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REVIEW ON SOME LATEST C-N BOND FORMATION REACTIONS BY USING HYPERVALENT IODINE REAGENT

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Abstract : Hypervalent iodine chemistry is a highly growing area in synthetic chemistry because of its environmentally benign nature, mild reaction conditions, short reaction time, and high yield. In synthetic chemistry metal free C-N bond formation reactions have high demand. This review summarizes the use of hypervalent iodine in carbon-nitrogen bond formation with emphasis on their application in heterocyclic compound synthesis.

Keywords – C-N bond formation, hypervalent iodine, diacetoxy iodobenzene, C-H bond functionalization

I. INTRODUCTION

The importance and value of compounds containing nitrogen stem from their extensive existence in nature and broad application in chemistry and biology.[1] The development of effective methods for the formation of C-N bonds is an intensively investigated area of great significance.[2] The N-substituted compounds are also potential building blocks for the synthesis of important pharmaceutical agents with biological activities.[3]Use of hypervalent iodine reagents in organic synthesis is an intensively investigated area. Many methods reported use of hypervalent iodine such as diacetoxy iodobenzene DIB 1, phenyliodine bis(trifluoroacetate) PIFA 2, diaryl iodonium chloride 3, iodosylbenzene 4, hydroxyl(tosyloxy) iodobenzene 5 dichloro iodobenzene 6, phenyliodine bis(*m*-chlorobenzoate) 7, benziodoxoles 8, pseudocyclic iodylarenes 9, 2-iodoxy benzoic acid 10, Iminoiodanes 11 and Dess Martin periodinane 12.[4] This review summarizes some latest C-N Bond Formation Reaction by Using Hypervalent Iodine Reagent.

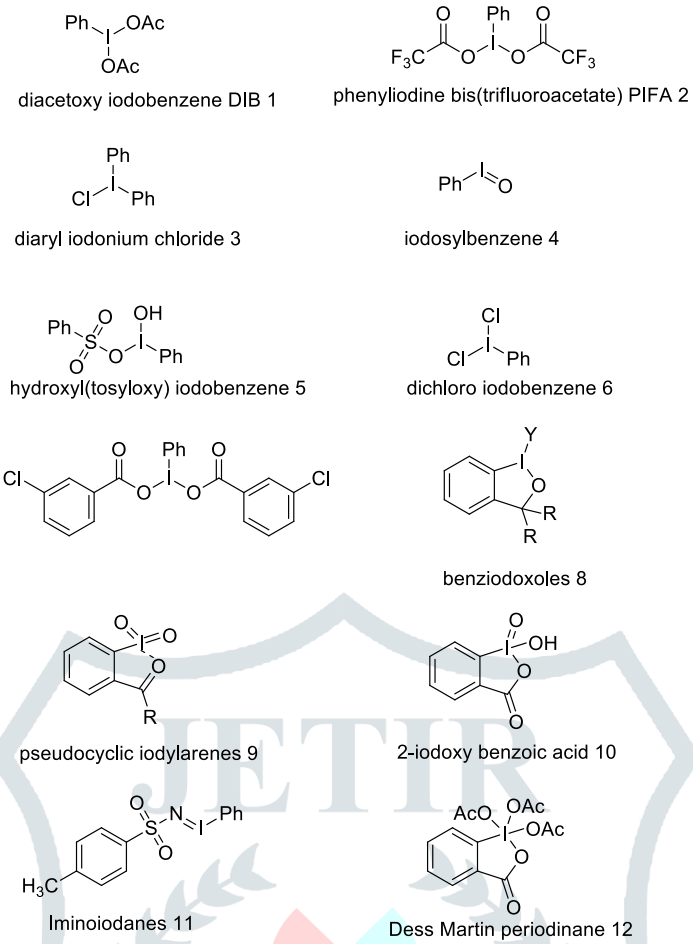
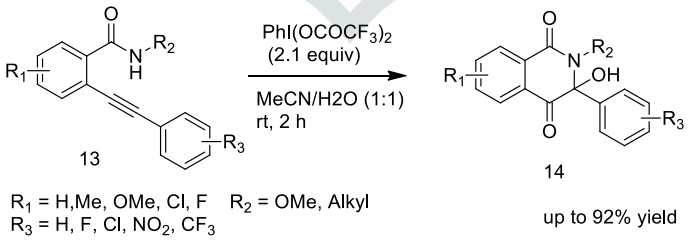


Figure 1. Some examples of hypervalent iodine reagents

II. IODINE (III) MEDIATED INTRAMOLECULAR C-N BOND FORMATION:

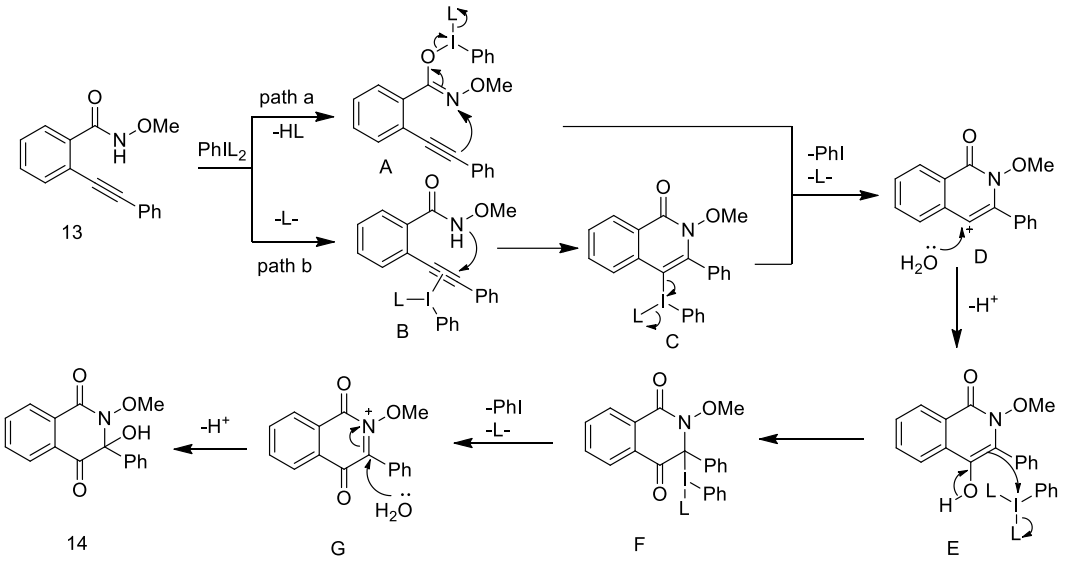
1. IODINE (III) MEDIATED INTRAMOLECULAR C(SP)-N BOND FORMATION:

In literature, there are very good results of C(sp)-N bond formation reactions by using hypervalent iodine that give very useful heterocyclic compound in step economic and environment-friendly way. When In 2015 Du et al developed a synthesis of 3- hydroxy-2,3-dihydroisoquinoline-1,4-diones 14 skeleton by hypervalent iodine (PIFA) mediated cyclization followed by oxidative hydroxylation of o-(1-alkynyl)benzamides 13 (Scheme 1).[5]



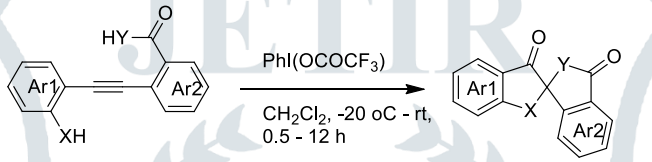
Scheme 1. Synthesis of 3-hydroxy-2,3-dihydroisoquinoline-1,4-diones.

They proposed a reaction mechanism in two ways in path a, the intermediate A is formed by reaction of the N-methoxyamide moiety 13 with PIFA by releasing one molecule of trifluoroacetic acid. Then intermediate D is formed by intramolecular cyclization of A with loss of iodobenzene and a trifluoroacetate anion. In path b, the PIFA coordinate with the triple bond to give intermediate B. This intermediate will undergo cyclisation to give intermediate C. The elimination of an iodobenzene and a trifluoroacetate anion will lead to the same intermediate D. Intermediate E formed by the attack of water molecule will be further oxidized by PIFA to give F intermediate which will reductively eliminate an iodobenzene molecule and a trifluoroacetate anion to give iminium ion G. nucleophilic attack of water on intermediate G followed by proton removal will give desired product 14.



