Iodonium ylides in organic synthesis

Mekhman S. Yusubov,*[,a] Akira Yoshimura,[b] and Viktor V. Zhdankin*[,a,b]

[a]Tomsk Polytechnic University, 634050 Tomsk, Russia
*[b]Department of Chemistry and Biochemistry, University of Minnesota Duluth,
Duluth, Minnesota, 55812, USA*
E-mail: vzhdanki@d.umn.edu; yusubov@mail.ru

Abstract
This review summarizes the chemistry of iodonium ylides with emphasis on their synthetic applications. The preparation, structure and chemistry of iodonium ylides of different structural types are overviewed. Iodonium ylides have found synthetic application as efficient carbene precursors, especially useful as reagents for cyclopropanation of alkenes and preparation of heterocyclic compounds. Recently iodonium ylides have been utilized as efficient reagents in the thiotrifluoromethylation and nucleophilic fluorination reactions.

Keywords: Hypervalent iodine, iodonium ylides, carbenes, carbenoids, thiotrifluoromethylation

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1. Introduction

Since the beginning of the 21st century, the organic chemistry of hypervalent iodine compounds has experienced an explosive development.[1-10] Hypervalent iodine reagents are now widely used in organic synthesis as versatile and sustainable reagents whose chemical properties are similar to the heavy metals derivatives, like mercury(II), thallium(III), lead(IV), osmium(VIII) and chromium(VI), but without the toxicity and environmental problems associated with these metals.

Previously we have published three reviews in Arkivoc summarizing synthetic applications of hypervalent iodine reagents[11,12] and aryliodonium salts.[13] Aryliodonium ylides, $ArI^+-^-CX_2$, where X is an electron-withdrawing substituent (e.g., carbonyl or sulfonyl group), represent an important class of iodonium compounds with numerous applications in organic synthesis. The chemistry of aryliodonium ylides has been discussed in several older reviews, which mainly summarized the use of ylides as precursors for generation of singlet carbenes or carbenoid species.[14-18] In the present review, the synthesis and structural studies of iodonium ylides are discussed, and recent developments in their synthetic applications are summarized. The literature coverage is through Spring 2016.

2. Preparation and Properties of Iodonium Ylides

The first stable iodonium ylide was prepared from (difluoroiodo)benzene and dimedone by Neiland and co-workers in 1957.[19] Since then, numerous stable aryliodonium ylides have been prepared and utilized as reagents for organic synthesis.

The vast majority of iodonium ylides have a relatively low thermal stability and can be handled only at low temperatures. The relatively stable dicarbonyl derivatives, $PhIC(COR)_2$,[19-23] and the disulfonyl derivatives, $PhIC(SO_2R)_2$,[24-27] are generally prepared by a reaction of $PhI(OAc)_2$ with appropriate dicarbonyl compounds or disulfones under basic conditions. In particular, phenyliodonium ylides **2** are obtained by the treatment of malonate esters **1** with (diacetoxyiodo)benzene in dichloromethane in the presence of KOH (Scheme 1).[22] An optimized procedure for the preparation of bis(methoxycarbonyl)(phenyliodonium)methanide **4** by a similar reaction of dimethyl malonate **3** in acetonitrile was published by the same authors in *Organic Syntheses*.[28] Ylides **2** and **4** can be stored for several weeks at –20 ^{o}C, however, they slowly decompose at room temperature.
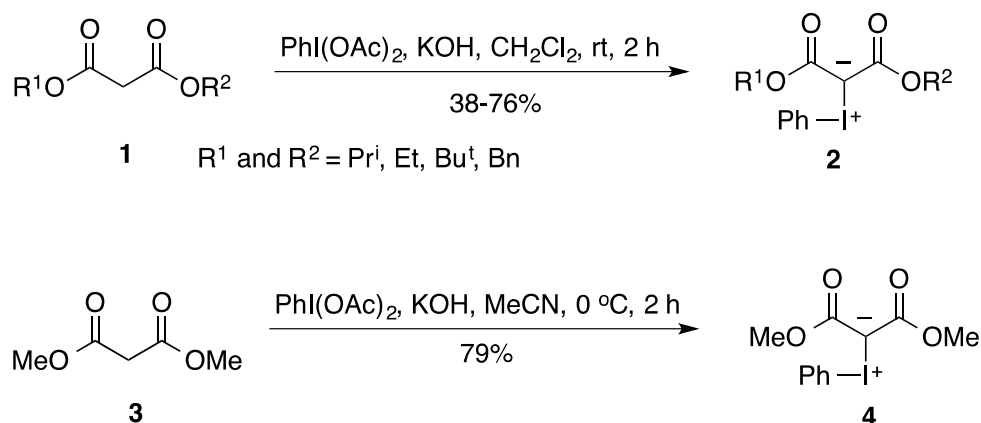
Scheme 1. Synthesis of iodonium ylides from malonate esters.

Zhang and co-workers have reported a convenient procedure for the preparation of dimedone-derived iodonium ylide **6** in excellent yield by treatment of dimedone **5** with iodosylbenzene in dichloromethane (Scheme 2).[29] Addition of a catalytic amount of zinc perchlorate (10 mol%) shortens the reaction time to 10 min with a slightly lower yield (80%) yield of ylide **6**. Zinc cation acts as a Lewis acid depolymerizing and activating iodosylbenzene.
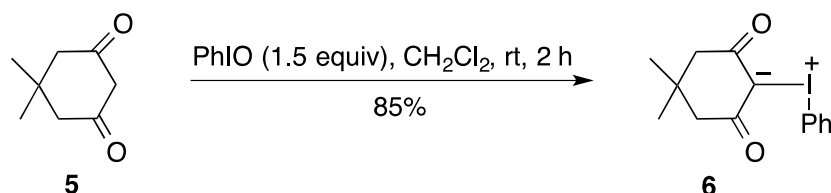

Scheme 2. Synthesis of dimedone-derived iodonium ylide **6**.

Practical applications of ylides **2**, **4** and **6** are limited by their poor solubility (insoluble in most organic solvents except DMSO) and low stability. Thermal stability and solubility of iodonium ylides can be significantly improved by introduction of a coordinating substituent in the *ortho* position of the phenyl ring.[30] In particular, 2-alkoxyphenyliodonium ylides **9** derived from malonate methyl ester and bearing an *ortho* alkoxy substituent on the phenyl ring, can be synthesized from commercially available 2-iodophenol **7** via diacetates **8** according to the procedure shown in Scheme 3. Ylides **9** are relatively stable compounds with excellent solubility in dichloromethane, chloroform, or acetone (e.g., the solubility of ylide **9**, R = Pr, in dichloromethane is 0.56 g/mL).[31] The higher thermal stability and a useful reactivity pattern are also characteristic for the dimedone-derived *o*-alkoxyphenyliodonium ylides **10**, which are prepared similarly by the reaction of diacetates **8** with dimedone **5** in methanol in the presence of KOH (Scheme 3).[32]
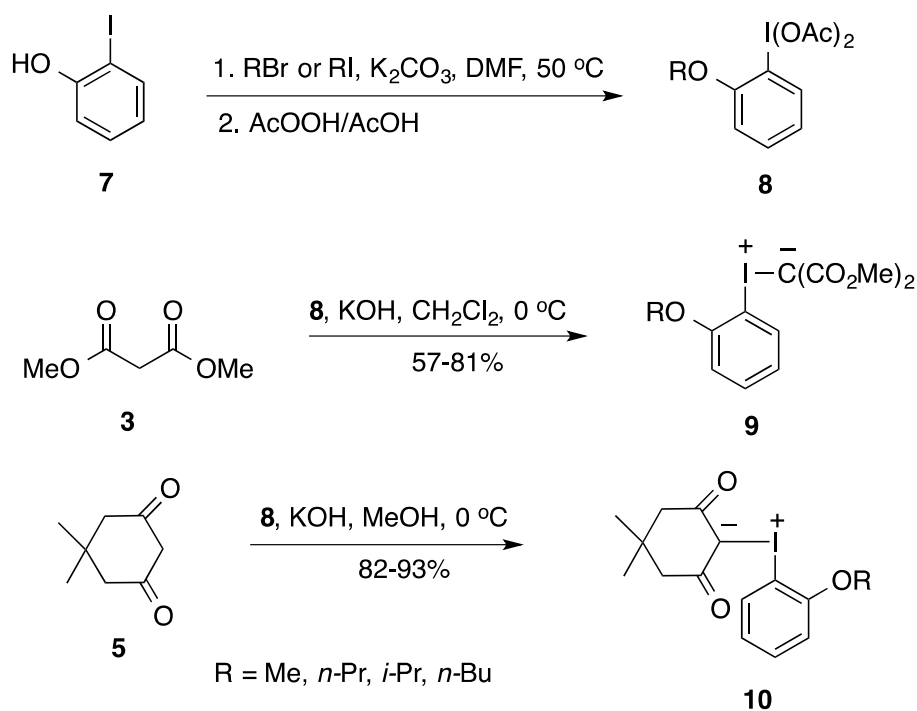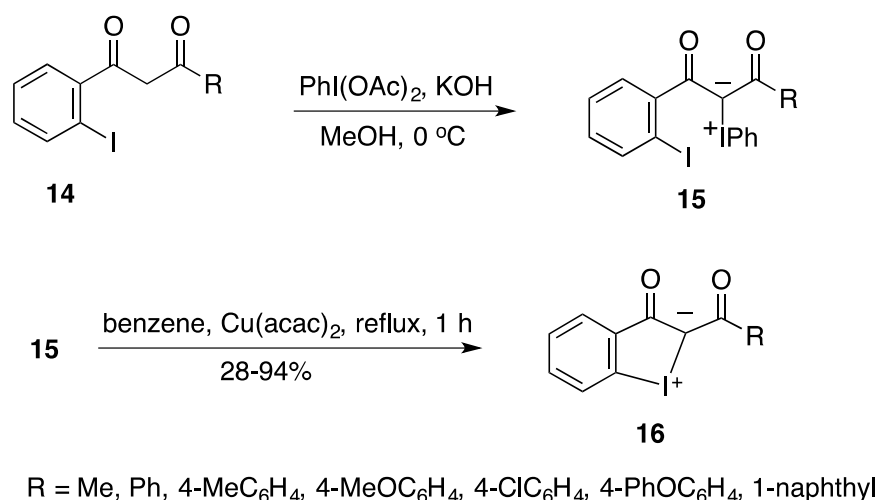
Scheme 3. Synthesis of 2-alkoxyphenyliodonium ylides.

