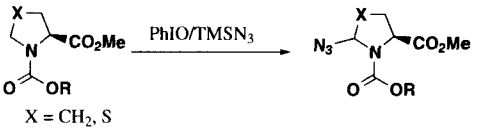
(85)



(86)

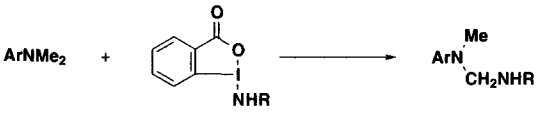
n = 1, 2; X = NPh_2, OPh, OR, Ar, Me

pyrrolidines are obtained and the pyrrolidines are more reactive. Similar α-azidonation by use of $PhIO/TMSN_3$ combination is conducted with a series of L-proline and thiaproline derivatives (Eq. 87).[176] These compounds are utilized as N-acyliminium ion precursor.

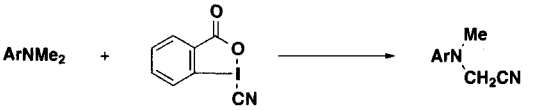


(87)

Amidation and cyanation of N,N-dimethylanilines also proceed with amido- and cyanobenziodoxoles (Eqs. 88,[66] 89[67]).



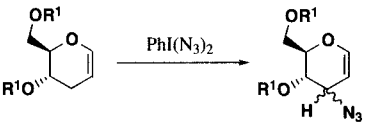
(88)



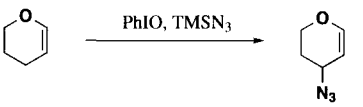
(89)

d) Other Compounds

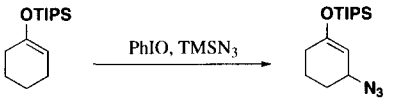
The allylic positions of glycals, enol ethers, and cyclohexene are azidonated (Eqs. 90-93).[177,140,139,162]



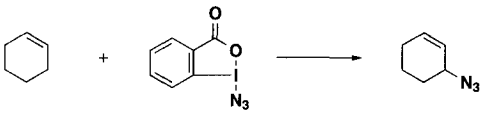
(90)



(91)

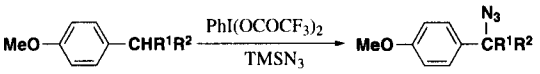


(92)



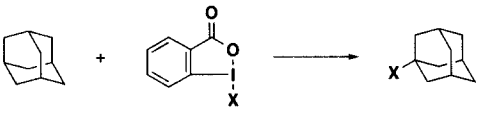
(93)

Azidonation of benzylic position also takes place (Eq. 94).[79] Interestingly, functionalizations of alkanes, cycloalkanes, and adamantanes occur in the presence of a radical initiator in the reactions with amido- and azidobenziodoxoles (Eq. 95).[62,66]



(94)

R^1, R^2 = H, Me, Et, CN, SMe, CO_2Me



(95)

X = NHR, N_3

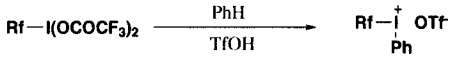
III. REACTIONS USING IODONIUM SALTS

Many types of iodonium salts are prepared from hypervalent iodine reagents and are used in organic synthesis. The advantage of the use of iodonium salts is their high reactivity. In most cases, the reaction conditions are mild and selective and efficient transformations are achieved. Solvolytic reaction of a cyclohexenyl(phenyl)iodonium salt indicates that vinyliodonium salts are solvolyzed much faster than the corresponding vinyl triflate.[178] The relative nucleofugality of phenyliodonio group (I^+Ph) is $8x10^5$ times higher than triflate (OTf). On the basis of the relative rate,[179] the rate enhancement by ca 10^{12} is obtained by the conversion of iodo group into phenyliodonio group. The high reactivity of the hypervalent iodine leaving group has been observed in the reaction of 1-iodonorbornane with bromine.[180] Because of this high reactivity, most of the iodonium salts available for organic synthesis have been previously restricted to diaryliodonium salts. Recently many functionalized iodonium salts have been prepared by using new types of hypervalent iodine reagents.

1. PREPARATION OF IODONIUM SALTS

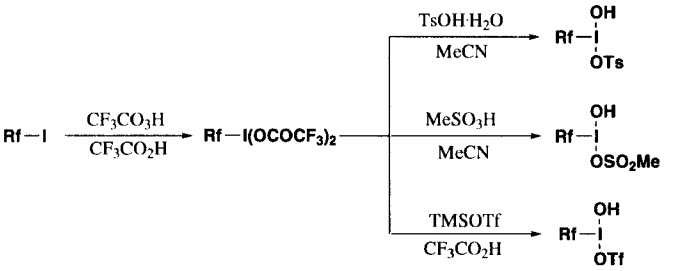
a) Polyfluoroalkyl(phenyl)iodonium Salts

Since polyfluoroalkyl(phenyl)iodonium salts have been first prepared by Yagupolskii *et al.* in 1971,[181] many have been synthesized by reaction of benzene with [bis(trifluoroacetoxy)iodo]polyfluoroalkanes (Eq. 96).[2,182]



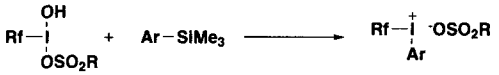
(96)

Recently [hydroxy(tosyloxy)iodo]perfluoroalkanes have been prepared by the reaction of [bis(trifluoroacetoxy)iodo]perfluoroalkanes with $TsOH•H_2O$ (Scheme 9).[71] The corresponding



Scheme 9

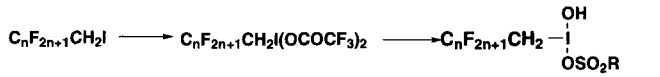
mesylates and triflates are also prepared by this method. The [(hydroxy)(trifyloxy)iodo]perfluoroalkanes react with trimethylsilylbenzenes to give aryl(perfluoroalkyl)iodonium triflates (Eq. 97).