Scheme 2. Plausible reaction mechanism

Later in the same year du group reported the reaction of di-orthosubstituted diarylacetylenes 15-17 with PIFA forming structurally novel spiro compound 18-20 by the cascade annulation process. The complex spiro cyclization of alkyne substrates under metal-free conditions involving two bond formations and one oxygen insertion in the form of a cascade reaction is reported for the first time (Scheme 3).[6]

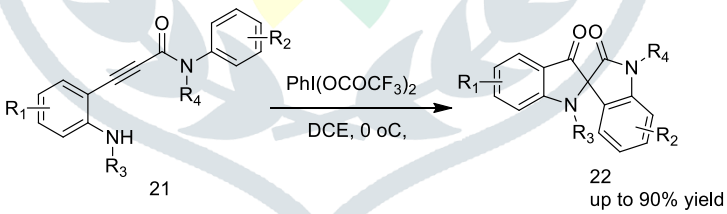


15 (X = N-Ts, Y = O)
16 (X = O, Y = O)
17 (X = O, Y = N-OMe)

18 (X = N-Ts, Y = O)
19 (X = O, Y = O)
20 (X= O, Y = N-OMe)

Scheme 3. Spirocyclization of di-orthosubstituted diarylacetylenes

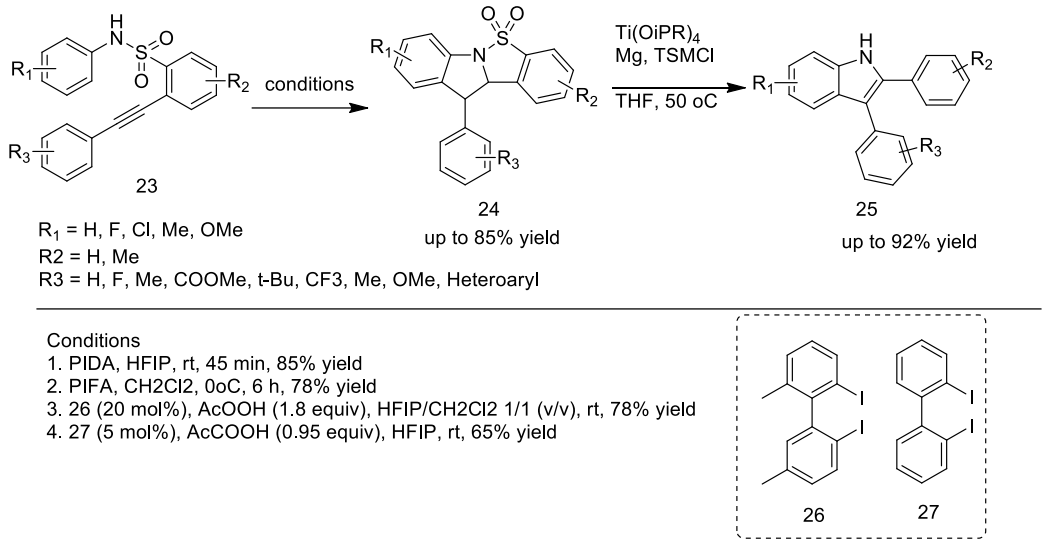
Further, the same group unveiled the method for the construction of a series of diversely functionalized 2-spiropseudoindoxyl compounds 22 from 2-sulfonamido-N-phenylpropiolamide derivatives 21 by using PIFA as an oxidant (Scheme 4).[7]



R1 = H, Cl, Br, F, CH_3, OMe
R2 = H, Cl, Br, F, CH_3, OMe
R3 = Ts, Ms, $PhSO_2$, p-Cl-$PhSO_2$
R4 = Me, Et, n-Bu

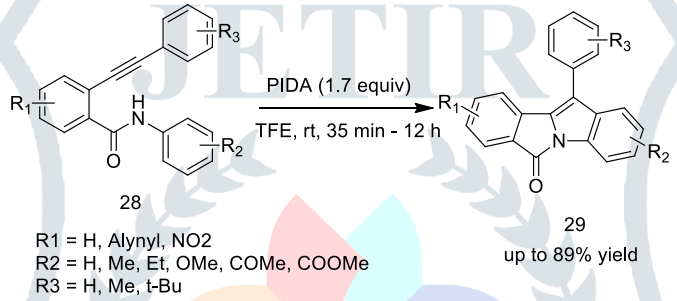
Scheme 4. Synthesis of 2-spiropseudoindoxyl.

In 2016 Muniz group synthesized 2,3-diarylated indoles 25 from 24 by traceless tether removal. The compound 24 is prepared by an intramolecular electrophilic N-H and C-H bond functionalization of 23 by reaction with PIDA (Scheme 5).[8]



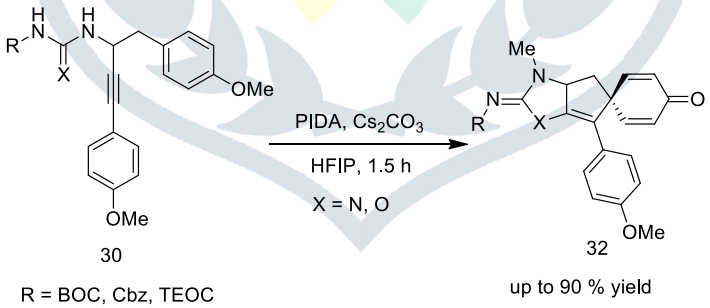
Scheme 5. Synthesis of 2,3-diarylated indoles

Maurya et al in 2015 developed PIDA-mediated intramolecular cascade oxidative cyclization of 2-(1-arylethynyl)benzamides 28 that gives 11-aryl-6H-isoindolo [2,1-a] indol-6-ones 29 at room temperature in good to excellent yields (Scheme 6).[9]



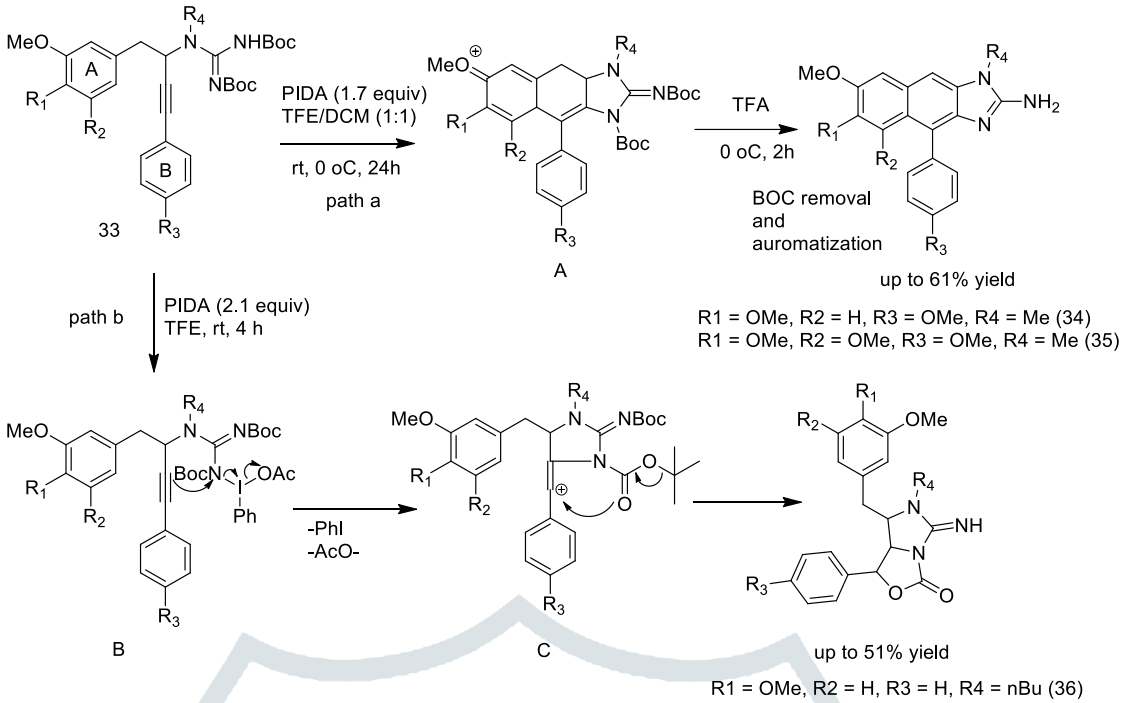
Scheme 6. Cascade oxidative cyclization of 2-(1-arylethynyl)benzamides

In 2017 Lovely et al demonstrated Tandem Oxidative Dearomatizing Spirocyclization of Propargyl Guanidines 30 promoted by PIDA and Cs_2CO_3, to construct complex spiro heterocyclic frameworks 31. The complete framework of the Leucetta alkaloids, spirocalcaridine A and B is directly prepared by this method (Scheme 7).[10]



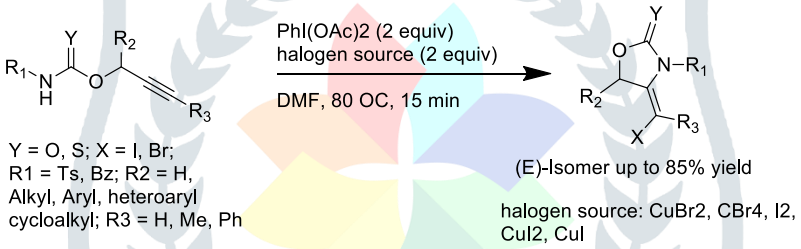
Scheme 7. Spirocyclization of Propargyl Guanidines

In the same year Eycken group revealed similar type of transformation. In this Cascade Cyclization of Propargylguanidines 33 is mediated by PIDA to give either Kealiinine B 34 and C 35 or ring-fused guanidine 36 depending on the electronic nature of the acetylene substituent. The former product was given by substrates that had two or three methoxy groups on the phenyl ring A and an electron-rich aromatic ring B while later was given by a substrate lacking this substituent (Scheme 8).