Recently, several stable *ortho*-substituted iodonium ylides **13** have been prepared by reactions of β-dicarbonyl compounds **11** with benziodoxole **12** in the absence of any base (Scheme 4).[33] The new iodonium ylides **12** bearing an *ortho*-propan-2-ol group in the phenyl ring are surprisingly stable for acyclic iodonium ylides owing to the intramolecular coordination of iodine by the hydroxyl group. Not only are these iodonium ylides stable at room temperature, but they could be purified by column chromatography on silica gel.
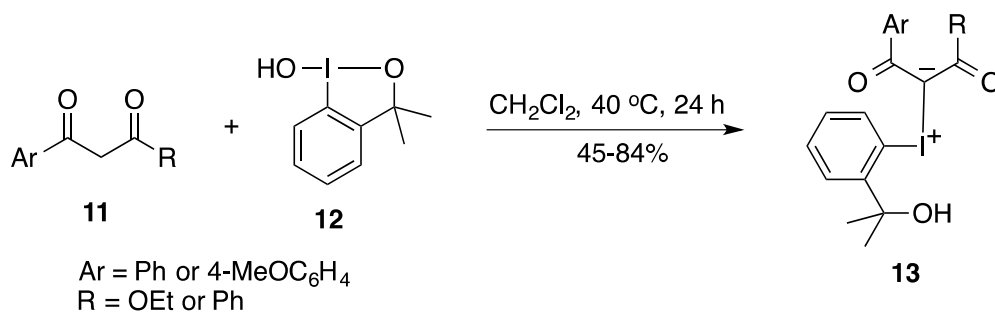
Scheme 4. Synthesis of iodonium ylides **13** from benziodoxole **12**.

Cyclic iodonium ylides, in which the iodonium atom is incorporated in a five-membered ring, have even higher thermal stability. The unusually stable cyclic iodonium ylides **16** were

prepared via the intramolecular transylidation of the acyclic ylides **15**, which were synthesized by the known method from β-diketones **14** (Scheme 5).[34]

R = Me, Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-PhOC$_6$H$_4$, 1-naphthyl

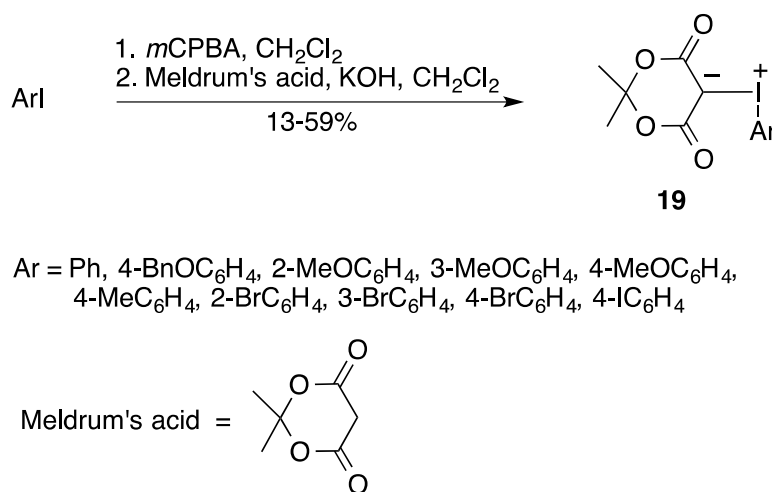**Scheme 5.** Synthesis of cyclic iodonium ylides **16**.

Bis(perfluoroalkanesulfonyl)(phenyliodonium)methanides **17**, synthesized from (diacetoxyiodo)benzene and bis[(perfluoroalkyl)sulfonyl]methane (Scheme 6), also have a relatively high thermal stability; they can be stored without decomposition at room temperature for several months.[26] The nonsymmetric, cyano[(perfluoroalkyl)sulfonyl]-substituted ylides **18** (Scheme 6)[25] or bis(fluorosulfonyl)(phenyliodonium)methanide, PhIC(SO$_2$F)$_2$,[35] were prepared from (diacetoxyiodo)benzene and appropriate bis(sulfonyl)methanes as starting materials.
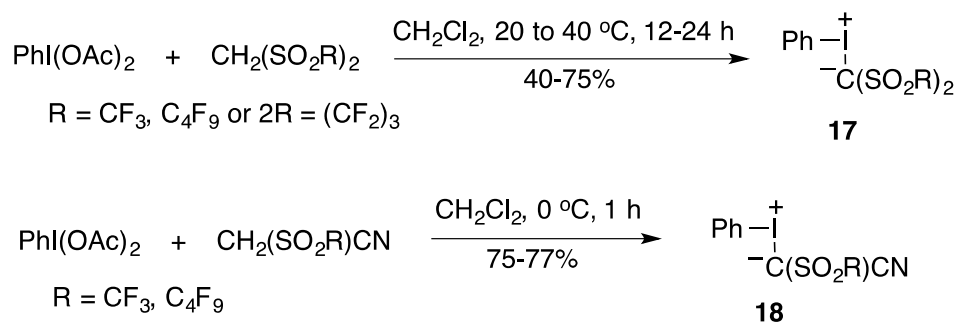
Scheme 6. Preparation of bis(perfluoroalkanesulfonyl)(phenyliodonium)methanides.
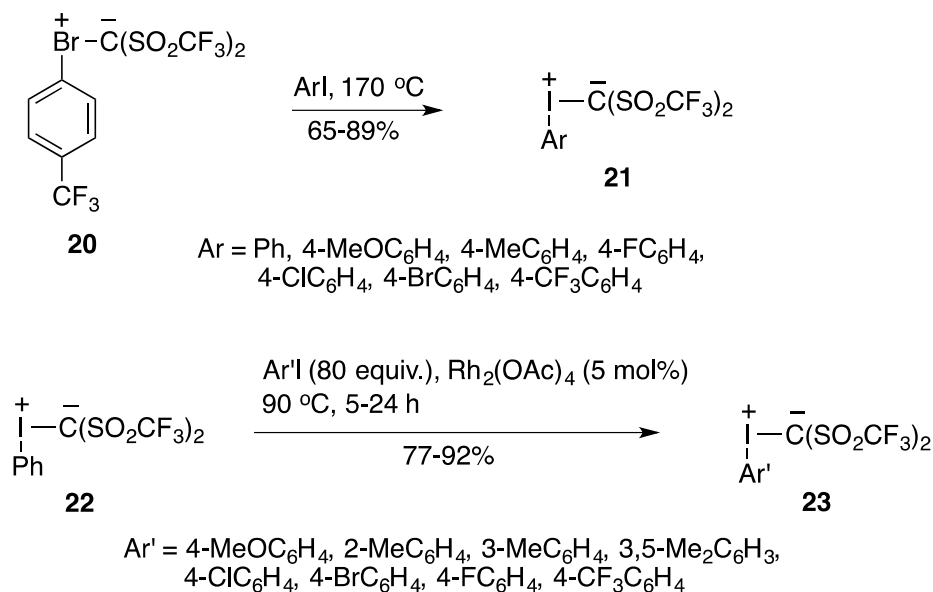
Cardinale and Ermert have developed a simplified method for preparing aryliodonium ylides in a one-pot procedure starting from the respective aryl iodides.[23] In particular, aryliodonium ylides **19** were synthesized by a two-step, one-pot procedure shown in Scheme 7. Aryl iodides were first oxidized with *m*-chloroperoxobenzoic acid (*m*CPBA) in dichloromethane

followed by the addition of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) and KOH to give ylides **19** in moderate yields.[23]


Ar = Ph, 4-BnOC$_6$H$_4$, 2-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 2-BrC$_6$H$_4$, 3-BrC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-IC$_6$H$_4$

Meldrum's acid =

Scheme 7. Preparation of aryliodonium ylides in one-pot starting from aryl iodides.

Ochiai and co-workers developed a new synthetic approach to iodonium ylides **21** by the intermolecular transylidation reactions between halonium ylides under thermal or catalytic conditions (Scheme 8).[36,37] The transylidation of bromonium **20** to iodonium **21** ylides proceeds under thermal conditions and probably involves generation of a reactive carbene intermediate.[36] Heating of phenyliodonium ylide **22** with iodoarenes in the presence of 5 mol% of rhodium(II) acetate as a catalyst results in the transfer of the bis(trifluoromethylsulfonyl)methylidene group to the iodine(I) atom of iodoarene to afford substituted aryliodonium ylides **23** in good yields.[37]

Ar = Ph, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-FC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$

Ar' = 4-MeOC$_6$H$_4$, 2-MeC$_6$H$_4$, 3-MeC$_6$H$_4$, 3,5-Me$_2$C$_6$H$_3$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-FC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$

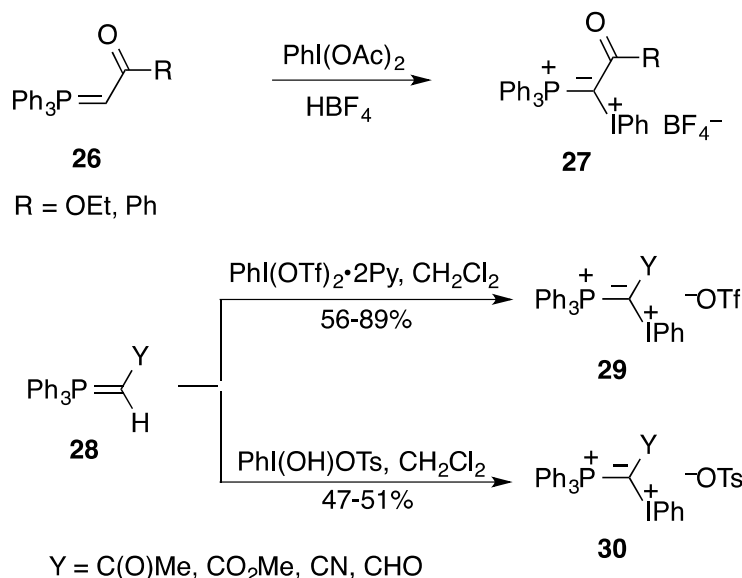**Scheme 8.** Preparation of aryliodonium ylides by the intermolecular transylidation reactions.

Iodonium ylides derived from phenolic substrates represent an important class of zwitterionic iodonium compounds.[17,18] The preparation of phenolic iodonium ylides **24** was first reported in 1977 via a reaction of *para*-substituted phenols with (diacetoxyiodo)benzene followed by treatment with pyridine (Scheme 9).[38] The system of an iodonium phenolate is stabilized by the presence of at least one electron–withdrawing substituent on the aromatic ring. Monosubstituted iodonium phenolates **24** are relatively unstable and easily rearrange to iodo ethers **25** under heating.
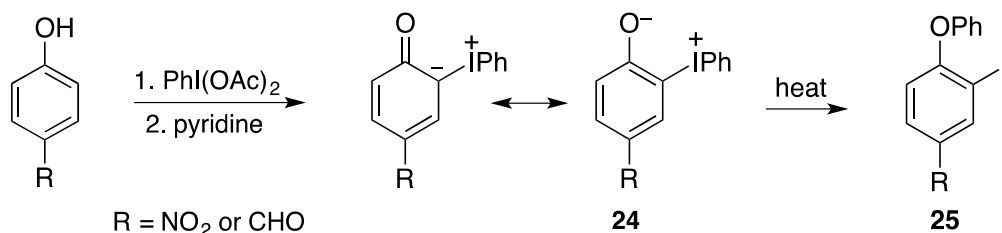

Scheme 9. Preparation and rearrangement of phenolic iodonium ylides.