(97)

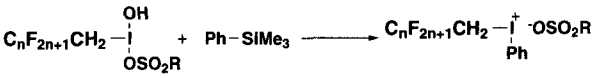
R = Me, *p*-MeC_6H_4, CF_3

The same method has been applied to CF_3CH_2I and $C_nF_{2n+1}CH_2I$. The corresponding 1-[(hydroxy)(sulfonyloxy)iodo]polyfluoroalkanes thus obtained are used for the synthesis of phenyl(polyfluoroalkyl)iodonium triflates (Eqs. 98 and 99).[72,183]



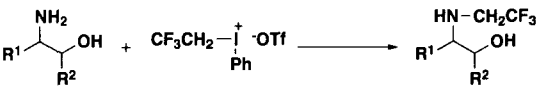
(98)

R = Me, *p*-MeC_6H_4, CF_3



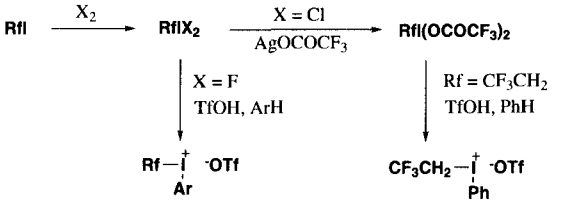
(99)

Aryl(polyfluoroalkyl)iodonium salts are very useful reagents for polyfluoroalkylation. Polyfluoro- and perfluoroalkyl groups may be introduced under mild conditions into various nucleophilic substrates. The results have been reviewed by Yagupolskii[182] and Umemoto.[2] A recent example is N-trifluoromethylation of aminoalcohols (Eq.100).[183]



(100)

Other routes to polyfluoroalkyliodonium salts involve the halogenation of polyfluoroalkyl iodides. Fluorination[184] and recently, chlorination[183] have been achieved (Scheme 10). Very recently, *bis*-trifluoroacetylation by xenon *bis*(trifluoroacetate) has been reported.[185]

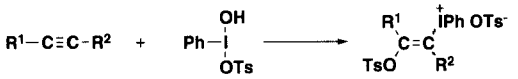


Scheme 10

b) Alkenyl(phenyl)iodonium Salts

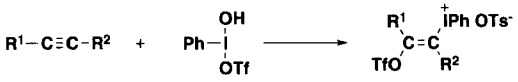
Compared with diaryliodonium salts, alkenyliodonium salts were not commonly known until recently because the methodology had not been available for their synthesis. The limited number of methods[3,6,8,11,12,16,17] for their preparation prior to the 1980's gave low yields.

More general routes to alkenyliodonium salts have been developed only recently . Addition of PhI(OH)OTs to alkynes provides β-tosyloxyalkenyliodonium tosylates (Eq. 101).[43] A highly stereoselective *anti* addition to alkynes has been achieved by using PhI(OH)OTf which is prepared *in*

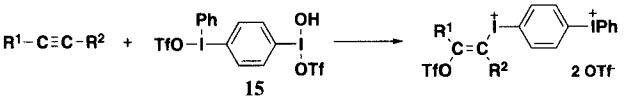


(101)

situ from PhIO and TfOH (Eq. 101).[141,183] A similar type of *anti* addition has been observed with (*p*-phenylene)bisiodine(III) reagent (**15**) prepared from PhIO and TfOH (1:2) or PhIO and Tf_2O (1:1) (Eq. 102).[81,187,188]



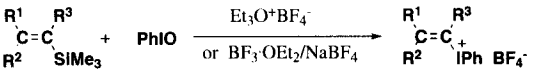
(102)



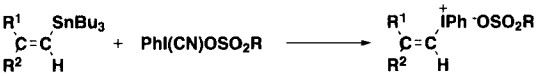
15

(103)

Electrophilic displacement of alkenylsilanes or alkenylstannanes by hypervalent iodine reagents affords a more general approach to alkenyliodonium salts. Reaction of alkenylsilanes with PhIO/Et_3O^+ BF_4^- or PhIO/BF_3•Et_2O followed by treatment with $NaBF_4$ yields alkenyliodonium tetrafluoroborates (Eq. 104).[51,189,190] Reaction of alkynyltributylstannanes with cyano(sulfonyloxy)iodobenzenes gives alkynyl(phenyl)iodonium tosylates and triflates (Eq. 105).[74,191]



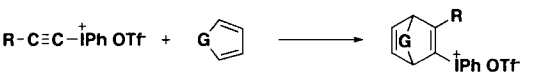
(104)



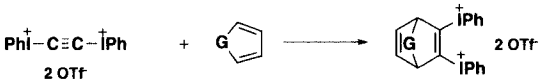
R = CF_3, *p*-MeC_6H_4

(105)

Cyclic alkenyliodonium salts are prepared by the cycloaddition of alkynyliodonium salts to dienes. Alkynyliodonium salts bearing electron-withdrawing groups such as CN, Ts, and RCO undergo facile cycloadditions under mild conditions to give cyclic alkenyliodonium salts (Eq. 106).[192] *bis*(Phenyliodonium)ethyne ditriflate also undergoes the Diels-Alder reaction to give the corresponding bisiodonium ditriflates (Eq. 107).[193]

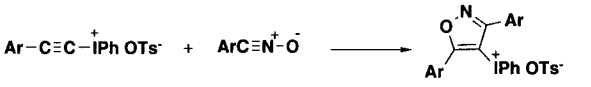


(106)

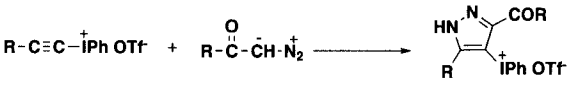


(107)

1,3-Dipolar cycloaddition also occurs in the reaction of alkynyliodonium salts by using nitrile oxides (Eq. 108),[194] nitrones,[194] α-diazocarbonyl compounds (Eq. 109),[195] and azides.[195]

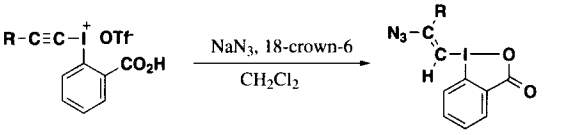


(108)



(109)

Although alkenyliodonium salts are not generally prepared by the reaction of alkynyliodonium salts with nucleophiles, vinylbenziodoxolones are obtained by the reaction of alkynyl(*o*-carboxyphenyl)iodonium triflates with azide ion (Eq. 110).[196]



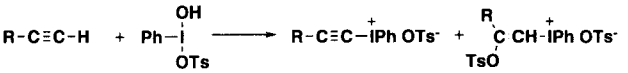
(110)

c) Alkynyl(phenyl)iodonium Salts

In 1965, phenylethynyl(phenyl)iodonium chloride was first prepared according to Eq. 111 but the yield was low.[197] Since 1980, synthetic procedures for alkynyliodonium salts have been reported. General and reliable methods involve terminal alkynes bearing aryl or bulky alkyl groups, alkynylsilanes, and alkynylstannanes.

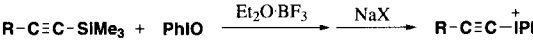
(111)

Treatment of terminal alkynes with hydroxy(tosyloxy)iodobenzene provides alkynyl-(phenyl)iodonium tosylates together with β-tosyloxyalkenyliodonium tosylates (Eq. 112).[43,44,198,199] Good yields of alkynyliodonium salts are obtained in cases where the substituent are secondary or tertiary alkyl and aryl groups.