Scheme 8. Cascade Cyclization of Propargylguanidines

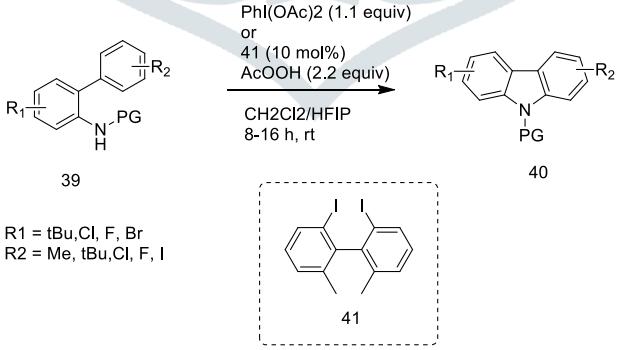
In 2017 Xiang et al reported 1,2-aminohalogenation of prop-2-yn-1-yl carbamates 1 with $PhI(OAc)_2$ 2 and different halogen sources. This reaction affords diverse (E)-4-(halomethylene)oxazolidin-2-ones 3 with excellent stereoselectivity through intramolecular cyclization of nitrogen radical (Scheme 9).[11]



Scheme 9. 1,2-aminohalogenation of alkynes

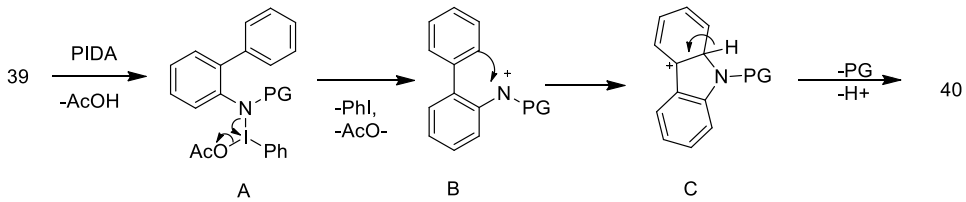
2. INTRAMOLECULAR C(SP2)-N BOND FORMATION

In 2011 Antonchick et al demonstrated the synthesis of carbazole derivatives 40 by hypervalent iodine-mediated Oxidative, Intramolecular C-H Bond Amination of acetaminobiphenyl 39 (Scheme 10).[12]



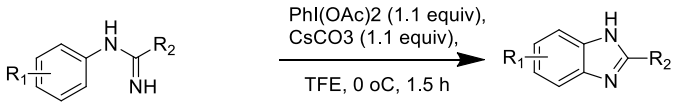
Scheme 10. Synthesis of carbazole derivatives

At first PIDA reacts with the acetaminobiphenyl 39 to give intermediate A which is then transformed into nitrenium ion B through an oxidative process. The electron-rich arene attacks the electron-deficient nitrenium ion B to give the desired product 40 (Scheme 11).



Scheme 11. Proposed mechanism

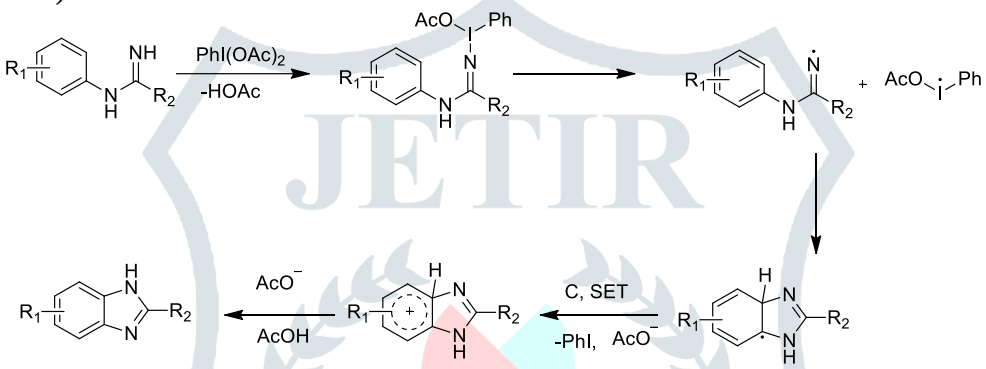
Zhu et al developed a simple and efficient method for the synthesis of 2-substituted benzimidazoles by oxidative imidation of aromatic C-H bond of N-arylamidines with the help of $PhI(OAc)_2$. It is possible to prepare Diversified 2-alkylbenzimidazoles by this method which is difficult to prepare by similar Pd or Cu catalysed approaches (Scheme 12).[13]



R1 = Me, Br, Cl, F, tBu, NO2
R_2 = Me, Cyclopropyl, Cyclohexyl, tBu, Iso propyl and Substituted aryl

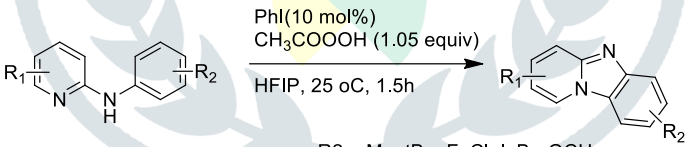
Scheme 12. Synthesis of 2-substituted benzimidazoles

Initially, PIDA and amidine substrate react to give N-iodoimido species, which on homolysis generates the n-centered free-radical intermediate b and hypervalent iodine- (iii)-centered radical, then this n-centered free-radical attack on aromatic ring to generate intermediate 6 which is oxidized by intermediate c to give cyclohexadienyl cation E finally in situ acetate ion will abstract proton from E to give desired product (Scheme 13).



Scheme 13. Plausible mechanism

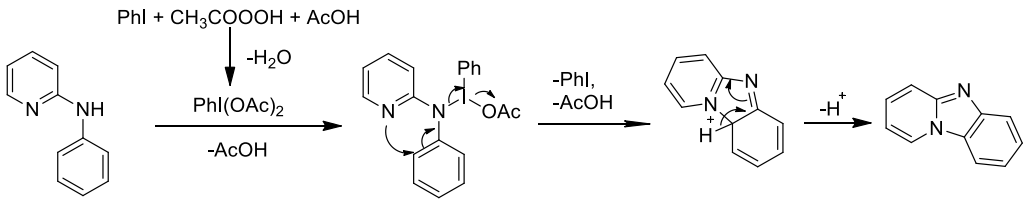
Further in 2013 Zhu et al developed a synthesis of pyrido[1,2-a]benzimidazoles by oxidation of N-aryl-2-aminopyridines with in situ generated $Ph(IOAc)_2$ from iodobenzene and peracetic acid. In the same way they synthesized 1H-benzo[d]imidazoles from N-arylamidines (Scheme 14).[14]



R1 = Me, Cl, F, CO2Et, CF3 R2 = Me, tBu, F, Cl, I, Br, OCH_3

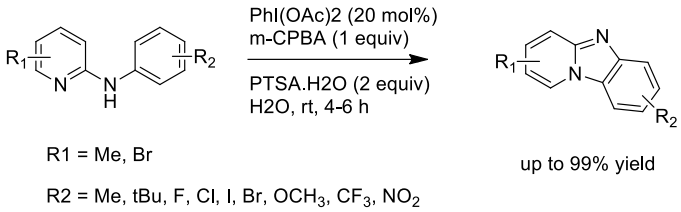
Scheme 14. Synthesis of pyrido[1,2-a]benzimidazoles

In the first instance, iodobenzene and peracetic acid react in the presence of acetic acid to give $PhI(OAc)_2$ which reacts with N-aryl-2-aminopyridines to give an intermediate which contains an electrophilic N-iodo moiety. Then nucleophilic attack of the pyridine nitrogen on the aromatic ring followed by release of PhI and AcO^- gives intermediate which on deprotonation gives the desired product (Scheme 15).