Mixed phosphonium-iodonium ylides represent a useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt. The preparation of the tetrafluoroborate derivatives **27** by the reaction of phosphonium ylides **26** with (diacetoxyiodo)benzene in the presence of HBF_4 was first reported by Neilands and Vanag in 1964.[39] Later, in 1984, Moriarty and co-workers reported the preparation of several new tetrafluoroborate derivatives **29** and X-ray crystal structure for one of the products.[40] The triflate **29** and tosylate **30** derivatives of phosphonium-iodonium ylides have been prepared in good yields by the reaction of phosphonium ylides **28** with the pyridine complex of iodobenzene ditriflate, $PhI(OTf)_2 \cdot 2Py$,[41] or with [hydroxy(tosyloxy)iodo]benzene, respectively (Scheme 10).[42-45] The analogous mixed arsonium-iodonium ylides were synthesized using a similar procedure.[45] Preparation of heteroaryl-substituted phosphonium-iodonium ylides was also reported.[46]

The unstable monocarbonyl iodonium ylides **32** can be generated from (*Z*)-(2-acetoxyvinyl)iodonium salts **31** by ester exchange reaction with lithium ethoxide in tetrahydrofuran at low temperature (Scheme 11). ^{1}H NMR measurements indicate that ylides **32** are stable up to −30 °C, and they can be conveniently used in subsequent transformations without isolation.[47-52]

Scheme 10. Preparation of mixed phosphonium-iodonium ylides.
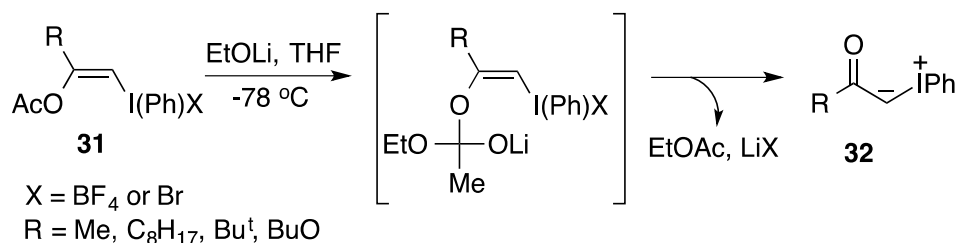
Scheme 11. Generation of monocarbonyl iodonium ylides.

3. General Structural Features of Iodonium Ylides

Single crystal X-ray structures have been reported for the following iodonium ylides: 3-phenyliodonio-1,2,4-trioxo-1,2,3,4-tetrahydronaphthalenide **33**,[53] 3-phenyliodonio-2,4-dioxo-1,2,3,4-tetrahydro-1-oxanaphthalenide **34**,[53] mixed phosphonium–iodonium tetrafluoroborates **35**[40] and **36**,[43] mixed arsonium–iodonium tetrafluoroborate **37**,[54] mixed phosphonium iodonium triflate **38**,[42] phenyliodonium bis(trifluoromethanesulfonyl)methide **39**,[24] cyclic iodonium ylide **40**,[34] 2-methoxyphenyliodonium bis(methoxycarbonyl)methanide **41**,[31] and the pseudocyclic *ortho*-substituted iodonium ylides **42**[33] (Figure 1). According to X-ray data, the geometry of aryliodonium ylides is similar to the geometry of iodonium salts with a C–I–C angle close to 90°, which is indicative of a zwitterionic nature of the ylidic C–I bond. In particular, phenyliodonium ylide **39** has a geometry typical for an iodonium ylide with the I–C ylidic bond length of about 1.9 Å and an C–I–C bond angle of 98°.[24] X-ray structural analysis for cyclic ylide **40** reveals a

distorted five-membered ring with the ylidic bond length about 2.1 Å and a C–I–C bond angle of 82°, which is smaller than the usual 90°.[34] 2-Methoxyphenyliodonium bis(methoxycarbonyl)-methanide **41** in solid state has a polymeric, asymmetrically bridged structure with a hexacoordinated geometry around the iodine centers formed by two short C–I bonds [2.117 Å for I–C(Ph) and 2.039 Å for I–C(malonate)] and two relatively long iodine-oxygen intramolecular interactions between iodine and the oxygen atom of the *ortho* substituent (2.928 Å) and the carbonyl oxygen atom of the methoxycarbonyl group (3.087 Å). In addition, a relatively weak intermolecular I–O secondary interaction of 2.933 Å between the iodine center and the carbonyl oxygen atom of the neighboring molecule is also present in the solid state structure of **41**.[31] Structure of the unusually stable pseudocyclic iodonium ylide **42** bearing an *ortho*-propan-2-ol group in the phenyl ring is characterized by the presence of additional intramolecular coordination of iodine by the hydroxyl group.[33]
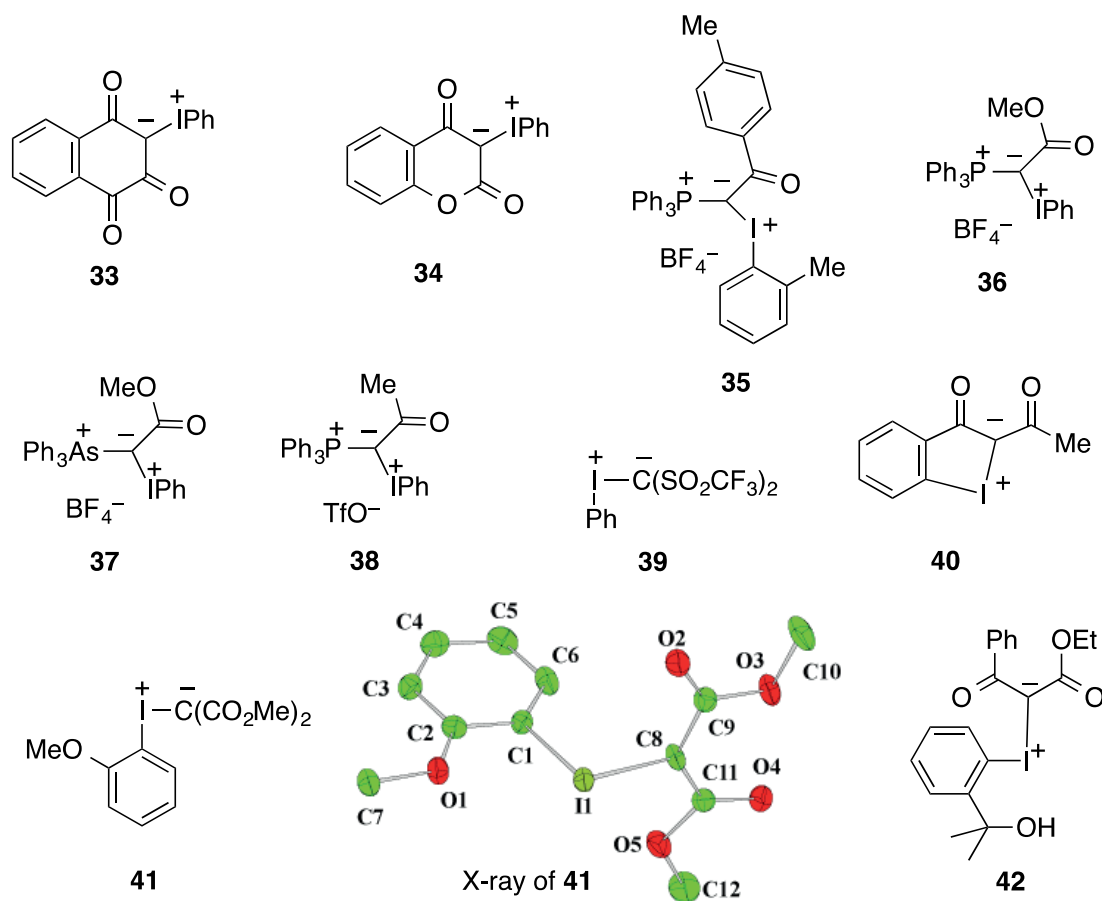

Figure 1. Iodonium ylides structurally characterized by single crystal X-ray diffractometry.

The structures of iodonium ylides have also been studied by various spectroscopic techniques. For example, an interesting Moessbauer spectral study has been published by

Nishimura and coauthors.[55] This study, in particular, confirmed that the ylidic I–C bond is mostly zwitterionic in nature.

In should be mentioned that the ylidic bond in iodonium ylides is commonly shown in the literature as the I=C double bond. However, according to high level computational study using adaptive natural density partitioning bond modeling technique (AdNDP), a double bond between iodine atom and other elements does not exist and the actual bonding in iodonium ylides has a dative 2c-2e nature.[56]

4. Synthetic Applications of Iodonium Ylides

4.1. Reactions of iodonium ylides as carbene precursors

Iodonium ylides can serve as efficient precursors to the respective carbene intermediates under thermal, photochemical, or catalytic conditions. A detailed discussion of the reaction mechanisms and synthetic applications of iodonium ylides as carbene precursors can be found in the earlier reviews.[14-18]

Bis(methoxycarbonyl)(phenyliodinio)methanide **4**, the most common iodonium ylide derived from malonate methyl ester, has found synthetic applications in the C–H insertion reactions,[57-61] and in the cyclopropanation of alkenes,[22,28,62-66] including enantioselective cyclopropanations in the presence of chiral rhodium complexes.[15,67,68] Representative examples of these reactions are shown in Scheme 12 and include the BF$_3$–catalyzed bis(carbonyl)alkylation of 2-alkylthiophenes **43**,[58] and the optimized procedure for rhodium–catalyzed cyclopropanation of styrene **44**.[28]

Rh$_2$(esp)$_2$ = bis[rhodium($\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,3-benzenedipropionic acid)]
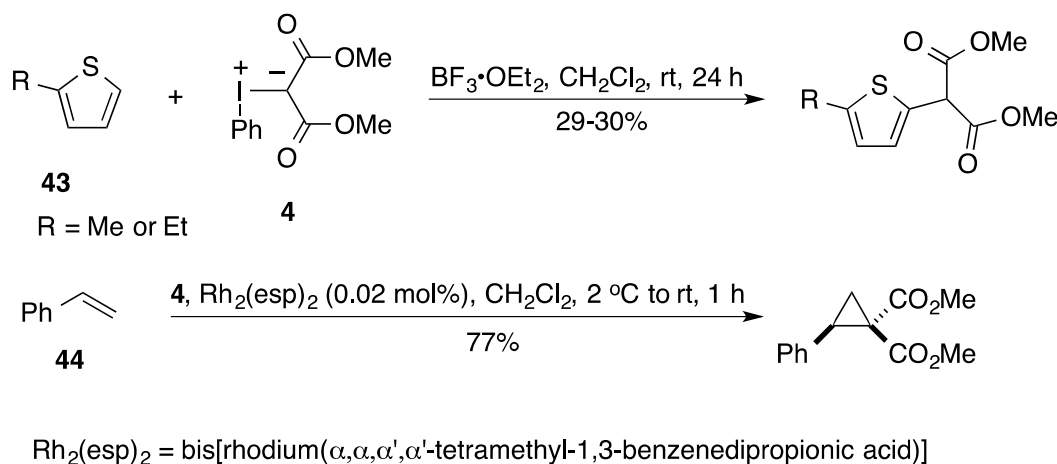
Scheme 12. Reactions of iodonium ylide **4** as carbene precursor.