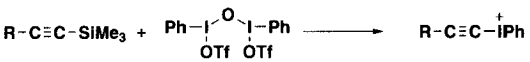


(112)

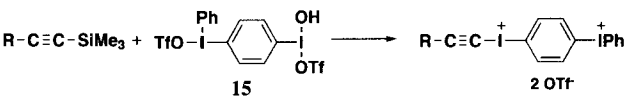
Reaction of alkynyltrimethylsilanes with $PhIO/Et_2O{\bullet}BF_3$ followed by $NaBF_4$[52] or NaOTs[200] gives alkynyliodonium tetrafluoroborates or tosylates (Eq. 113). Similar reactions with Zefirov's reagent, PhI(OTf)OI(OTf)Ph,[48] or a (*p*-phenylene)bisiodine reagent **15**[81,188] afford the corresponding alkynyliodonium or -(*p*-phenylene)bisiodonium triflates, respectively (Eqs. 114 and 115).



(113)

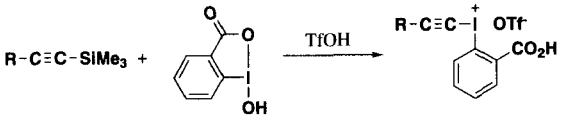


(114)



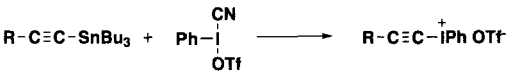
(115)

o-Iodosylbenzoic acid activated with TfOH also reacts with alkynyltrimethylsilanes to give the corresponding alkynyliodonium triflates (Eq. 116).[201]

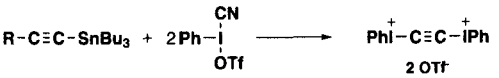


(116)

A more widely applicable method for the preparation of alkynyliodonium salts involves the use of alkynylstannanes and [(cyano)(trifluoromethylsulfonyloxy)iodo]benzene, PhI(CN)OTf. Treatment of alkynylstannanes with PhI(CN)OTf at low temperature gives the corresponding alkynyliodonium triflates. This method can be applied to electron-deficient alkynyl groups (Eq. 117)[192,202] and to a double transfer of phenyliodonio group to *bis*(tributylstannyl)acetylene (Eq. 118).[193,203]

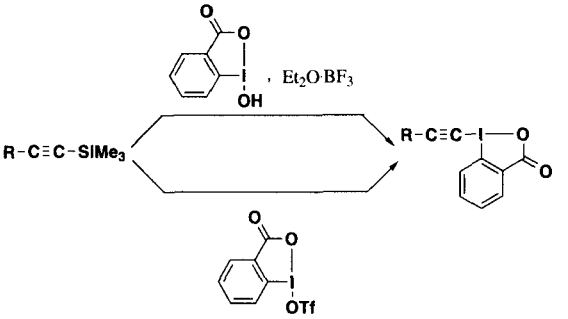


(117)

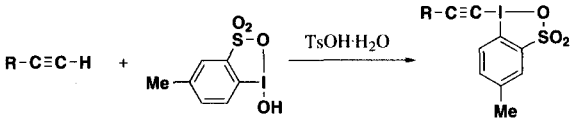


(118)

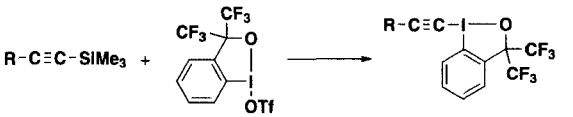
Recently alkynyliodanes bearing cyclic iodine structures have been prepared (Eqs. 119,[56,65] 120,[68] and 121[65]).



(119)



(120)



(121)

d) Diaryliodonium Salts

Since Hartmann and Meyer first reported the formation of (*p*-iodophenyl)(phenyl)iodonium bisulfate in 1894,[204] many diaryliodonium salts have been prepared by the use of iodylarenes ($ArIO_2$), iodosylarenes (ArIO), diacyloxyiodoarenes [$ArI(OCOR)_2$], dichloroiodoarenes ($ArICl_2$), and related organoiodine(III) compounds (Eqs. 121 and 122).[24,205]

$$\mathrm{ArIO} + \mathrm{Ar'H} \xrightarrow{\mathrm{HX}} \mathrm{ArIAr'\ X^-} \qquad (122)$$

$$\mathrm{ArI(OCOR)_2} + \mathrm{Ar'H} \xrightarrow{\mathrm{HX}} \mathrm{ArIAr'\ X^-} \qquad (123)$$

Recent methods have focused on the increasing reactivity of the iodine(III) reagents and the introduction of functional groups. Earlier preparations of diaryliodonium salts have been reviewed.[3,12,206] Koser's salt, PhI(OH)OTs, reacts with electron-rich anisole but not with toluene or benzene. Trimethylsilylarenes react with PhI(OH)OTs to give the corresponding diaryliodonium tosylates (Eq. 124).[207]

$$\mathrm{ArSiMe_3} + \mathrm{Ph{-}I(OH)OTs} \longrightarrow \mathrm{ArIPh\ OTs^-} \qquad (124)$$

More reactive hypervalent iodine reagents have been prepared by treatment of PhIO[141,186,208] or $PhI(OAc)_2$[209] with trifluoromethanesulfonic acid (Eqs. 125 and 126). The use of these reagents with

$$\mathrm{PhIO} + \mathrm{TfOH} \longrightarrow \mathrm{Ph{-}I(OH)OTf} \xrightarrow{\mathrm{ArH}} \mathrm{ArIPh\ OTf^-} \qquad (125)$$

$$\mathrm{PhI(OAc)_2} + 2\ \mathrm{TfOH} \longrightarrow \mathrm{[PhI(OAc)_2\text{-}2TfOH]} \xrightarrow{\mathrm{ArH}} \mathrm{ArIPh\ OTf^-} \qquad (126)$$

various substituted aromatic substrates affords the diaryliodonium triflates except for strongly deactivated substrates such as benzonitrile and nitrobenzene. The reactions with the hypervalent iodine reagents generally exhibit a high *para* selectivity.

Activation of PhIO by SO_3[210] and oxidation of aryl iodides by CrO_3[211,212] are also used for arylation (Eqs. 127, 128).

$$\mathrm{PhIO} \xrightarrow{SO_3,\ CH_2Cl_2} \xrightarrow{\mathrm{ArH}} \mathrm{PhIAr\ HSO_4^-} \qquad (127)$$

$$\mathrm{ArI} \xrightarrow{CrO_3,\ AcOH,\ Ac_2O,\ H_2O} \xrightarrow{\mathrm{Ar'H}} \xrightarrow{\mathrm{aq.\ KBr}} \mathrm{ArIAr'\ Br^-} \qquad (128)$$

Reaction of tetraarylborate ions with (diacetoxyiodo)arenes provides diaryliodonium tetraarylborates (Eq. 129).[213]

$$\mathrm{ArI(OAc)_2} + \mathrm{M^+\ B^-Ar'_4} \xrightarrow{\mathrm{AcOH}} \mathrm{ArIAr'\ B^-Ar'_4} \qquad (129)$$

