

HYPERVALENT IODINE MEDIATED OXIDATIVE ANNULATIONS AND CROSS DEHYDROGENATIVE COUPLINGS.

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By

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Indian Institute of Technology Hyderabad

to the

DEPARTMENT OF CHEMISTRY

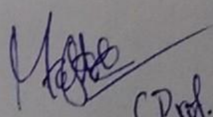
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INDIA

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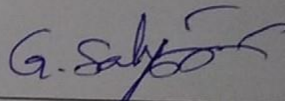
APPROVAL SHEET

This thesis entitled "**Hypervalent Iodine Mediated Oxidative Annulations and Cross Dehydrogenative Couplings**" by **Sitansu Muni** is approved for the degree of Master of Science from IIT Hyderabad.


(Prof. F. A. Khan)

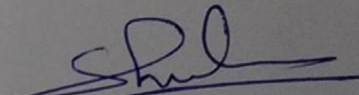
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DECLARATION

I declare that this written submission represents my ideas in my own words, and where others ideas or words have been included; I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/ data/ fact/ source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

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Sitansu Muni
CY14MSCST11020

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Finally I would like to thank the almighty for giving me a chance to work in this world.

HYPERVALENT IODINE MEDIATED OXIDATIVE ANNULATIONS AND CROSS DEHYDROGENATIVE COUPLINGS.

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1. INTRODUCTION

Iodine is a special element. Its speciality lies in the fact that it is the heaviest non radioactive element in the periodic table and it is the most polarizable of the halogens. Amongst many iodine compounds that we have observed hypervalent (polyvalent) iodine compounds are the best. The time from 1990 onwards has seen a streak advancement of the applications of Hypervalent Iodine in organic synthesis. Hypervalent iodine compounds have received considerable attention these years because of their non toxic, recyclable, oxidizing, electrophilic characteristics. Hypervalent Iodine compounds are not only used as SET reagents but also they are used in delivery of many functional groups. They are also used in Azidation, Aminations, Radical fragmentations, Oxidative Coupling of aromatic substrates, Oxidation of alkenes and alkynes, Thiocyanations, Arylselenations. Poly Iodide compounds are also used for facile and efficient oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. PhIO₂ can generate the alkoxy radicals from alcohols in certain photochemical reactions. Hypervalent iodine reagents are also used as polymerization initiators (ex Diaryl iodonium salts). There are many hypervalent iodine reagents. To name a few we have PIDA, PIFA, IBX, DMP etc. Chemists have successfully conducted the reactions of hypervalent iodine in water, recyclable organic solvents, and also in solvent free conditions. Several reviews and books have been published regarding hypervalent iodine which have described its characteristics. We have compiled authentic information from 2009-2016 regarding application of hypervalent iodine.

In this review we are mainly focussing on oxidative cyclisations and cross dehydrogenative couplings by hypervalent iodine.

2. Intramolecular Oxidative Annulations by Hypervalent Iodine Compounds.

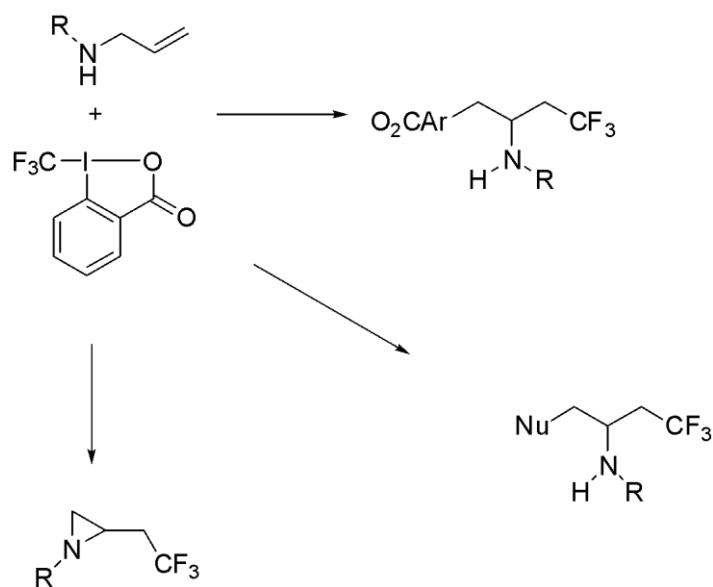
Oxidative annulations within a certain molecule is termed as intramolecular oxidative annulations. Defeating the metal reagents hypervalent iodine compounds have clearly shown that they are the best reagents for oxidative annulations. Whether it be oxylactonization of ketocarboxylic acids or Synthesis of Indoles from N-Aryl Enamines, hypervalent iodine compounds have shown certain reactive rates and properties which metals did not show.