A particularly useful reagent in these carbenoid reactions is the highly soluble and reactive iodonium ylide **45** derived from malonate methyl ester and bearing an *ortho* methoxy

substituent on the phenyl ring.[31] This reagent shows higher reactivity than common phenyliodonium ylides in the Rh–catalyzed cyclopropanation, C–H insertion, and transylidation reactions under homogeneous conditions. Examples of the carbenoid reactions of ylide **45** are shown in Scheme 13.[31]


Ar = Ph, 4-MeC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$, 4-BrC$_6$H$_4$, 4-ClC$_6$H$_4$, 3-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, etc.
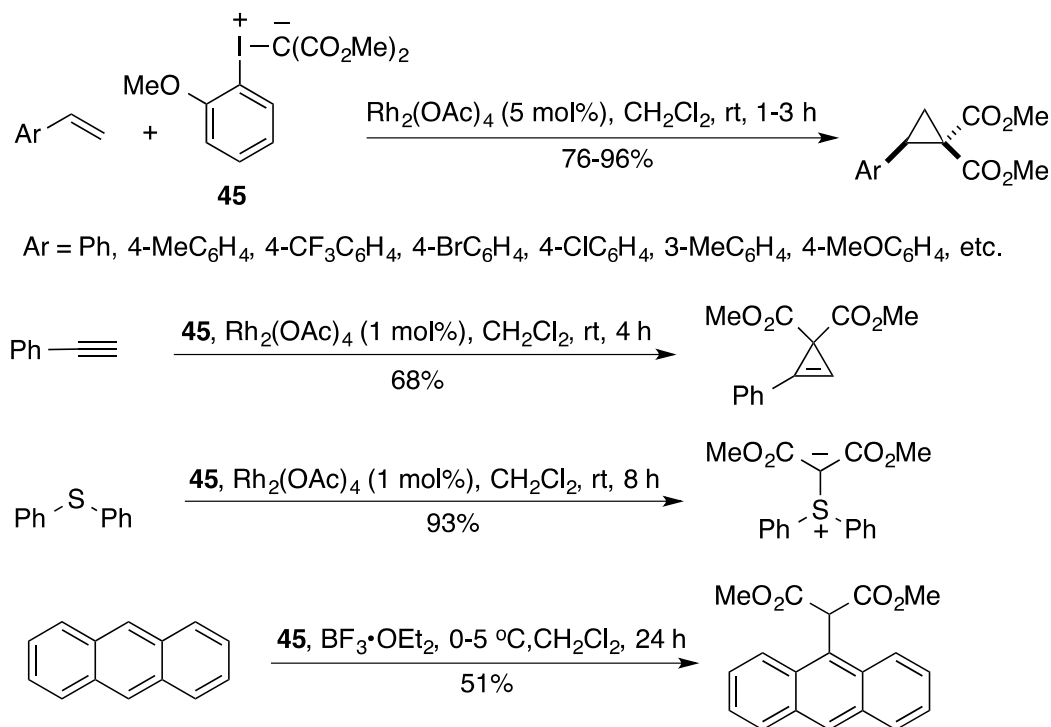
Scheme 13. Carbenoid reactions of the soluble iodonium ylide **45**.

The carbenoid reactions of iodonium ylides can be effectively catalyzed by rhodium(II) or copper complexes.[14-16] The product composition in the rhodium(II)–catalyzed reactions of iodonium ylides was found to be identical to that of the corresponding diazo compounds, which confirms that mechanisms of both processes are similar and involve metallocarbenes as key intermediates.[69] Hadjiarapoglou and co-workers have recently reported a mechanistic study of the reactions of cyclic β-dicarbonyl phenyliodonium ylide with various substituted styrenes under Rh$_2$(OAc)$_4$ catalysis confirming the carbenoid mechanism of these reactions.[70] Examples of the transition metal–catalyzed carbenoid reactions of iodonium ylides are illustrated by the following publications: Rh(II)- or Cu(I)-catalyzed cyclopropanation reactions using the unstable ylides PhIC(H)NO$_2$[71] and PhIC(CO$_2$Me)NO$_2$[72-74] generated in situ from nitromethane and methyl nitroacetate; Rh(II)-catalyzed three–component coupling of an ether with a nitromethane–derived carbenoid generated from PhIC(H)NO$_2$;[75] Rh(II)- or Cu(II)-catalyzed insertion of carbene into alkenyl C–H bond in flavones,[76] and highly phenylated ethylenes;[77] Rh(II)-catalyzed reaction of iodonium ylides with conjugated dienes and α,β-unsaturated carbonyl compounds leading to efficient synthesis of dihydrofurans, oxazoles, and dihydrooxepines;[78]

synthesis of various heterocycles by Rh(II)-catalyzed reactions of iodonium ylides with vinyl ethers, carbon disulfide, alkynes, and nitriles;[66] Rh(II)-catalyzed reaction of iodonium ylides with electron–deficient and conjugated alkynes leading to substituted furans;[79] efficient synthesis of β-substituted α-haloenones by Rh(II)-catalyzed reactions of iodonium ylides with benzyl halides and acid halides;[80,81] Rh(II)- or Cu(II)-catalyzed generation/rearrangement of onium ylides of allyl and benzyl ethers via iodonium ylides;[82] and Rh(II)- or Cu(II)-catalyzed stereoselective cycloaddition of disulfonyl iodonium ylides with alkenes leading to 1,2,3-trisubstituted benzocyclopentenes[83] or functionalized indanes.[84-86]

Moriarty and co-workers have investigated the intramolecular cyclopropanation of iodonium ylides to the tricyclic ketones in the presence of copper(I) chloride and also in the absence of conventional metal calalysts.[87] Synthetic utility of this methodology has been demonstrated by conversion of ylide **46** to a mixture of diastereomeric products **47** and **48** related to prostaglandins and vitamin D, respectively (Scheme 14).
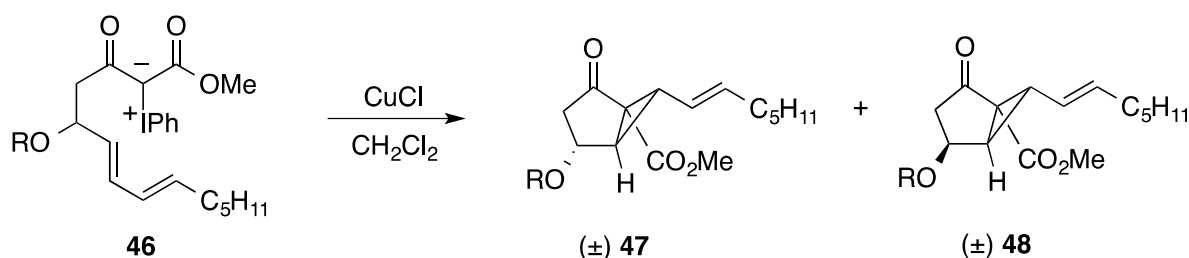
Scheme 14. Intramolecular cyclization of phenyliodonium ylide **46**.

The metal–catalyzed carbenoid reactions of iodonium ylides have been applied in asymmetric reactions.[60,64,73,74,88] For example, the copper(II)–catalyzed intramolecular C–H insertion of phenyliodonium ylide **49** in the presence of chiral ligands followed by hydrolysis and decarboxylation affords product **50** in moderate yield with up to 72% ee (Scheme 15).[60]
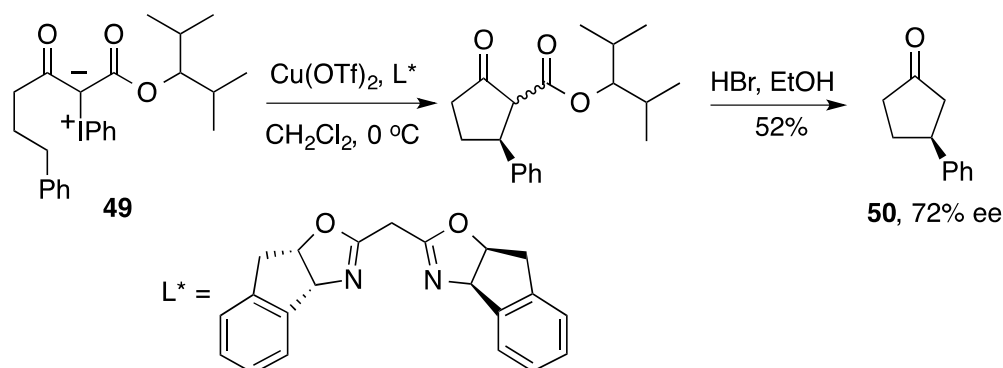
Scheme 15. Enantioselective intramolecular C–H insertion of phenyliodonium ylide **49**.