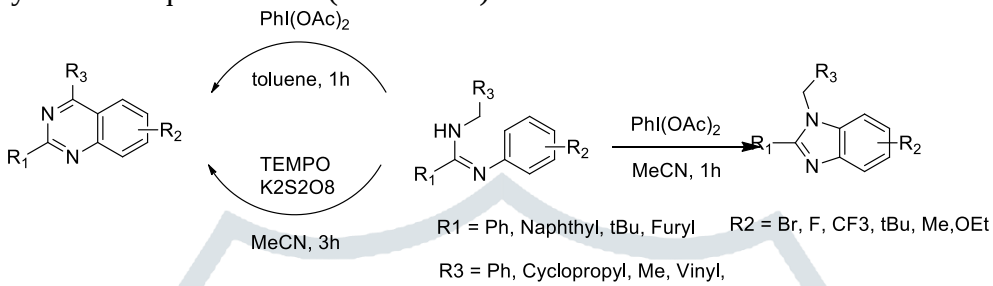
Scheme 15. Proposed reaction path way

Later in 2014 Das group did the same reaction in water by in situ generating HTIB (Koser's reagent). This approach is more economical due to water as a solvent and high regioselectivity is obtained (Scheme 16).[15]



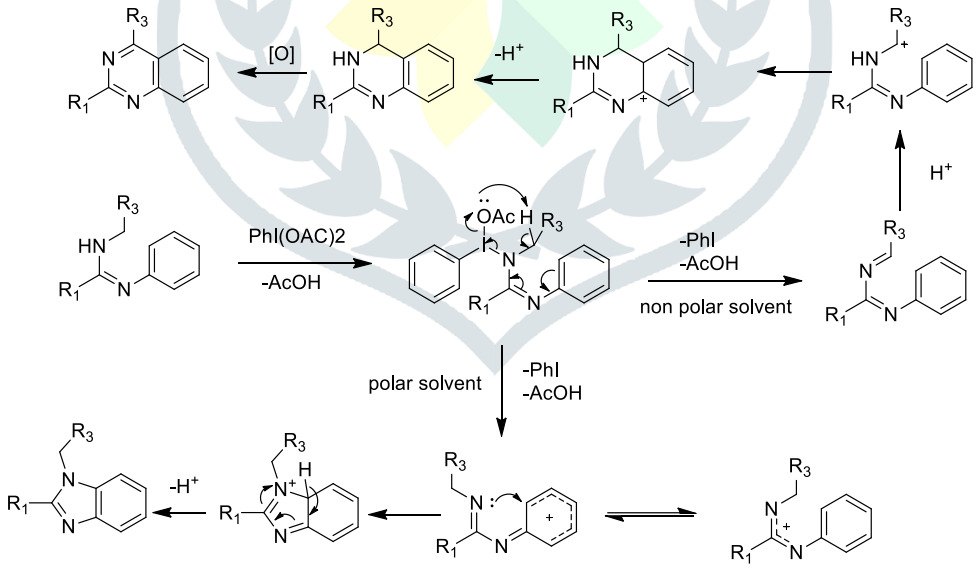
Scheme 16. Synthesis of pyrido[1,2-a]benzimidazoles in water

Long et al reported a simple method for the synthesis of multisubstituted quinazolines and benzimidazoles by the reaction of amidines with $PhI(OAc)_2$. The product of the reaction depends on the polarity of the solvent in polar solvent the reaction affords benzimidazoles while in nonpolar it gives quinazolines. The same reaction can be done by using TEMPO (catalytic) and $K_2S_2O_8$ (excess) as an oxidant for the synthesis of quinazolines (Scheme 17).[16]



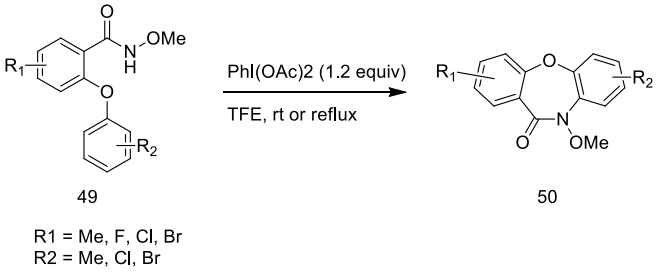
Scheme 17. Synthesis of benzimidazoles and quinazolines

The reaction pathway starts with the interaction of amidine and $PhI(OAc)_2$ to form N-(phenylacetoxyiodo)imidamido species. In nonpolar solvent, this species is converted to the neutral N-benzylidene-N′-phenylcarboxamidine by benzylic deprotonation assisted by the intramolecular acetate group. In situ generated acetic acid will protonate N-benzylidene-N′-phenylcarboxamidine to give benzylic cation species which will undergo an intramolecular Friedel−Craft reaction to give intermediate E, which is subsequently oxidized to afford the final product quinazoline. In a nonpolar solvent, the species is converted into a cationic intermediate due to the solvent stabilization effect. Then the nitrogen's lone pair will attack this cation giving an intermediate which on deprotonic rearomatization delivers the desired product (Scheme 18).



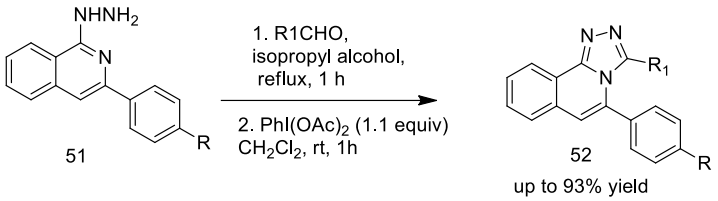
Scheme 18. Reaction mechanism

In 2015 Du's group unveiled a method for the synthesis of Dibenzoxazepinone compounds from 2-(aryloxy)benzamides through hypervalent iodine(III)-mediated oxidative cyclization. Reaction is thought to precede through nitrenium ion intermediate (Scheme 19).[17]



Scheme 19. Synthesis of Dibenzoxazepinone

Khan et al demonstrated $PhI(OAc)_2$ mediated intramolecular oxidative cyclization of 1- (3-arylisoquinolin-1-yl)-2-(arylmethylene)hydrazines 51 to 5-aryl-3-(aryl)- [1,2,4]triazolo[3,4-a] isoquinolines 52 in very proficient way (Scheme 20).[18]

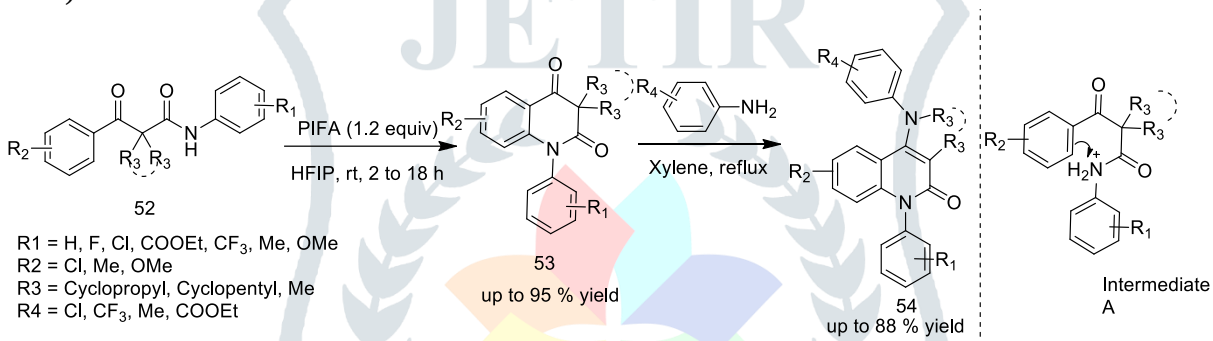


R = H, R1 = 2-thiophenyl, 4-cyanophenyl, 4-methoxyphenyl, 2-benzothiophenyl, 4-chlorophenyl, 2-trifluoromethylphenyl

R = Cl, R1 = 2-Furanyl, 4-N,N-Dimethylaminophenyl, 3-Indolyl, 2,5-Dimethyl-4-thiazolyl, 4-methylphenyl

Scheme 20. Oxidative cyclization of 1- (3-arylisoquinolin-1-yl)-2-(arylmethylene)hydrazines