Aryl(cyano)iodonium triflates react with tributyltin derivatives of aromatic and heteroaromatic compounds to form the corresponding diaryliodonium triflates (Eq. 130).[73] (Dicyano)iodonium triflate prepared *in situ* by the reaction of O=I-OTf with Me_3SiCN, reacts with tributyltin derivatives of aromatic compounds to form the corresponding diaryliodonium triflates (Eq. 131).[76]

$$\overset{+}{\text{ArI}}\text{CN OTf}^- + \text{Ar'SnBu}_3 \longrightarrow \overset{+}{\text{ArI}}\text{Ar' OTf}^- \quad (130)$$

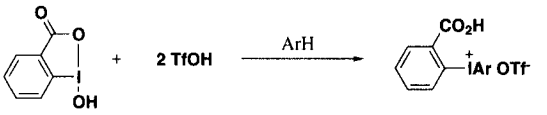
$$\text{O=I-OTf} + 2\,\text{Me}_3\text{SiCN} \longrightarrow (\text{NC})_2\text{I}^+\ \text{OTf}^- \xrightarrow{2\ \text{ArSnBu}_3} \text{Ar}_2\text{I}^+\ \text{OTf}^- \quad (131)$$

Iodosyl fluorosulfate ($O=IOSO_2F$) reacts with aromatic compounds to give diaryliodonium hydrosulfates (Eq. 132).[78] This reagent is highly reactive toward deactivated substrates such as halobenzenes and even nitrobenzene. *bis*(Pentafluorophenyl)iodonium salts are prepared by the reaction of pentafluorobenzene, iodine *tris*(trifluoroacetate), and trifluoromethanesulfonic acid or 2,4,6-trinitrobenzenesulfonic acid in trifluoroacetic acid (Eq. 133).[214]

$$\text{ArH} + \text{O=IOSO}_2\text{F} \longrightarrow \text{Ar}_2\text{I}^+\ \text{HOSO}_3^- \quad (132)$$

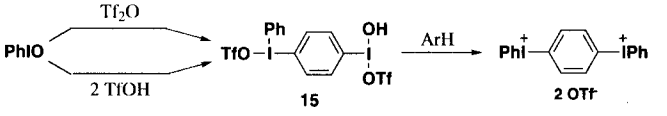
$$2\,\text{C}_6\text{F}_5\text{H} + \text{I(OCOCF}_3)_3 + \text{RSO}_3\text{H} \longrightarrow (\text{C}_6\text{F}_5)_2\text{I}^+\ {}^-\text{OSO}_2\text{R} \quad (133)$$

o-Iodosylbenzoic acid activated by trifluoromethanesulfonic acid reacts with aromatic compounds to give *o*-carboxydiaryliodonium triflates (Eq. 134).[201]



(134)

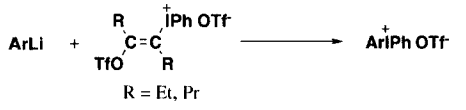
1-[(Hydroxy)(trifyloxy)iodo]-4-[(phenyl)(trifyloxy)iodo]benzene (**15**) may be prepared by the reaction of PhIO with Tf_2O or TfOH (2 equiv) and reacts with aromatic compounds to give (*p*-phenylene)bis(aryliodonium) ditriflates (Eq. 135).[80,81,187]



(135)

Ligand exchange reactions using vinyliodonium salts proceeds at the iodine atom to give diaryliodonium salts regioselectively (Eqs. 136,[215] 137[216]).

(136)



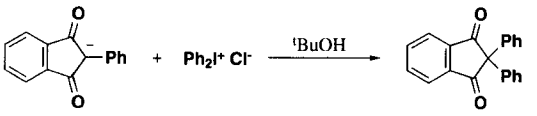
(137)

2. SYNTHETIC USE OF IODONIUM SALTS

a) Arylation

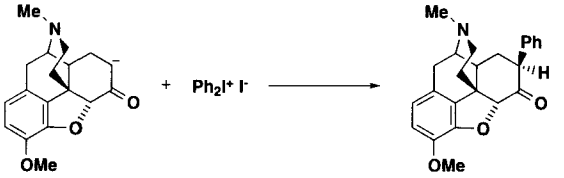
One of the synthetic applications using diaryliodonium salts is arylation of nucleophilic substrates. A wide variety of substrates can undergo arylation. Arylations at carbon, oxygen, nitrogen, sulfur, and other elements have been reviewed.[4,9,12,109,145]

In the arylation at carbon, the reactions are limited to the substrates bearing active methylene groups. For example, the reaction of sodium 2-phenyl-1,3-indandione with diphenyliodonium chloride affords 2,2-diphenyl-1,3-indanedione in 86% yield (Eq. 138).[217]



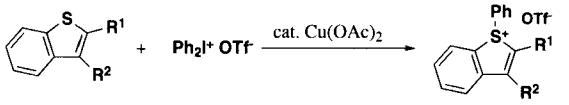
(138)

Recent application of the arylation is the conversion of hydrocodone to 7-phenylhydrocodone (Eq. 139).[218] The method using trimethylsilyl enol ether of hydrocodone followed by diphenyliodonium fluoride, however, results in a low yield (11%) of monophenylated product.



(139)

A direct phenylation of benzothiophenes is successfully conducted by using diphenyliodonium triflate and a catalytic amount of copper(II) acetate (Eq. 140).[219] This method provides a wide variety of 1-phenylbenzo[b]thiophenium salts.

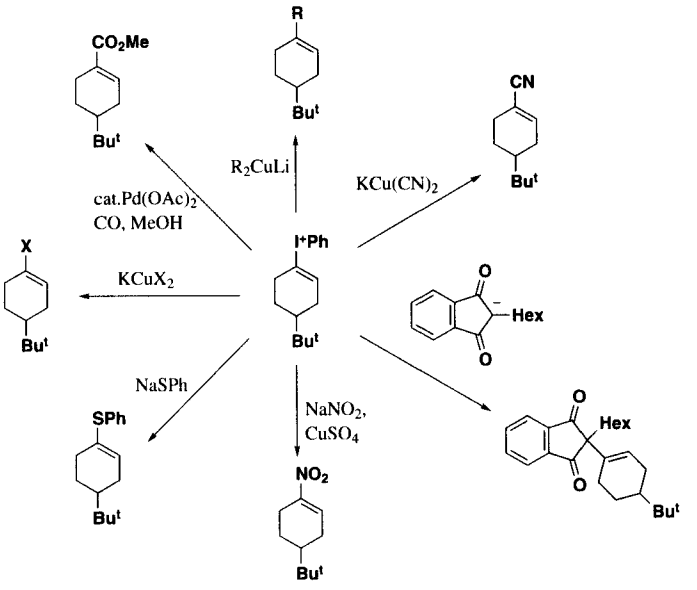


(140)

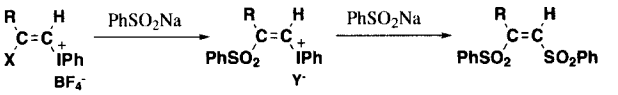
b) Alkenylation

Alkenyl(phenyl)iodonium salts react with soft nucleophilic reagents to give alkenylated products.[6,8,11,12,16,17] A typical scheme is given in Scheme 11.[51,189] The phenyliodonio group is effectively replaced by nucleophiles.