Charette and co-workers have developed a Cu(I)-catalyzed asymmetric cyclopropanation of alkenes with an iodonium ylide generated in situ from iodosylbenzene and m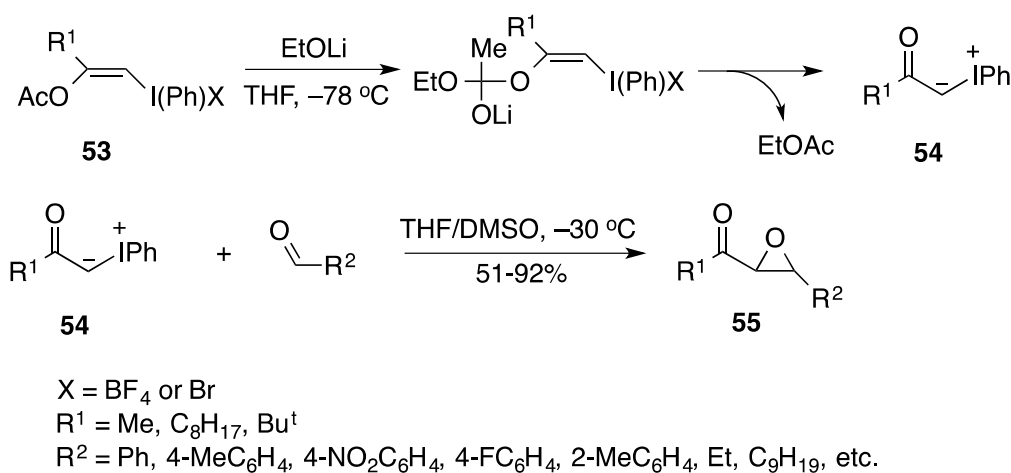ethyl nitroacetate (Scheme 16).[74] High enantioselectivity (up to 98% ee) and diastereoselectivity (95:5 dr trans/cis) were achieved for a wide range of aryl- or alkyl-substituted alkenes **51**. This synthetically useful reaction allows facile preparation of various 1-nitrocyclopropyl carboxylates **52** which can be further transformed into the corresponding substituted cyclopropane amino acids and aminocyclopropanes.
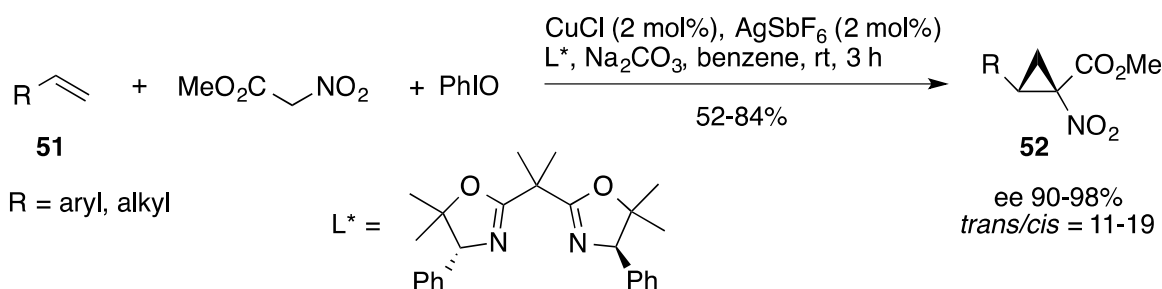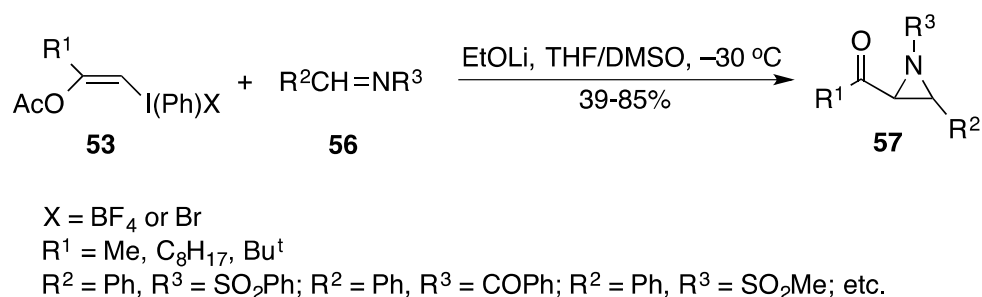

Scheme 16. Preparation of 1-nitrocyclopropyl carboxylates by enantioselective cyclopropanation of alkenes.

Ochiai and co-workers have reported several useful reactions of the unstable monocarbonyl iodonium ylides **54**, which can be quantitatively generated from (Z)-(2-acetoxyvinyl)iodonium salts **53** via an ester exchange reaction with lithium ethoxide in THF at low temperature (Scheme 17).[47-49] Ylide **54**, generated in situ from iodonium salts **53**, reacts with aldehydes in THF/DMSO at low temperature to afford α,β-epoxy ketones **55** with the predominant formation of the *trans* isomers. A Hammett reaction constant ($\rho = 2.95$) for this reaction indicates that monocarbonyl iodonium ylides **54** are moderately nucleophilic in nature.[49]
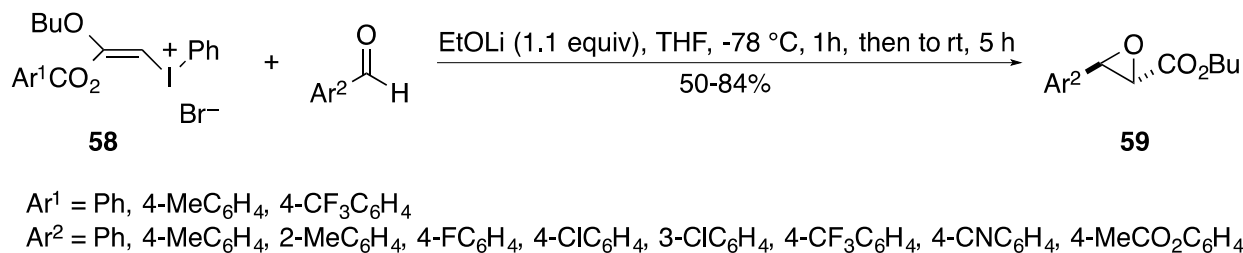

$X = BF_4$ or Br
$R^1 = Me, C_8H_{17}, Bu^t$
$R^2 = Ph, 4\text{-}MeC_6H_4, 4\text{-}NO_2C_6H_4, 4\text{-}FC_6H_4, 2\text{-}MeC_6H_4, Et, C_9H_{19}$, etc.

Scheme 17. Reactions of monocarbonyl iodonium ylides **54** with aldehydes.

Monocarbonyl iodonium ylides, generated in situ from iodonium salts **53**, undergo alkylidene transfer reactions to activated imines **56** yielding 2-acylaziridines **57** in good yields (Scheme 18). The stereochemical outcome of this aziridination is dependent on both the activating groups of the imines and the reaction solvents; for example, the aziridination of *N*-(2,4,6-trimethylbenzenesulfonyl)imines in THF affords *cis*-aziridines as a major product, while that of *N*-benzoylimines in THF/DMSO or THF gives the *trans* isomer stereoselectively.[47,48]

X = BF$_4$ or Br
R^1 = Me, C$_8$H$_{17}$, Bu^t
R^2 = Ph, R^3 = SO$_2$Ph; R^2 = Ph, R^3 = COPh; R^2 = Ph, R^3 = SO$_2$Me; etc.

Scheme 18. Preparation of 2-acylaziridines **57** using monocarbonyl iodonium ylides.

Miyamoto and co-workers have investigated reactions of β-butoxycarbonyliodonium ylides, Darzens reagent analogues, which were prepared by the ester exchange reaction of β-butoxy-β-acyloxyvinyl-λ^3-iodane **58** with lithium bases.[52] The iodonium ylide generated in situ from **58** cleanly undergoes Darzens condensation with aromatic aldehydes to selectively give the *trans* epoxyesters **59** (Scheme 19).


Ar^1 = Ph, 4-MeC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$
Ar^2 = Ph, 4-MeC$_6$H$_4$, 2-MeC$_6$H$_4$, 4-FC$_6$H$_4$, 4-ClC$_6$H$_4$, 3-ClC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$, 4-CNC$_6$H$_4$, 4-MeCO$_2$C$_6$H$_4$

Scheme 19. Darzens-type condensation of alkenyliodonium salt with aromatic aldehydes.

Murphy and co-workers have investigated the suitability of monocarbonyl iodonium ylides as metallocarbene precursors.[89] They have developed a new method for generating monocarbonyl iodonium ylides **61** in situ by treatment of phosphonium ylides **60** with iodosylbenzene. Ylides **61** were subsequently intercepted by transition-metal catalysts to generate metallocarbenes, which then underwent either dimerization or cyclopropanation reactions with alkenes (Scheme 20). Though the authors were unable to improve the yields of cyclopropanes **62** to be synthetically viable, this study proves that monocarbonyl iodonium ylides **61** can serve as metallocarbene precursors.

tfacac = trifluoroacetylacetonate
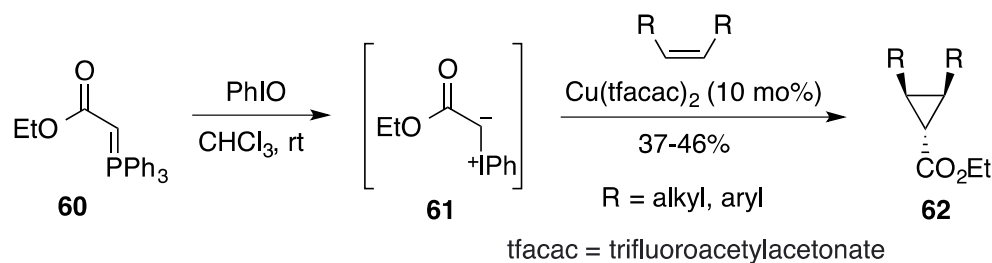
Scheme 20. Reactions of monocarbonyl iodonium ylides as metallocarbene precursors.