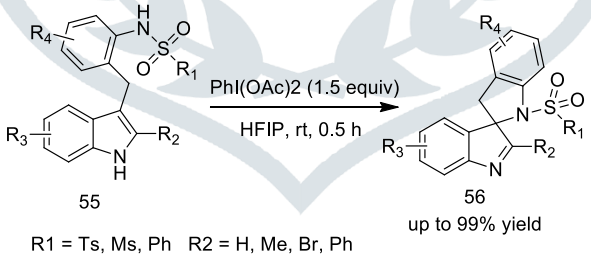
In 2017 Zhang group reported PIFA-Mediated oxidative cyclization of 1-aroyl-N-arylcyclopropane-1-carboxamides 52 which furnishes spirocyclopropane quinolinedione 53, which further refluxed with an amine in xylene to give pyrrolo[3,2-c]quinolinones 54. The reaction goes through nitrenium ion intermediate A, which is formed by oxidation of 1-aroyl-N-arylcyclopropane-1-carboxamides 52 by PIFA (Scheme 21).[19]



R1 = H, F, Cl, COOEt, CF_3, Me, OMe
R2 = Cl, Me, OMe
R3 = Cyclopropyl, Cyclopentyl, Me
R4 = Cl, CF_3, Me, COOEt

Scheme 21. Synthesis pyrrolo[3,2-c]quinolinones 54

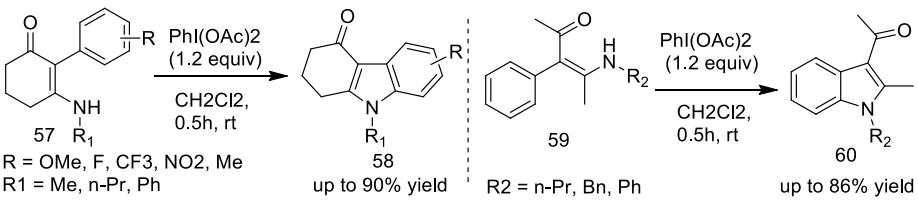
Another interesting transformation of Zhu group is facile construction of the spiro[indoline-3,2'-pyrrolidine] skeleton 56 via $PhI(OAc)_2$-mediated dearomative C–N coupling of C3 sulfonamide linked indole derivatives 55 (Scheme 22). [20]



R1 = Ts, Ms, Ph R2 = H, Me, Br, Ph
R3 = H, Me, OMe, F, Cl R4 = H, OMe, Me

Scheme 22. Construction of the spiro[indoline-3,2'-pyrrolidine] skeleton 56

In 2012 du group described PIFA-mediated intramolecular cyclization of 2-aryl enaminones 57 for the synthesis of carbazolones derivatives 58 and 3-acetylindoles 59, which proceed via oxidative C–N bond formation (Scheme 23).[21]



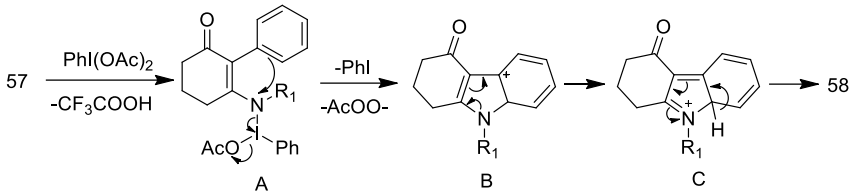
R = OMe, F, CF3, NO2, Me
R1 = Me, n-Pr, Ph

R2 = n-Pr, Bn, Ph

Scheme 23. Cyclization of 2-aryl enaminones 57

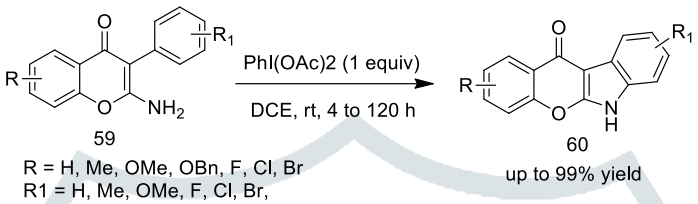
At first, PIDA reacts with enaminone 57 to give N-iodo intermediate A, which will undergo cyclization to give Wheland intermediate B. Intermediate B is stabilized by the lone pair on nitrogen

through conjugation to give the iminium salt C, which will spontaneously undergo deprotonation to give desired compound 58 (Scheme 24).



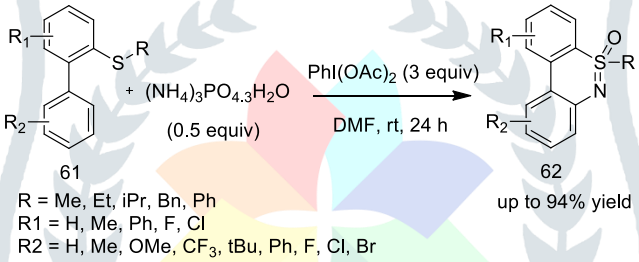
Scheme 24. Reaction pathway

Later in 2015 same group reported similar type of reaction where the 2-Amino-3-phenyl-4H-chromen-4-one 59 is treated with PIDA which affords chromeno[2,3-b]indol-11(6H)-ones 60 via Intramolecular Oxidative C(sp2)–N(H_2) Bond Formation (Scheme 25).[22]



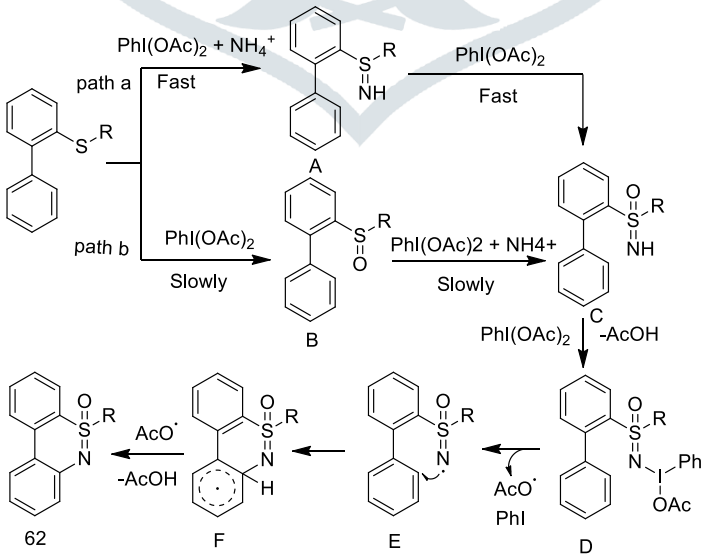
Scheme 25. Synthesis of chromeno[2,3-b]indol-11(6H)-ones 60

In 2018 Chen group unveiled synthesis of dibenzothiazines 62 from 2-biphenyl sulfides 61 via one-pot N, O transfer and intramolecular C-H amination assisted by PIDA (Scheme 26).[23]



Scheme 26. Dibenzothiazines synthesis

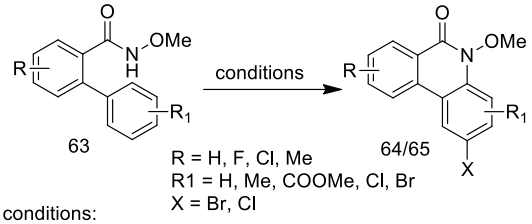
Initially PIDA oxidize sulfide 61 to sulfoximine C via sulfilimine A or sulfoxide B. sulfoximine C further oxidized by PIDA to give N-centered radical E through D. This electrophilic N-centered radical E directly attacks on aromatic ring to give intermediate F, which on Re-aromatization furnishes title compound 62 (Scheme 27).



Scheme 27. Proposed mechanism

In 2012 Xue group reported one-pot sequential hypervalent iodine promoted amindation/halogenation reaction to synthesize 2-substituted-phenanthridinones 64 and 65. In this protocol,

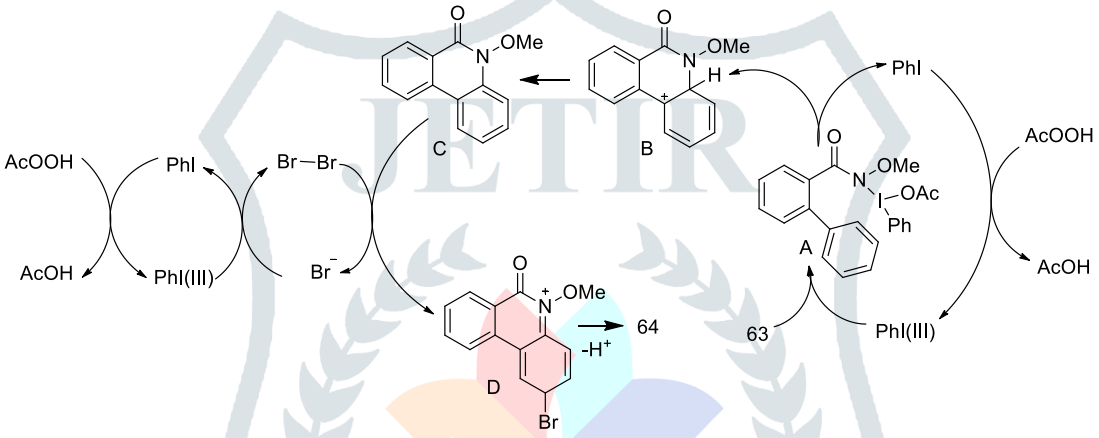
N-Methoxybenzamides 63 was treated with peracetic acid and a catalytic amount of iodobenzene in the presence of TBAB or TBAC as bromide or chloride source respectively (Scheme 28).[24]



conditions:
1) PhI (20 mol %), AcOOH (2.5 equiv.) TBAB (1.2 equiv.), HFIP, air, 3 h, 64, up to 89% yield
2) PhI (20 mol %), AcOOH (2.5 equiv.) TBAC (1.2 equiv.), HFIP, 3 h, 65, up to 88% yield
3) PIDA (2.5 equiv), TBAC (1.2 equiv.), HFIP, air, 3 h, 65, up to 77% yield