Recent studies include the reactions with benzenesulfinate ion and with alkynylcopper reagents. Nucleophilic substitution of (Z)-β-haloalkenyliodonium tetrafluoroborates with sodium benzenesulfinate gives (Z)-1,2-bis(phenylsulfonyl)alkenes (Eq. 141).[220] The first step proceeds by a Michael-type addition of benzenesulfinate ion to alkenyliodonium salts. The second vinylic substitution takes place with retention of the configuration.[221]

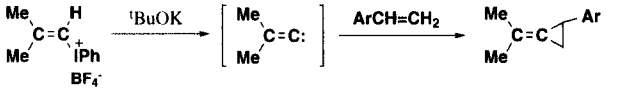


Scheme 11

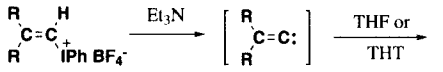


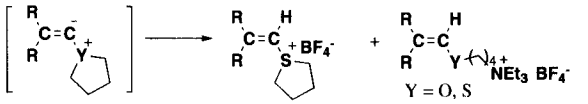
(141)

Additions of an alkylidenecarbenes to styrenes and to THF or tetrahydrothiophene give methylenecyclopropanes (Eq. 142)[222] and the products derived from onium ylides or sulfonium ylides (Eq. 143),[223] respectively. Double alkynylation of alkenylbisiodonium salts is achieved by using alkynylcopper reagents (Eq. 144).[180]

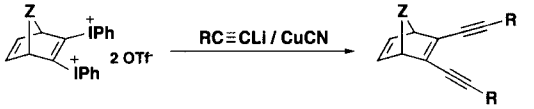


(142)





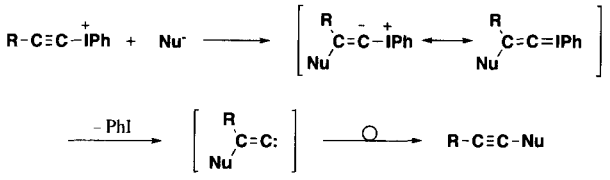
(143)



(144)

c) Alkynylation

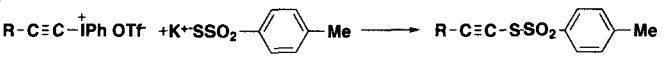
The reaction of alkynyl(phenyl)iodonium salts with soft nucleophiles proceeds with initial Michael addition followed by elimination of iodobenzene to form alkylidenecarbenes (Scheme 12). When the substituent or the nucleophile is able to migrate, a 1,2-shift leading to alkynes occurs in the



Scheme 12

alkylidenecarbenes. As the result, alkynylation is achieved by a sequence of the above processes. Many alkynylations have been reviewed.[6,8,11,12,16,17]

Recently sulfur nucleophiles have been used for alkynylation. Thiocyanate,[201,225-227] *p*-toluenethiosulfonate,[228] and arylsulfinate[229] react with alkynyliodonium salts to give the corresponding alkynyl thiocyanates, *p*-toluenethiosulfonates, and arylsulfones, respectively (Eqs. 145-149). Similarly, reaction of alkynyliodonium tosylates with potassium *O,O*-dialkyl phosphorodithioates gave alkynyl phosphorodithioates in good yields (Eq. 150).[230]



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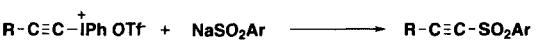

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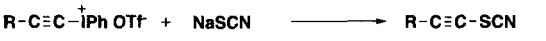

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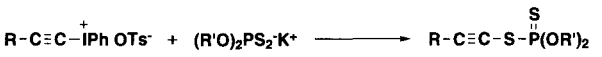
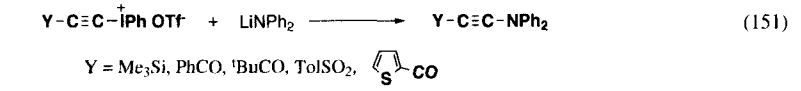


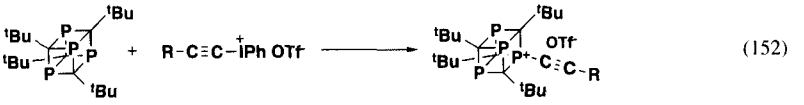
(150)

Alkynylations using nitrogen nucleophiles are rare. The sole example involves the reaction of electron-deficient alkynyliodonium triflates with lithium diphenylamide (Eq. 151).[231] Push-pull ynamines are prepared by this method.



(151)

Alkynyl onium salts are easily prepared by the reaction of alkynyliodonium salts with tetraphosphacubane (Eq. 152),[232] triphenylphosphine (Eqs. 153, 154),[233-235] and triphenylarsine (Eq. 155).[236] Alkynyliodonium triflates with triphenylphosphine reacts in the dark or under photochemical conditions to give alkynyltriphenylphosphonium triflates.[233-235] Similarly, this reaction is applied to bisphosphonium salts[233] and monoalkynylation of tetra-*tert*-butyltetraphophacubane.[232] The reaction of alkynyliodonium salts with triphenylarsine takes place easily to provide a useful tool for synthesis of alkynyltriphenylarsonium salts.[236]



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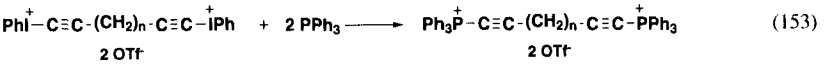

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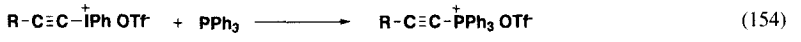

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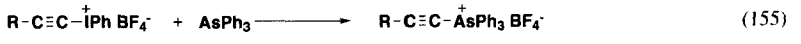
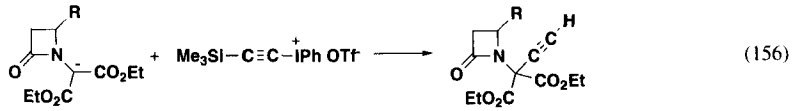


(155)

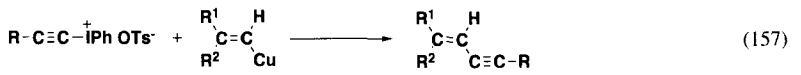
Alkynylation of carbon nucleophiles is limited to alkynyliodonium salts bearing phenyl, trimethylsilyl, and unsubstituted ethynyl groups since these groups have a high migratory aptitude.[197,227,237,238] A recent advance is the alkynylation of 2-oxazetidin-1-yl malonates using trimethylsilylethynyliodonium triflate (Eq. 156).[239]