The mixed phosphonium–iodonium ylides represent a useful class of reagents that combine in one molecule synthetic advantages of a phosphonium ylide and an iodonium salt.[42,44-46,54,90-95] For example, phosphorane–derived phenyliodonium tosylate **63** reacts with soft nucleophiles, such as iodide, bromide, benzenesulfinate, thiocyanate, and thiophenolate anions, with a selective formation of the respective α-functionalized phosphonium ylides **64** (Scheme 21), which can be further converted to alkenes (e.g., **65**) by the Wittig reaction with aldehydes.[44] The analogous arsonium–iodonium ylides have a similar reactivity toward nucleophiles.[45,54,96]

Nu = I, Br, PhS, SCN, PhSO$_2$, etc.
solvent = MeOH, CH$_2$Cl$_2$, or CH$_2$Cl$_2$/DMSO
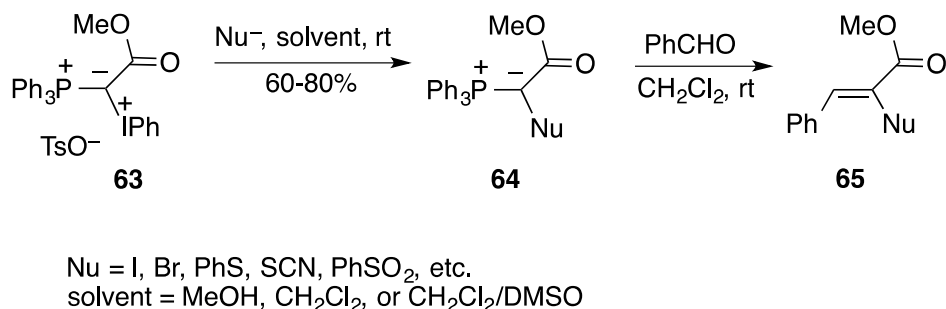
Scheme 21. Reactions of mixed phosphonium–iodonium ylides **63**.
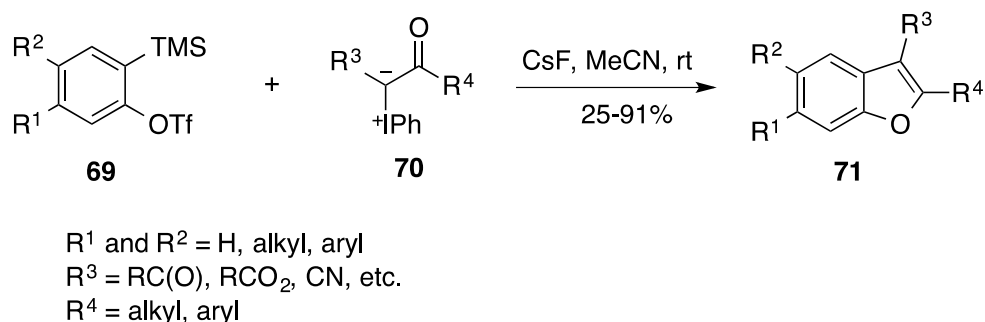
4.2. Cycloaddition reactions of iodonium ylides leading to heterocycles

Iodonium ylides of different structural types have been used in various heterocyclization reactions under transition metal free conditions or in the presence of metal catalysts. Liang and co-workers have developed a metal-free approach to synthesis of indolines from *N*-(ortho-chloromethyl)aryl amides and iodonium ylides.[97] In particular, *N*-[2-(chloromethyl)phenyl]tosylamides **66** react with iodonium ylides **67** at room temperature to afford indolines **68** in moderate yields (Scheme 22). The mechanism of these reactions involves the initial conversion of *N*-[2-(chloromethyl)phenyl]tosylamides into the aza-o-quinodimethane intermediate under basic conditions, followed by Michael addition and N-alkylation with iodonium ylide to generate indoline by loss of iodobenzene.[97]

R^1 and R^2 = H, Cl, OMe
R^3 = H, Me
R^4 and R^5 = RC(O), RCO$_2$, CN, etc.
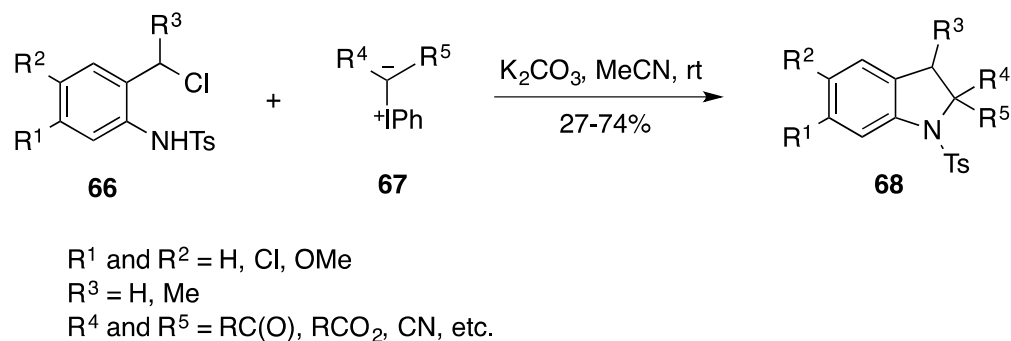
Scheme 22. Synthesis of indolines from *N*-(ortho-chloromethyl)aryl amides and iodonium ylides.

Liang, Li and co-workers have also reported a mild and general synthesis of benzofurans by cycloaddition of arynes with iodonium ylides.[98] The aryne intermediates, generated from 2-silylaryltriflates **69** in the presence of CsF, undergo the cycloaddition reaction with iodonium ylides **70** at room temperature to afford the corresponding benzofurans **71** in moderate to good yields (Scheme 23).

R^1 and R^2 = H, alkyl, aryl
R^3 = RC(O), RCO$_2$, CN, etc.
R^4 = alkyl, aryl

Scheme 23. Synthesis of benzofurans by cycloaddition of arynes with iodonium ylides.

Stabilized β-dicarbonyl iodonium ylides **72** react with isocyanates **73** under mild conditions to afford substituted oxazolin-2-ones **74** in moderate yields (Scheme 24).[99] It has been suggested that this reaction proceeds via carbenoid intermediates, as supported by isolation of the products of carbene dimerization from the reaction mixture.

R = Me or OEt; Ar = 2,4-Cl$_2$C$_6$H$_3$
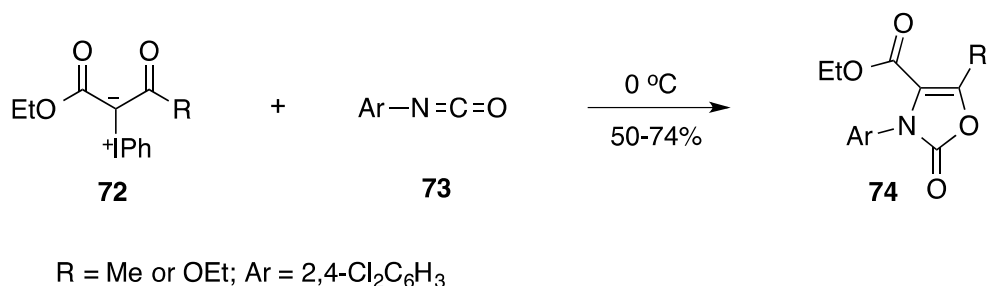
Scheme 24. Synthesis of oxazolin-2-ones from isocyanates and iodonium ylides.

The cyclic, dimedone-derived phenyliodonium ylide **75** serves as an excellent carbenoid precursor useful for synthesis of various heterocycles. Under catalytic, thermal, or photochemical conditions, ylide **75** can t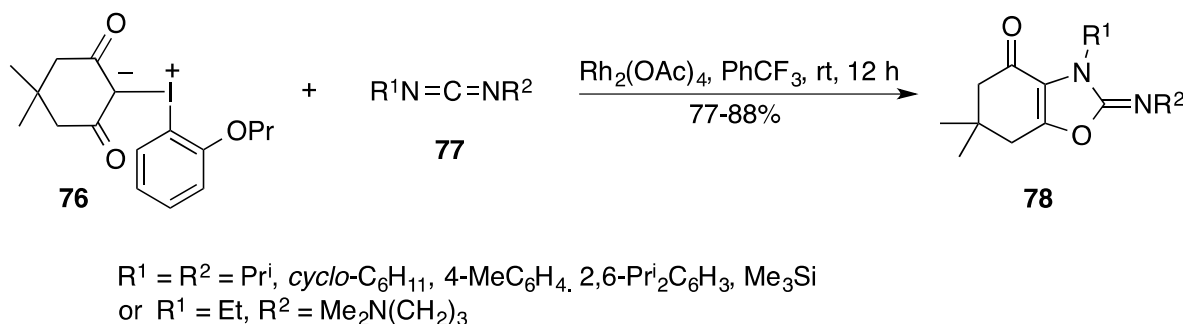ransfer the carbenoid moiety to a suitable acceptor resulting in the synthesis of five–membered heterocycles as outlined in Scheme 25. Cycloadditions are typically observed in the reactions of ylide **75** with acetylenes,[100,101] alkenes,[70,102,103] aldehydes,[104] ketenes,[105] nitriles,[100,106] isocyanates,[105,107] isothiocyanates,[108,109] and dienes.[78,110]
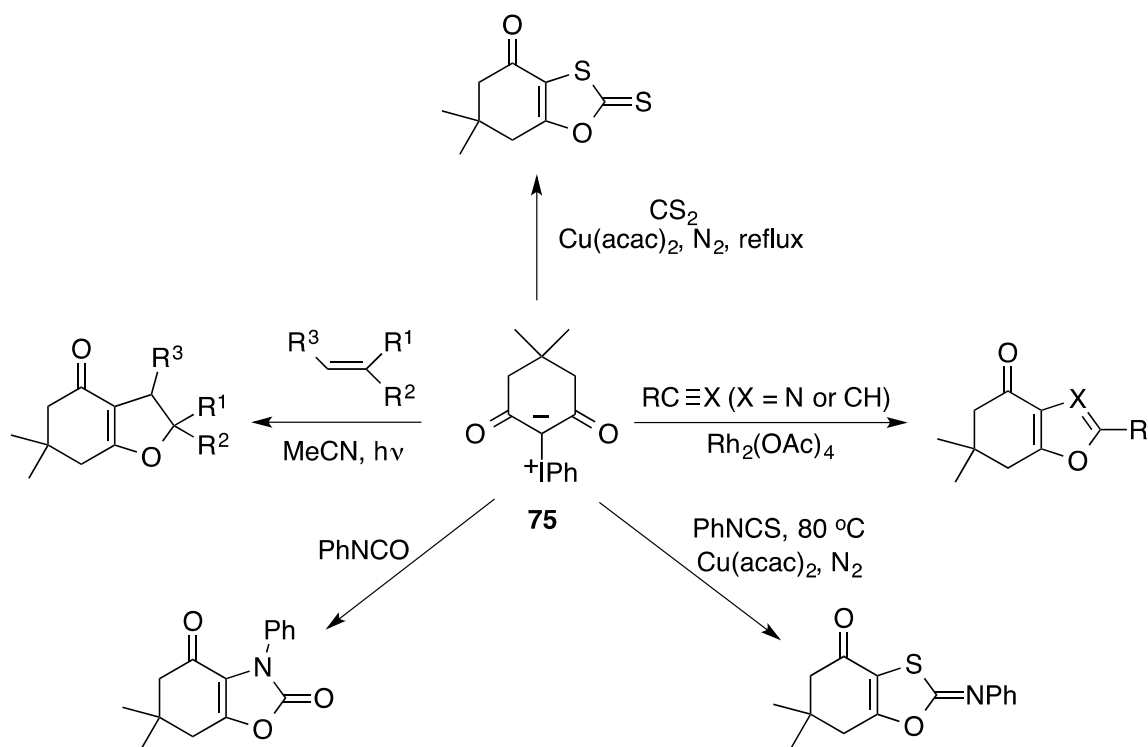
Scheme 25. Synthesis of heterocycles using dimedone-derived phenyliodonium ylide **75**.