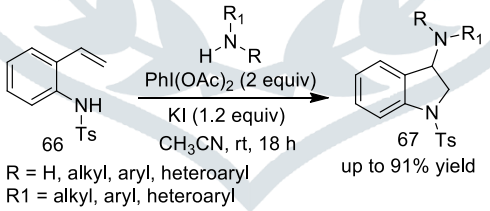
Scheme 28. One-pot synthesis of 2-substituted-phenanthridinones 64 and 65

At the beginning Methoxybenzamide reacts with the in situ generated hypervalent iodine reagent to give intermediate A. Electrophilic attack of nitrogen on adjacent aromatic ring provides B. Rearomatization of B with loss of proton gives compound C. This C further reacts with Br_2, Which is in-situ generated from the reaction of hypervalent iodine reagent with the bromide source (Scheme 29).



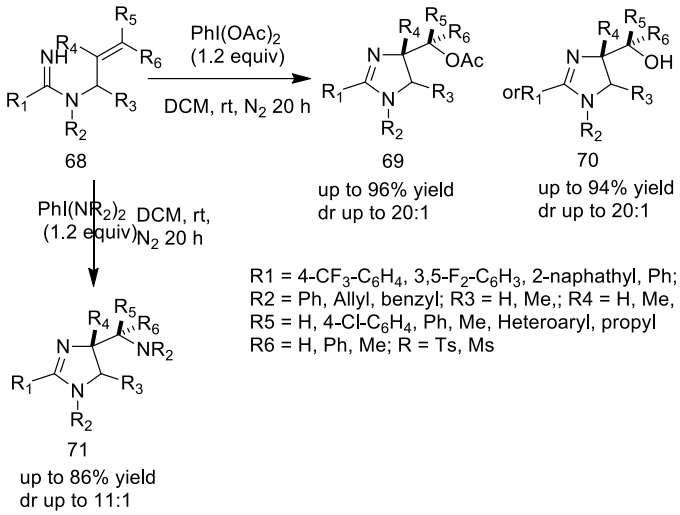
Scheme 29. Possible reaction pathway

In 2014 Johnston demonstrated inter and intramolecular oxidative diamination of terminal alkenes assisted by PIDA for the synthesis of 3-aminoindolines 67. In this approach, terminal alkene 66 is treated with primary or secondary amines in the presence of stoichiometric amounts of iodide salt and PIDA (Scheme 30).[25]



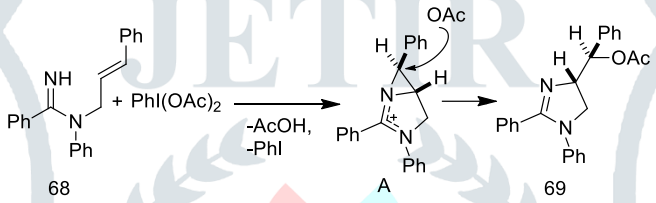
Scheme 30. Oxidative diamination of terminal alkenes

Later in 2014, Chiba group described diastereoselective anti-aminooxygenation and anti-diamination of Alkenes with Amidines by Hypervalent Iodine Reagents. In this protocol N-allylamidines 68 is made to react with $PhI(OCOCF_3)_2$ or $PhI(OAc)_2$ for the aminooxygenation which afford 69 or 70 and with $PhI(NTs_2)_2$ for diamination to synthesize 71 (Scheme 31). [26]



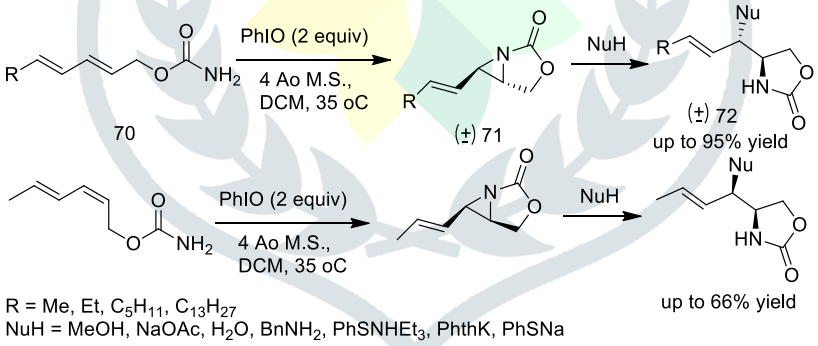
Scheme 31. Diastereoselective anti-aminooxygenation and anti-diamination of Alkenes

At the beginning PIFA oxidises N-allylamidines to generate nitrenium ion, which will add on alkene to give syn-aziridinium ion A. Further nucleophilic ring-opening of aziridinium ion A, with counter carboxylate ion furnishes anti-aminooxygenated product 69 (Scheme 32).



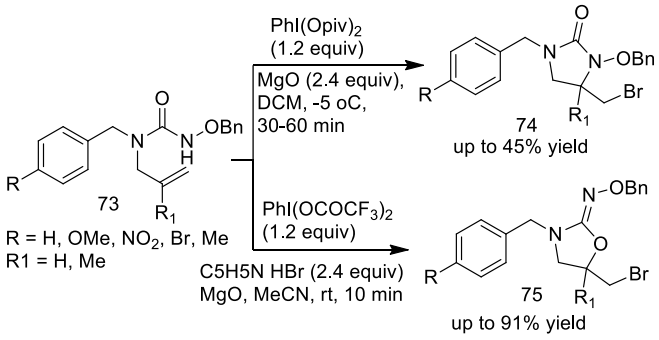
Scheme 32. Possible mechanism

Diaz group in 2014 reported PhIO catalyzed aziridination of dienyl carbamates 70 to give vinylaziridines 71, which were further treated with nucleophiles to synthesize oxazolidinones 72 in a regio- and stereoselective manner (Scheme 33).[27]



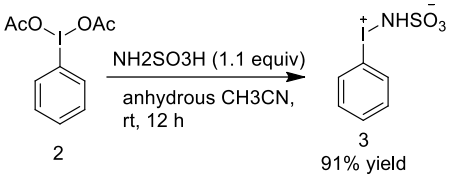
Scheme 33. Aziridination of dienyl carbamates

In 2019 Cariou et al described hypervalent iodine mediated oxybromocyclization and aminobromocyclization of N-benzyloxy urea. When N-benzyloxy urea 73 is treated with $PhI(OPiv)_2$ in presence of tetrabutylammonium bromide and magnesium oxide chemoselectively afforded aminobromocyclized product 74. While oxybromocyclization 75 is chemoselectively achieved by treatment with $PhI(OCOCF_3)_2$, pyridinium bromide, and magnesium oxide (Scheme 34).[28]

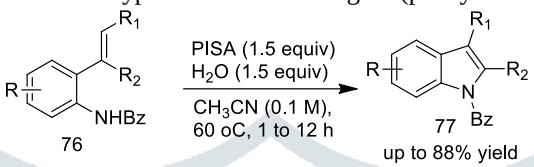


Scheme 34. Oxybromocyclization and aminobromocyclization of N-benzyloxy urea

In 2018 Zhang group synthesized bench-stable, water-soluble novel hypervalent iodine reagent (phenyliodonio)sulfamate (PISA) 3 with an I−N bond. Subsequently they used same reagent 3 for the synthesis of various indoles 77 by C-H amination of 2-alkenylanilines 76 (Scheme 35A). Total synthesis of indometacin zidometacin and pravadoline is also reported (Scheme 35B).[29]



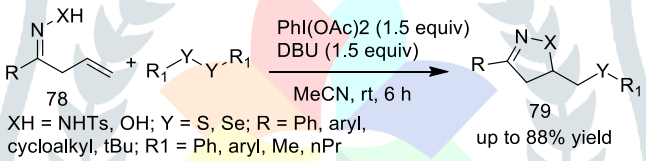
Scheme 35A. Synthesis of novel hypervalent iodine reagent (phenyliodonio)sulfamate (PISA) 3