(156)

R = $PhSeCH_2$, ^tBuS

Organocopper reagents are suitable reagents for the wide-spread alkynylation of carbon nucleophiles. Alkyl, alkenyl, alkynyl, and arylcopper reagents react with alkynyliodonium salts to give alkynes, enynes, diynes, and arylalkynes, respectively (Eqs. 157-159).[240-242] Recently this method has been applied to synthesis of liquid-crystalline diaryldiacetylenes and chiral diacetylenic liquid crystals (Eq. 160).[243-245]



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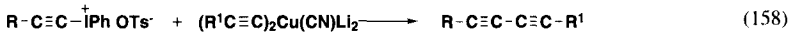

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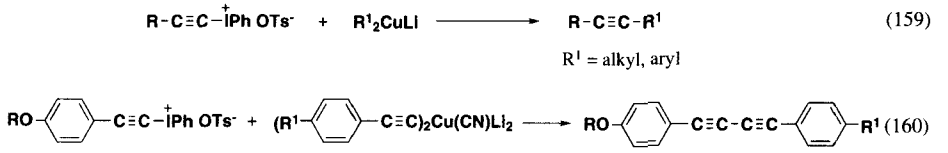


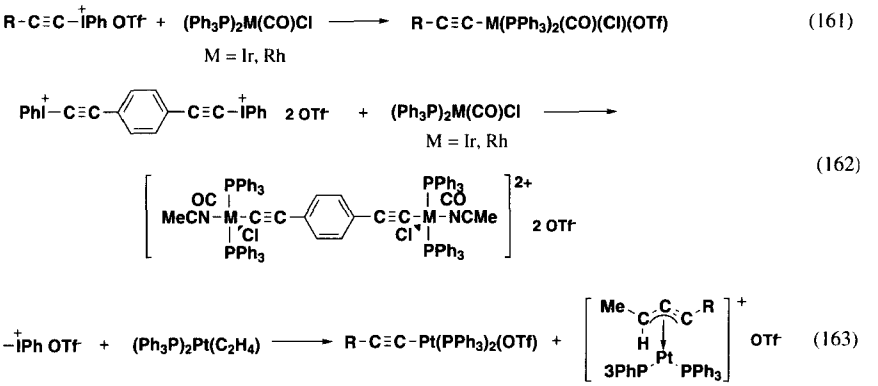
(159)

(160)

R = *n*-C_8H_{17}, *n*-$C_{10}H_{21}$, *n*-$C_{12}H_{25}$, *n*-$C_{14}H_{29}$; $C_2H_5C^*H(CH_3)CH_2O$, $C_2H_5C^*H(CH_3)CH_2OCO$

R^1 = MeO, Me, NO_2, CN, *n*-C_4H_9, *n*-C_6H_{13}, *n*-C_8H_{17}

Metal complexes, such as Vaska's complex and its rhodium analog, react with alkynyliodonium triflates to yield σ-alkynyl metal complexes, respectively, in high yields (Eq. 161).[246] This reaction is applied to preparation of novel rigid-rod, cationic, bimetallic σ-complexes (Eq. 162).[247] On the other hand, the reaction of $(Ph_3P)_2PtC_2H_4$ results in formation of either η^3-propargyl/allenyl- or σ-acetylide-Pt complexes (Eq. 163).[248]



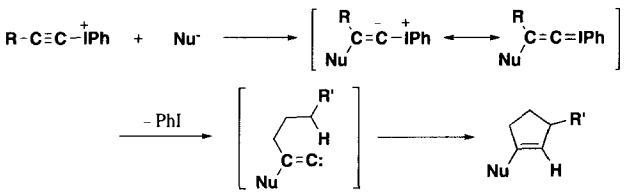
(161)

(162)

(163)

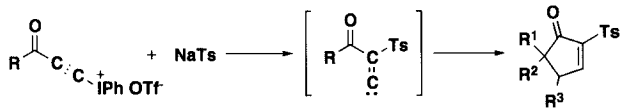
d) Cyclopentene Synthesis

Reaction of alkynyl(phenyl)iodonium salts with soft nucleophiles proceeds by Michael addition followed by elimination of iodobenzene leading to generation of alkylidenecarbenes. When the substituent of the alkylidenecarbene have a γ-hydrogen and are not subject to rearrangement, intramolecular 1,5-C-H insertion takes place to give cyclopentene derivatives (Scheme 13). Enolate anions of 1,3-diketones,[227,239] azide ion,[249] and benzenesulfinic acid[250] have been used as the nucleophiles.



Scheme 13

Cyclopentenone derivatives are prepared by the reaction of β-ketoethynyl(phenyl)iodonium triflates with sodium *p*-toluenesulfinate (Eq. 164).[251] Similarly, γ-lactams are prepared by reaction of β-amidoethynyl(phenyl)iodonium triflates with sodium *p*-toluenesulfinate (Eq. 165).[251]



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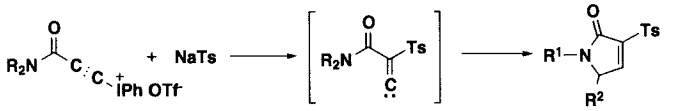
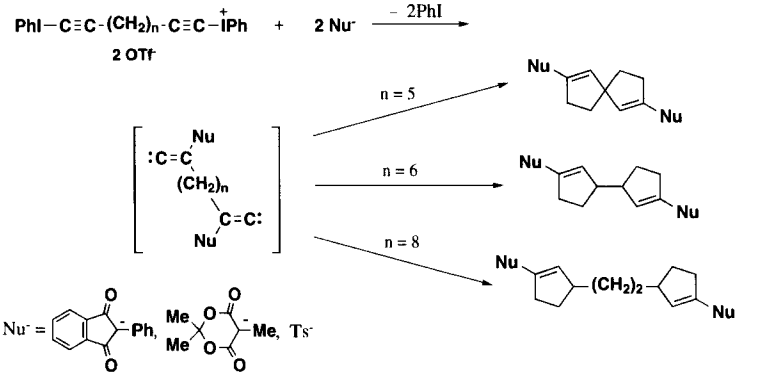


(165)

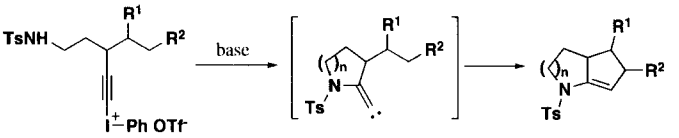
Double cyclopentenations are conducted by use of *bis*(phenyliodonio)diyne ditriflates (Scheme 14).[252] Reaction of *bis*(phenyliodonio)diyne ditriflates with potassium 2-phenyl-1,3-indandionate, potassium 2,2,5-trimethyl-1,3-dioxa-4,6-dionate, and sodium *p*-toluenesulfinate undergoes



Scheme 14

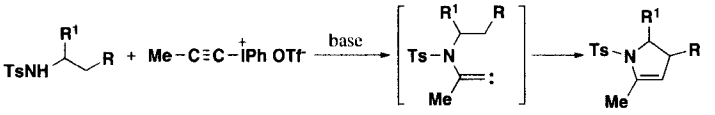
Michael addition followed by generation of two alkylidenecarbenes in the same molecule. Dual intramolecular 1,5-C-H insertions of the carbenes afford the *bis*-cyclopentene derivatives.