A modified, *o*-alkoxy–substituted ylide **76**, has an improved solubility in nonpolar solvents, such as aromatic hydrocarbons, and has a generally higher reactivity compared to ylide **75**.[32] Ylide **76** is a useful reagent for the preparation of oxazole derivatives **78** in the reaction with carbodiimides **77** under homogeneous conditions in the presence of Rh(II) or Cu(II) catalysts (Scheme 26).[32]

R^1 = R^2 = Pr^i, *cyclo*-C$_6$H$_{11}$, 4-MeC$_6$H$_4$, 2,6-Pr$^i_2$C$_6$H$_3$, Me$_3$Si
or R^1 = Et, R^2 = Me$_2$N(CH$_2$)$_3$

Scheme 26. Synthesis of oxazole derivatives using stabilized phenyliodonium ylide **76**.

Zefirov, Matveeva, and co-workers have demonstrated the utility of mixed phosphonium-iodonium ylides as reagents for the synthesis of various heterocyclic systems such as: substituted oxazoles,[92,111] phosphonium-substituted furans,[46] substituted phosphinolines,[46,91,93,94] and annelated phosphorus-containing heterocycles.[112-115] All these cycloadditions proceed under photochemical conditions. In particular, irradiation of mixed phosphonium iodonium ylides **27** in a nitrile solution with a mercury light source (254 nm) affords the corresponding oxazole derivatives **79** in moderate yields (Scheme 27).[92,116]

R^1 = OMe, OEt, Ph
R^2 = Me, Et, Ph
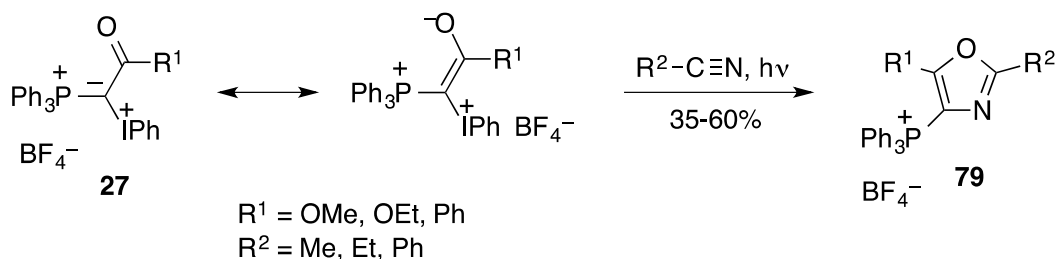
Scheme 27. Synthesis of phosphonium-substituted oxazoles by cycloaddition reactions of mixed phosphonium-iodonium ylides.

The reactions of heteroaryl-substituted (in the phosphonium part) phosphonium-iodonium ylides **80** with alkynes afford either furyl annelated phosphinolines **81** or phosphonium substituted furans **82** depending on the nature of the substituent R in the alkyne (Scheme 28).[46,117] The authors proposed a mechanism involving the initial elimination of PhI upon UV-irradiation with the formation of an electrophilic intermediate, which interacts with the alkyne to give the corresponding products of cationic cyclization.
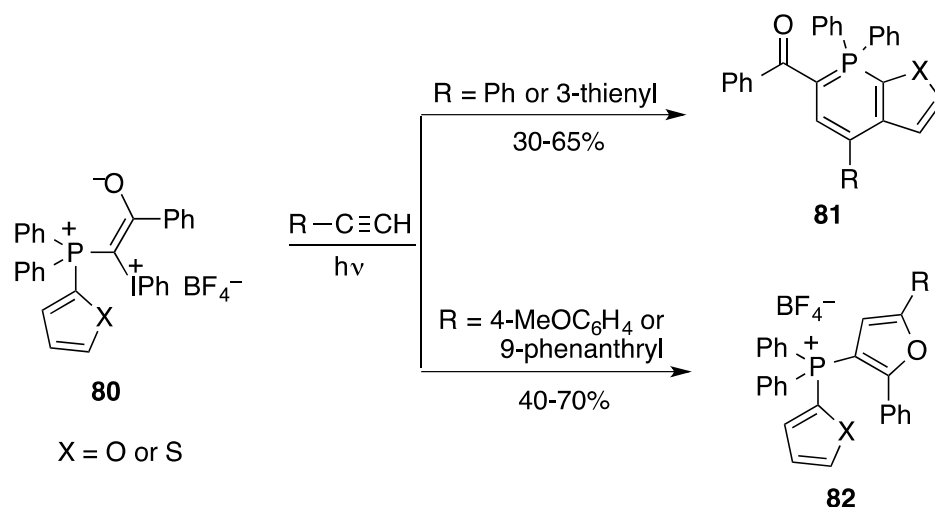
Scheme 28. Reactions of heteroaryl-substituted phosphonium-iodonium ylides **80** with alkynes.

4.3. Introduction of fluorine using iodonium ylides

Iodonium ylides have recently attracted some interest as efficient precursors for nucleophilic fluorination in Positron Emission Tomography (PET).[118-121] Iodonium ylides have an advantage over diaryliodonium salts as the selective PET precursors. Due to the carbanionic character of the ylidic carbon, the attack of an external nucleophile in principle should be directed exclusively toward the aromatic ring of the Ar group of an aryliodonium ylide. However, it was previously demonstrated that the reaction of various organic and inorganic acids with phenyliodonium ylides leads to nucleophilic substitution of the iodobenzene substituent by the anion.[122,123] Gondo and Kitamura have recently reported that the reaction of iodonium ylides **83** derived from 1-phenylbutan-1,3-dione, ethyl benzoylacetate, and ethyl *p*-nitrobenzoylacetate with Et$_3$N•3HF gave the corresponding fluorinated products **84** in low yields (Scheme 29).[124] These products are formed through the C-protonation of the ylide, followed by displacement of the PhI by the fluoride ion.
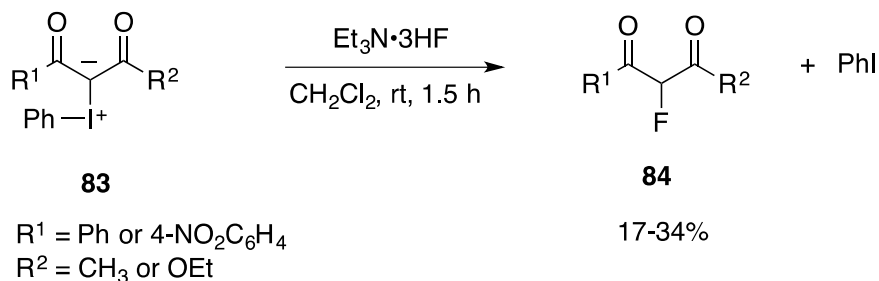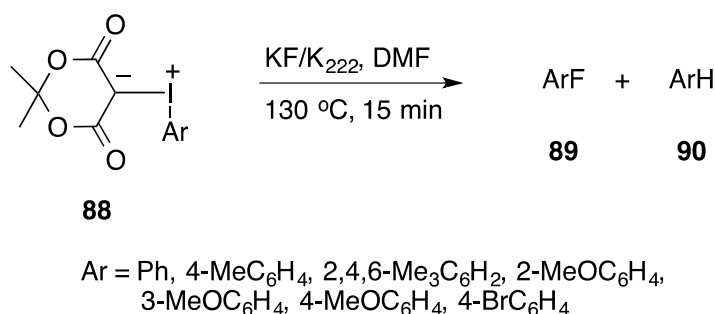

Scheme 29. Reactions of iodonium ylides with Et$_3$N•3HF.

Stuart and co-workers have investigated a similar fluorination of the stable iodonium ylide **85** with Et₃N•3HF resulting in the formation of monofluorinated product **86** in 64% isolated yield along with a small amount of the difluorinated product **87** (Scheme 30).[33]
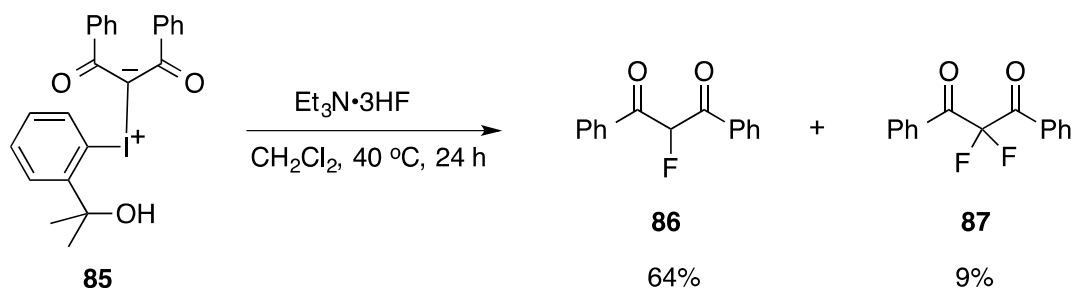
Scheme 30. Fluorination of stable iodonium ylide **85** with Et₃N•3HF.

In sharp contrast to the reactions of aryliodonium ylides with acids, Satyamurthy and Barrio have found that the reactions of ylides with nucleophiles (F⁻, Cl⁻, Br⁻, etc.) in polar aprotic solvents such as acetonitrile, tetrahydrofuran, dimethylsulfoxide, dimethylacetamide and dimethylformamide lead to regioselective substitution of the nucleophile on the aromatic ring instead of the dione ring.[125] For example, heating of phenyliodonium ylides **88** with dried KF-Kryptofix (K₂₂₂) complex in dry DMF affords fluoroarenes **89** as main product and hydrocarbon **90** as a byproduct due to a radical channel competing with the nucleophilic substitution reaction (Scheme 31). No product of fluorination of the β-dicarbonyl moiety has been detected in this reaction.[125]

Ar = Ph, 4-MeC₆H₄, 2,4,6-Me₃C₆H₂, 2-MeOC₆H₄,
3-MeOC₆H₄, 4-MeOC₆H₄, 4-BrC₆H₄

Scheme 31. Reaction of iodonium ylides with fluoride anion in DMF.

This approach has been employed for the radiofluorination of protected L-DOPA derivatives.[125] A radiochemically pure amino acid L-6-[¹⁸F]fluoroDOPA **91** has been produced in amounts usable for human PET studies as shown in Scheme 32. The fluorine-18 labeled L-DOPA is a useful PET imaging agent for mapping dopamine related brain disorders and is the PET biomarker of choice for the diagnosis of Parkinson's disease.

Scheme 32. Radiosynthesis of L-6-[^{18}F]fluoroDOPA **91**.