R = H, F, Cl, Br, CF_3, Me, Ph, furyl, thienyl, OMe, CO_2Me
R1 = H, Me, nPr, Bn,
R2 = Me, Et, n-pentyl, cyclopropyl, Ph, H

Scheme 35B. C-H amination of 2-alkenylanilines 76

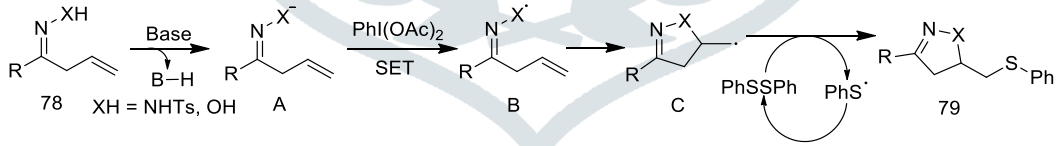
In 2018 Chun Cai unveiled the synthesis of pyrazoline and isoxazoline derivatives 79 from β, γ-unsaturated hydrazones and oximes 78 via oxidative cascade radical cyclization/sulfenylation or selenylation of β, γ-unsaturated hydrazones and oximes mediated by PIDA (Scheme 36).[30]



XH = NHTs, OH; Y = S, Se; R = Ph, aryl, cycloalkyl, tBu; R1 = Ph, aryl, Me, nPr

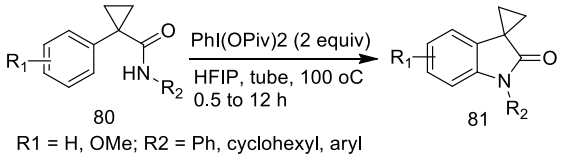
Scheme 36. Synthesis of pyrazoline and isoxazoline derivatives 79

At the start base removes the proton from β,γ-unsaturated hydrazone or oxime 78 to give anionic intermediate A. Further, a single electron oxidation of A by PIDA gives the N-centered or O-centered radical B, which will undergo cyclization to form C-centered radical C. This C-centered radical C will react with diphenyl disulfide to afford the desired product 79 (Scheme 37).



Scheme 37. Proposed reaction mechanism

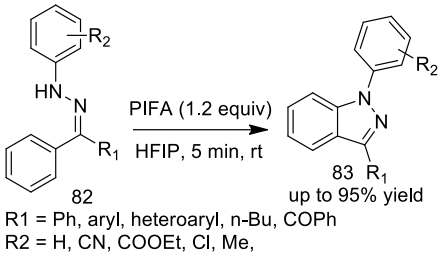
Zhang group in 2017 demonstrated oxidative cyclization of secondary cyclopropyl carboxamides 80 promoted by $PhI(OPiv)_2$ for the synthesis of cyclopropyl spirooxindoles 81 (Scheme 38).[31]



R1 = H, OMe; R2 = Ph, cyclohexyl, aryl

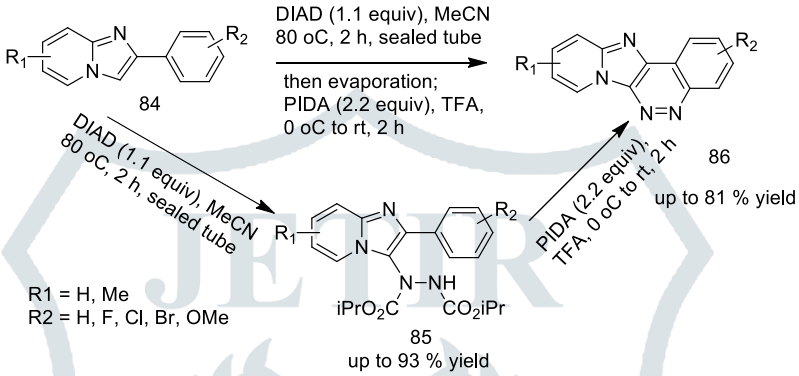
Scheme 38. Oxidative cyclization of secondary cyclopropyl carboxamides 80

In the same year same group reported PIFA mediated oxidative C-N bond formation for the synthesis of 1H-indazoles 83 from readily available arylhydrazones 82 (Scheme 39).[32]



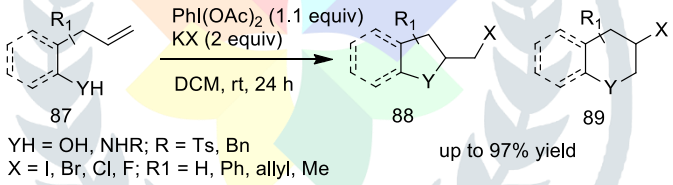
Scheme 39. Synthesis of 1H-indazoles 83

In 2016 Gowravaram Sabitha group published a two-step synthesis of pyrido[2',1':2,3]imidazo[4,5-c]cinnoline derivatives. The first step involves C-3 regioselective hydrazination of 2-arylimidazo[1,2-a]pyridines by using diisopropyl azodicarboxylate to furnish intermediate compounds diisopropyl 1-(2-arylimidazo[1,2-a] pyridin-3-yl)hydrazine-1,2-dicarboxylates, which further oxidised with PIDA to give title compound (Scheme 40). [33]



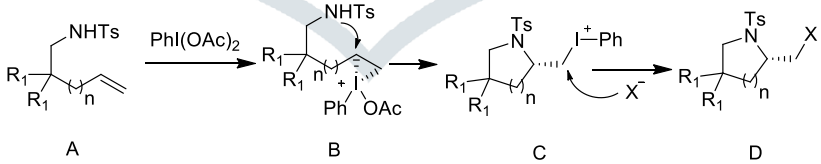
Scheme 40. Synthesis of pyrido[2',1':2,3]imidazo[4,5-c]cinnoline derivatives

Li group in 2014 published haloamidation, haloetherification and halolactonization of unfunctionalized olefins by using PIDA and potassium halide (Scheme 41).[34]



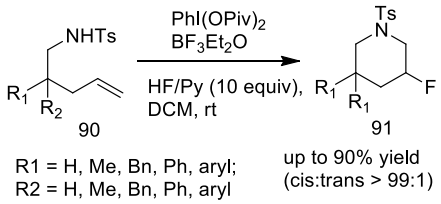
Scheme 41. Haloamidation, haloetherification and halolactonization of unfunctionalized olefins

At first, PIDA activates the C=C double bond in substrate A, then the intramolecular nucleophilic attack of nitrogen atom on the three-membered ring in B gives the intermediate C. the attack of halide ion on C afford desired product D (Scheme 42).



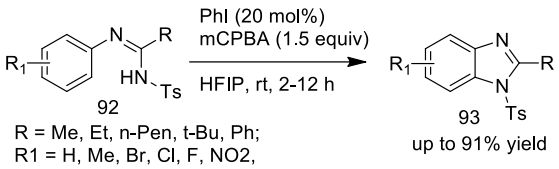
Scheme 42. Reaction mechanism

In 2012 li group reported Metal-free aminofluorination of tosyl-protected pent-4-en-1-amines mediated by PhI(OPiv)$_2$/hydrogen fluoride–pyridine system for the synthesis of 3-F-piperidines (Scheme 43).[35]



Scheme 43. Aminofluorination of tosyl-protected pent-4-en-1-amines

In 2012 Punniyamurthy et al discovered oxidative C–H amination of N″-aryl-N′-tosyl/N′-methylsulfonylamidines and N,N′-bis(aryl)amidines 92 with the help of mCPBA and catalytic amount of iodobenzene for the synthesis of 1,2-disubstituted benzimidazoles 93 (Scheme 44).[36]

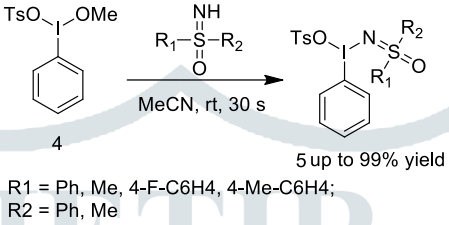


Scheme 44. Synthesis of 1,2-disubstituted benzimidazoles 93

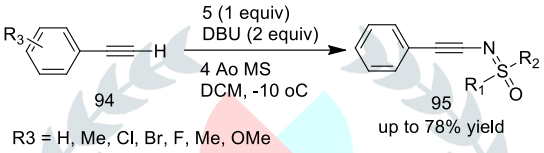
III. INTERMOLECULAR C-N BOND FORMATION

1. INTERMOLECULAR C(sp)-N BOND FORMATION

In 2016 Bolm group reported the synthesis of novel sulfoximidoyl-containing hypervalent iodine reagent 5 by ligand exchange reactions of methoxy- (tosyloxy)iodobenzene 4 (MTIB) with NH sulfoximines (Scheme 45). Further sulfoximidations of terminal alkyne 94 is achieved by using synthesized hypervalent iodine to afford 95 in excellent yield (Scheme 46).[37]