Tosylamine-bearing alkynyliodonium triflates are applied to synthesis of cyclopentylamine-containing alkaloid skeletons (Eq. 166).[253] This reaction is induced by base and proceeds by intramolecular Michael addition of the *p*-toluenesulfonamide anion and the successive intramolecular C-H



(166)

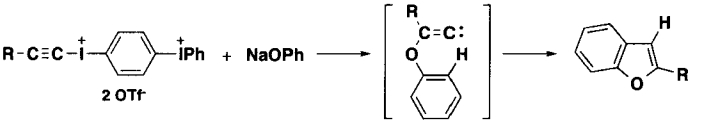
insertion of the alkylidenecarbenes. Similarly, intermolecular reaction of phenyl(propynyl)iodonium triflate with tosylamide anions provides dihydropyrrole derivatives (Eq. 167).[254,255]



(167)

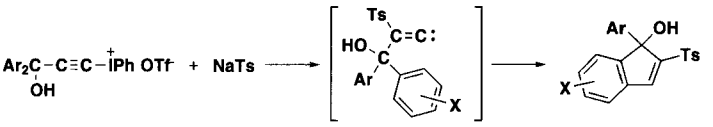
Cyclopentene synthesis is based on intramolecular aliphatic 1,5-C-H insertion of alkylidenecarbenes. Although many aromatic C-H insertion reactions of alkylidenecarbenes have been

observed in gas phase at a high temperature,[256] there are no examples of the aromatic C-H insertion reaction in solution under mild conditions. Very recently, aromatic C-H insertion of alkylidenecarbenes has been observed by using the reaction of alkynyliodonium salts. Reaction of alkynyl(*p*-phenylene)*bis*-iodonium ditriflates with phenoxide ion leads to formation of benzofurans *via* aromatic C-H insertion of alkylidenecarbenes (Eq. 168).[257] Intramolecular aromatic C-H insertion occurs selectively even in the presence of aliphatic C-H bond.



(168)

Reaction of sodium *p*-toluenesulfinate with alkynyliodonium triflates bearing aryl group at the γ-position affords indene derivatives by intramolecular aromatic C-H insertion (Eq. 169).[258] Similarly, reaction of tosylamide anion with phenyl(propynyl)iodonium triflate gives indole derivatives, probably arising form aromatic C-H insertion of alkylidenecarbenes (Eq. 170).[254,255]



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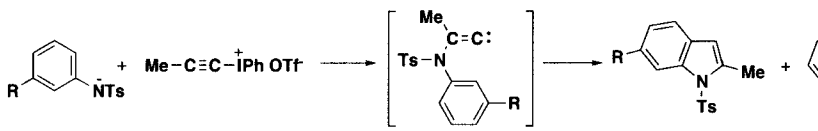
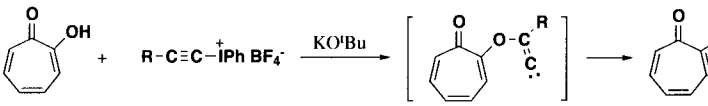


(170)

Reaction of alkynyliodonium salts with tropolones in the presence of potassium butoxide gives 2-substituted furotropones (Eq. 171).[259] On the other hand, the reaction with thioamides in the presence of K_2CO_3 yields thiazoles (Eq. 172).[260]



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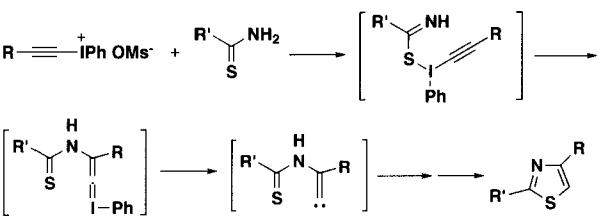
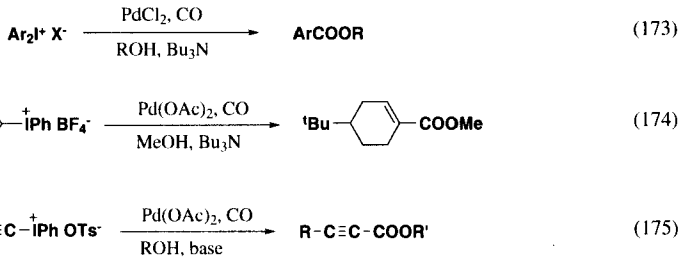


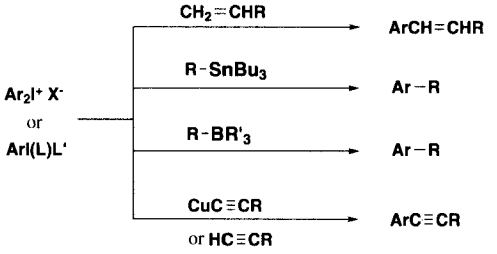
(172)

e) Palladium-Catalyzed Reactions

Hypervalent iodine compounds undergo palladium-catalyzed reactions under milder conditions than the corresponding iodides. Diaryl,[261-263] alkenyl,[189] and alkynyliodonium salts[264] react with carbon monoxide in alcohols in the presence of palladium catalyst to yield aryl- (Eq. 173), alkenyl- (Eq. 174), and alkynylcarboxylic esters (Eq. 175), respectively.

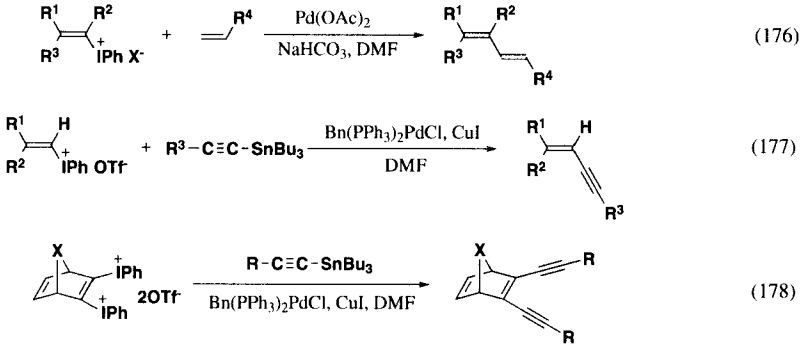


The palladium-catalyzed coupling reaction using hypervalent iodine compounds proceeds efficiently under mild conditions. Diaryliodonium salts and aryliodanes may be used for the arylation of olefins,[256-269] organotin compounds,[270,271] organoboron compounds,[272,273] copper acetylide,[274] and terminal alkynes[275,276] (Scheme 15). Similarly, copper-catalyzed reactions[277] and reductive coupling of diaryliodonium salts to biaryls[278,279] also take place.