Scheme 33. Radiosynthesis of ([^{18}F]FPEB **91**.
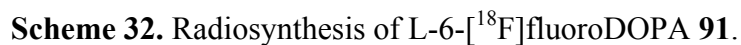
Vasdev, Liang, and co-workers have demonstrated that the spirocyclic hypervalent iodine(III) ylides can serve as synthetically versatile precursors for efficient radiolabelling of a diverse range of non-activated (hetero)arenes, highly functionalized small molecules, building blocks, and radiopharmaceuticals from [^{18}F]fluoride ion.[126,127] In particular, the reactions of ylides **92** and **94** under continuous-flow microfluidic condition offers automated synthetic procedure for the preparation of a radiopharmaceutical, 3-[^{18}F]fluoro-5-[(pyridin-3-yl)ethynyl]benzonitrile ([^{18}F]FPEB) **93**, and a routinely used building block for click-radiochemistry, 4-[^{18}F]fluorobenzyl azide **95** in 68% radiochemical conversion (RCC) (Scheme 33).

4.4. Thiotrifluoromethylation using iodonium ylides

In 2013, Shibata and co-workers have introduced a novel electrophilic-type trifluoromethylthiolation reagent, trifluoromethanesulfonyl iodonium ylide **96**, which can react with various nucleophiles to afford CF_3S-substituted products **97** (Scheme 34).[128] These reactions have a complex mechanism involving in situ reduction of the trifluoromethanesulfonyl group in the presence of a copper catalyst to give the trifluoromethylthio group. The key steps of this mechanism are shown in Scheme 34.
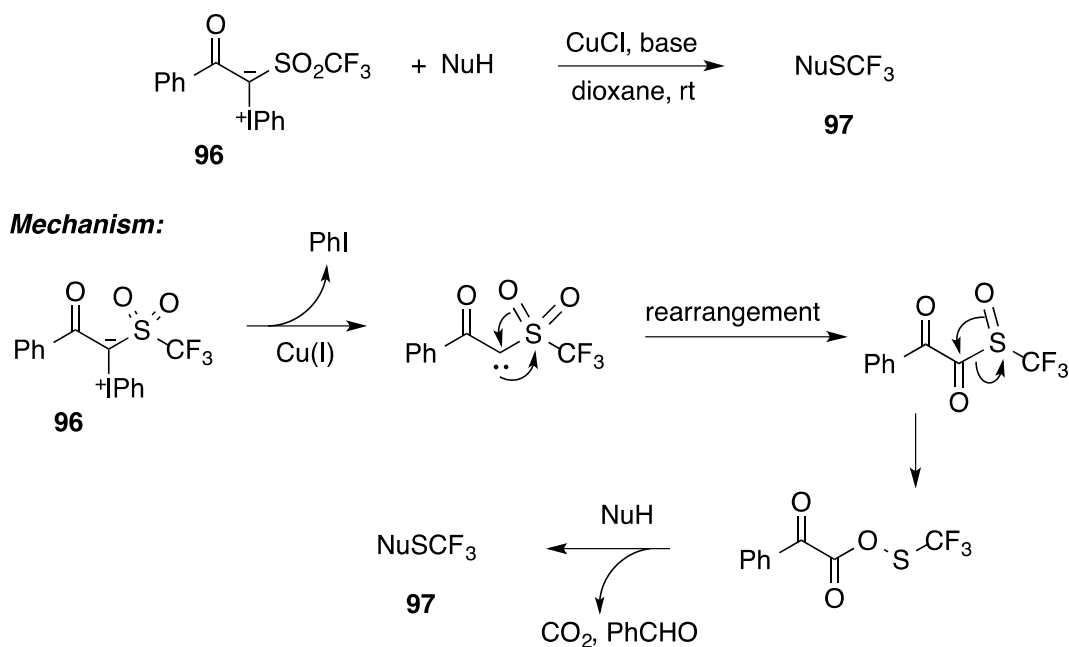
Scheme 34. Copper-catalyzed trifluoromethylthiolations by iodonium ylide **96**.

In the original work, Shibata and co-workers have reported thiotrifluoromethylation of enamines, β-keto esters, and indoles using iodonium ylide **96**.[126] For example, indoles **98** smoothly react with reagent **96** affording trifluoromethylthiolated products **99** in generally high yields (Scheme 35).
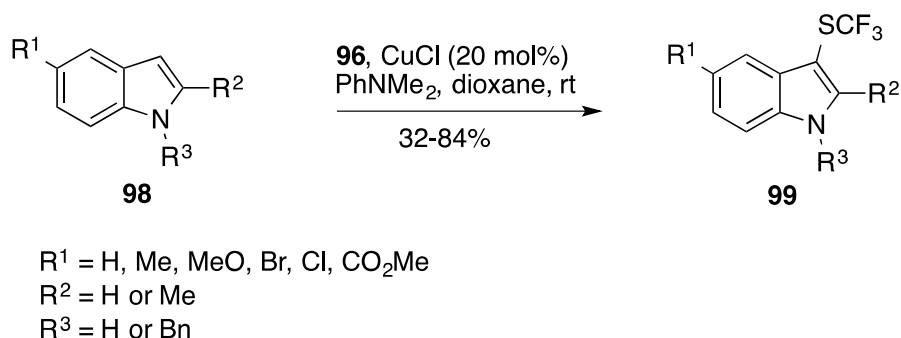
Scheme 35. Thiotrifluoromethylation of indoles.

In a series of more recent publications, reagent **96** has been used for thiotrifluoromethylation of various other nucleophilic substrates, such as: allyl alcohols and boronic acids,[129] arylamines,[130] allylsilanes and silyl enol ethers,[131] and pyrroles.[132] Several examples of thiotrifluoromethylation reactions of these substrates are shown in Scheme 36.
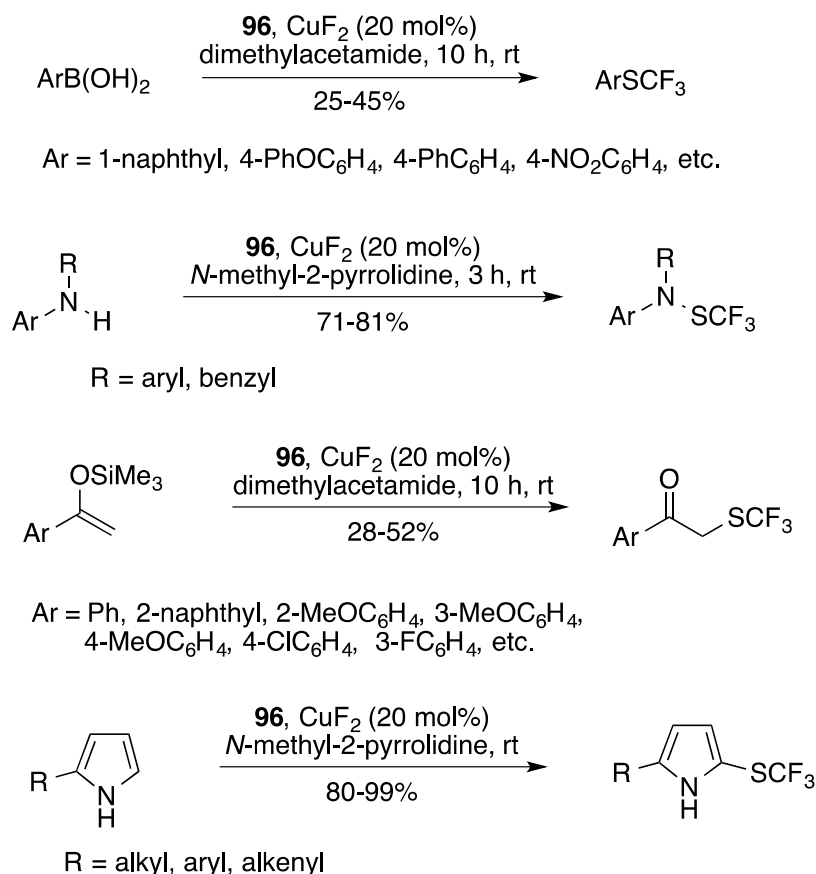
Scheme 36. Thiotrifluoromethylation of organic substrates.

5. Conclusions

This review demonstrates that iodonium ylides of different structural types are becoming increasingly popular reagents in organic synthesis. Iodonium ylides are widely used as efficient carbene precursors, especially useful as reagents for cyclopropanation of alkenes and preparation of heterocyclic compounds. Recently iodonium ylides have been utilized as efficient reagents in the thiotrifluoromethylation and nucleophilic fluorination reactions, which find practical application in Positron Emission Tomography. We anticipate that this synthetically important area of hypervalent iodine chemistry will continue to attract significant research activity in the future.

6. Acknowledgements

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Authors Biographies

Mekhman S. Yusubov born in Georgia. His M.S. (1985), Ph.D. (1991), and Doctor of Chemical Sciences (1998) degrees were earned at Tomsk Polytechnic University in the laboratory of Professor Victor D. Filimonov. He is a Professor and Department Head at Tomsk Polytechnic University. Since 1994 he has been involved in intense international collaborative research programs with leading research laboratories in South Korea, Germany and United Kingdom. In 2004 he started a joint research in the area of hypervalent iodine chemistry with Professor V. V. Zhdankin at the University of Minnesota Duluth. His main research interests are in the fields of chemistry of natural products and hypervalent iodine reagents. Professor M. S. Yusubov has published over 100 scientific papers.

Akira Yoshimura, a native of Osaka, Japan, received his M.S. in 2007 and Ph.D. in 2010, both from Tokushima University, under the supervision of Professor Masahito Ochiai. During 2010-2014 he carried his postdoctoral work with Professor Viktor Zhdankin at the University of Minnesota Duluth, and in 2015 he was appointed to a Research Associate position in the same university. His research interests are in the fields of synthetic and mechanistic organic chemistry of hypervalent main-group elements and heterocyclic chemistry. He published over 30 research papers, mainly related to the chemistry of hypervalent iodine and bromine.

Viktor V. Zhdankin was born in Ekaterinburg, Russian Federation. His M.S. (1978), Ph.D. (1981), and Doctor of Chemical Sciences (1986) degrees were earned at Moscow State University. He moved to the University of Utah in 1990, where he worked for three years as Instructor of organic chemistry and Senior Research Associate with Professor Peter J. Stang. In 1993, he joined the faculty of the University of Minnesota Duluth, where he is currently a Professor of Chemistry. He also has the status of a visiting Professor at Tomsk Polytechnic University. Dr. Zhdankin has published over 250 research papers, gave over a hundred research presentations in many countries, edited several books, co-authored the *Handbook of Heterocyclic Chemistry* (3rd Edition, 2010) with Professors A. R. Katritzky, C. A. Ramsden, and J. A. Joule, and authored a book on *Hypervalent Iodine Chemistry* (Wiley, 2013). His main research interests are in the areas of synthetic and mechanistic organic chemistry of hypervalent main-group elements and organofluorine chemistry. In 2011 he received the National Award of the American Chemical Society for *Creative Research & Applications of Iodine Chemistry*. Since 2003 he is Scientific Editor and a Member of Control Board of *Arkivoc*.