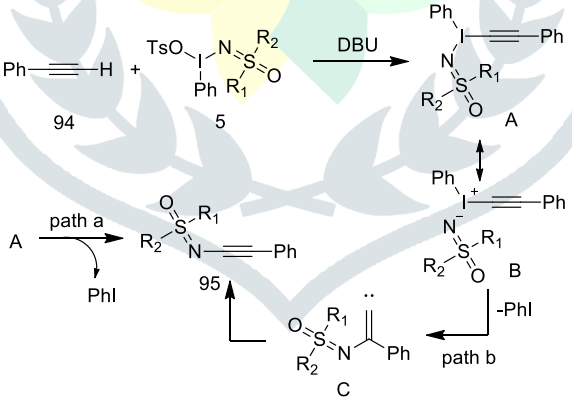


Scheme 45. synthesis of novel sulfoximidoyl-containing hypervalent iodine reagent



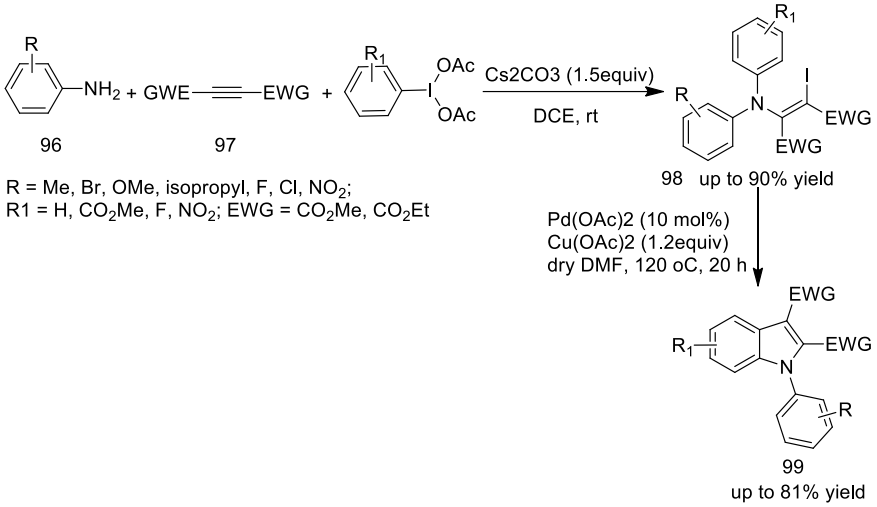
Scheme 46. sulfoximidations of terminal alkyne

At first alkyne 94 and iodine(III) reagent 5 react in the presence of DBU to give intermediate A. This intermediate A react in two way. In path, a reductive elimination of phenyliodide gives product 95. Path b proceeds via alkylidenecarbene C generated from ionic species B



Scheme 47. Proposed reaction mechanism of sulfoximidations

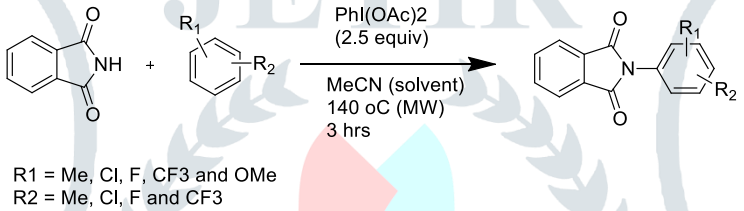
Sharada et al synthesized Iodinated Enamines by Stereoselective Aminoiodination of Activated Alkynes with PIDA and amines. This iodinated enamine is further treated with Pd for the synthesis of indole derivatives (Scheme 47).[38]



Scheme 47. Stereoselective Aminoiodination of Activated Alkynes with PIDA

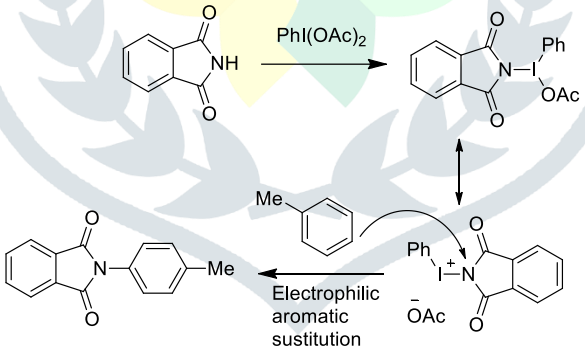
2. INTERMOLECULAR C(sp2)-N BOND FORMATION

DeBoef group reported the synthesis of anilines by oxidative coupling of phthalimide 4 with an unfunctionalized arenes 5 by using $PhI(OAc)_2$ 2 under microwave heating. This method is orthogonal to the conventional method of synthesizing anilines, which relies on electrophilic nitration/reduction strategies or metal-catalyzed coupling of prefunctionalized arenes (Scheme 48).[39]



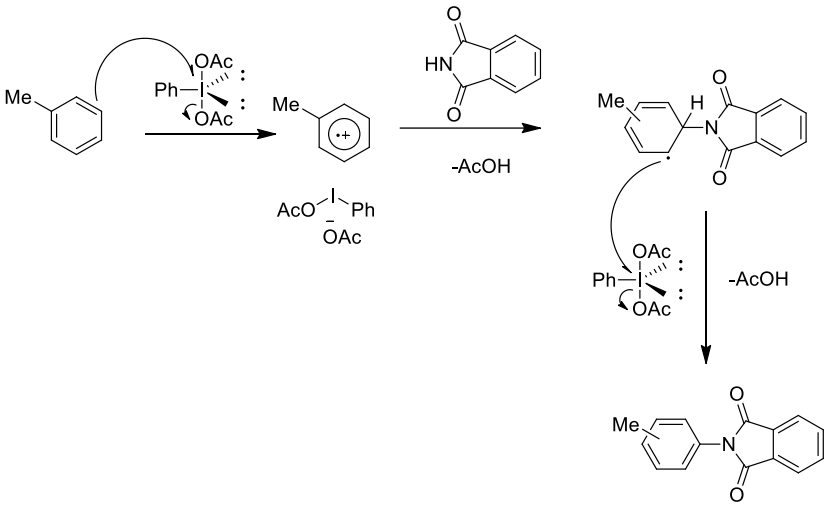
Scheme 48. synthesis of anilines by oxidative coupling of phthalimide

They proposed two mechanistic approaches for this reaction, in the first mechanistic approach $PhI(OAc)_2$ 2 reacts with phthalimide to give intermediate 6 which is in equilibrium with 7. This intermediate 7 will attack on arene to give the product (Scheme 49).



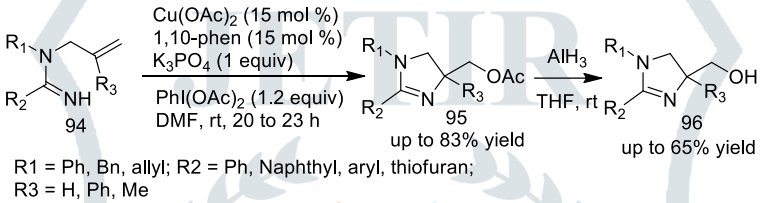
Scheme 49. Proposed reaction mechanism of oxidative coupling of phthalimide

Alternatively, $PhI(OAc)_2$ could oxidize the electron-rich arene substrate to a radical cation (27), and nucleophilic attack on such a radical cation should be relatively nonregioselective. The consequent radical intermediate could then be oxidized to form a Wheland-type arenium ion. These two individual oxidation steps may indicate why two equivalents of $PhI(OAc)_2$ are required to achieve complete conversion (Scheme 50).



Scheme 50. Proposed reaction mechanism of oxidative coupling of phthalimide

A Cu-catalyzed aminoacetoxylation of N-alkenylamidines has been achieved using $PhI(OAc)_2$ as an oxygen source for the synthesis of 4-acetoxymethyl-4,5-dihydroimidazoles, which could be further converted into 2,3-diaminopropanol derivatives using AlH_3 as a reductant (Scheme 51).[40]



Scheme 51. Aminoacetoxylation of N-alkenylamidines

IV. Conclusion

Literature regarding the latest C-N bond formation reactions are thoroughly reviewed and discussed in this review which is useful for academicians and researchers in this field. Researchers will get a brief idea about this field after reading this review.

V. Acknowledgment

The authors are thankful to the Director, Institute of Science, Nagpur.

VI. References

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