Scheme 15

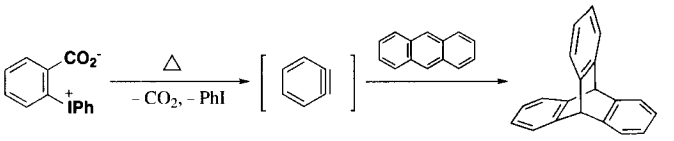
Palladium-catalyzed coupling reactions of alkenyliodonium salts afford dienes (Eq. 176),[280-282] enynes (Eq. 177),[282] and endiynes. (Eq. 178).[283]



IV. MISCELLANEOUS REACTIONS

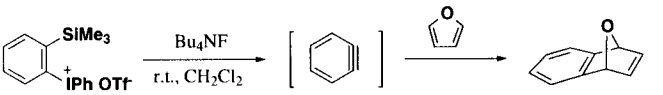
1. BENZYNE FORMATION

The well-known benzyne precursor of diaryliodonium salts is diphenyliodonium-2-carboxylate. However, this iodonium salt is quite stable and high temperatures (> 220°) are required for the generation of benzyne (Eq. 179).[284]



(179)

On the other hand, (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate is an excellent source of benzyne under mild and neutral conditions and efficiently provides the Diels-Alder adducts (Eq. 180).[83] Similarly, methyl-substituted iodonium salts afford methyl-substituted benzynes regioselectively (Eq. 181). The cycloaddition reaction of thiobenzophenones with benzyne has been achieved by using this benzyne precursor (Eq. 182).[84] Very recently, this method was applied to generate 3,4-dehydrothiophene (Eq. 183).[285]



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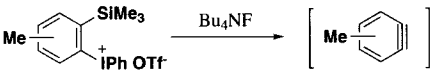

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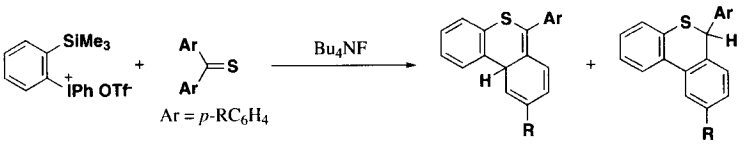

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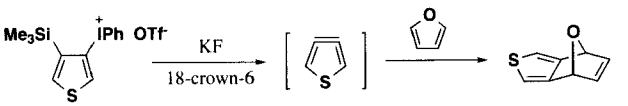
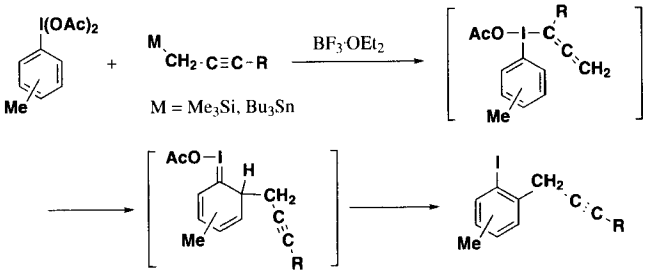


(183)

2. IODONIO-CLAISEN REARRANGEMENT

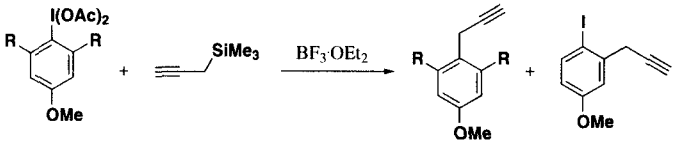
Reaction of propargylsilanes with aryliodanes in the presence of BF_3-OEt_2 undergoes a reductive iodonio-Claisen rearrangement to yield *o*-propargylic iodoarenes in good yields (Scheme 16).[286] The reductive *ortho* propargylation involves the intermediate formation of allenyl(aryl)iodanes



Scheme 16

that is subject to a [3,3]-sigmatropic rearrangement. This rearrangement also occurs with propargylgermanes and stannanes.

The *para*-methoxy group plays an important role in the iodonio-Claisen rearrangement of the intermediate allenyl(aryl)iodanes and undergoes *ipso* iodonio-Claisen rearrangement (Eq. 184 and Scheme 17).[287,288] Similar reactions involving allenyliodanes are observed in the reaction of Zefirov's



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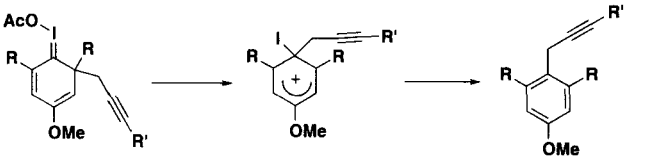
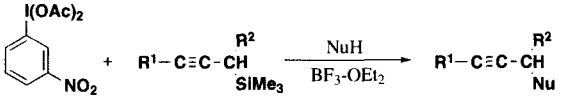


Scheme 17

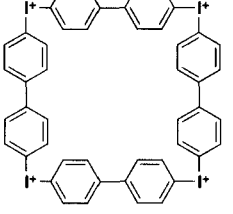
reagent with propargylsilanes and stannanes.[284] However, the reaction of propynylsilanes with diacetoxy(*m*-nitrophenyl)iodane in nucleophilic solvents gives the substitution products (Eq. 185).[290]



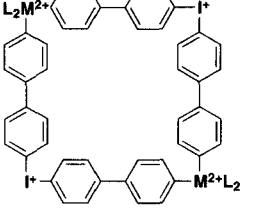
(185)

3. *MACROCYCLIC MOLECULAR SQUARES*

Recent application in this field has been devoted to the synthesis of macrocyclic iodonium salts. Diaryliodonium salts are approximately T-shaped and their geometry around iodine is a trigonal bipyramid including the non-bonding electron pairs.[3,12,16,19,20] The aryl rings lie in the apical and equatorial positions with ca 90° angle and can form the corner of the molecular squares. Two types of the molecular squares, macrocyclic tetraaryltetraiodonium cationic molecular square **16** and a hybrid, iodonium-transition metal macrocyclic squares **17**, have been prepared.[291-295]



16



17

V. CONCLUSION

Since the first hypervalent iodine compound, $PhICl_2$, was prepared by Willgerodt in 1886,[296] many hypervalent iodine compounds have been synthesized and applied to organic synthesis.

However, those hypervalent iodine compounds have not been widely utilized for organic synthesis except for oxidation. Recent development on hypervalent iodine chemistry provides reliable synthetic methods of various types of hypervalent iodine compounds and suggests possible applications to sophisticated organic syntheses. We hope that this review will induce investigators to explore the use of hypervalent iodine compounds in mechanistic and synthetic organic chemistry.

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