2.1 C-Heterocyclic bond formation.

2.1.1. Aminotrifluoromethylation of Olefins

Trifluoromethylated compounds have attracted much attention as candidate agrochemicals and pharmaceuticals because of their unique biological activities, high hydrophobicity, lipophilicity, and metabolic stability.

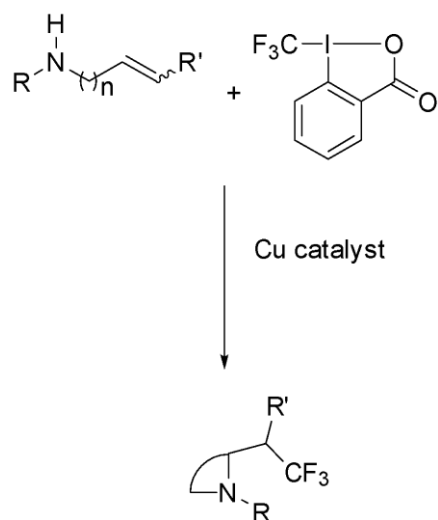
Scheme 1.



$\text{Nu}=\text{BuOH}$

Present work of chemists.

Scheme 2.

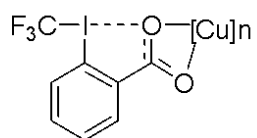
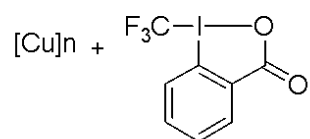
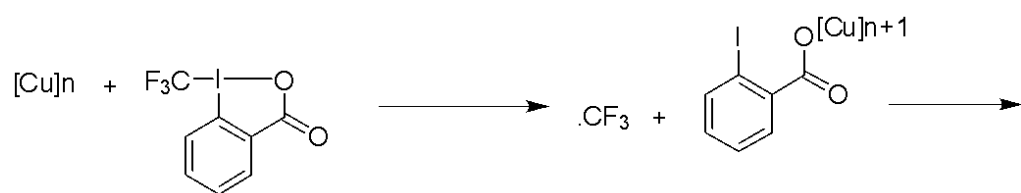


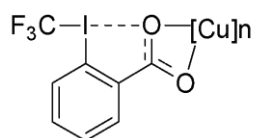
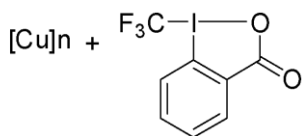
Envisioned Mechanism

This splendid work has been done by Shintaro Kawamura et al.

One of the proposed mechanisms requires generation of trifluoromethyl radical as a key intermediate, which either reacts directly with olefins or is a precursor of $Cu-CF_3$ species.²⁰ The other proposed mechanism involves activated Togni reagent as the reactive species, in which the electrophilicity of the hypervalent iodine is enhanced by copper as a Lewis acid. The latter is based on Togni's originally proposed mechanism of trifluoromethylation of alcohols in the presence of zinc salts.

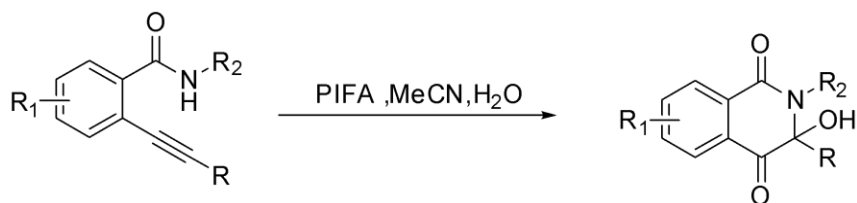
Scheme 3





2.1.2 . Cyclization of o-(1-Alkynyl)benzamides.

The nucleophilic moiety in the proximity of the carbon intramolecular cyclization of alkynes possessing a $\text{-C}\equiv\text{C}$ bond¹ has been reported to be a convenient and effective process for the construction of a variety of heterocycles. Among these transformations is the construction of N-containing heterocycles through intramolecular cyclization reactions between an amide moiety and the carbon-carbon triple bond. For this reason, during the past decades o-(1-alkynyl) benzamide derivatives have been widely studied as a basic enyne-amide system for exploring novel and useful cyclization transformations.

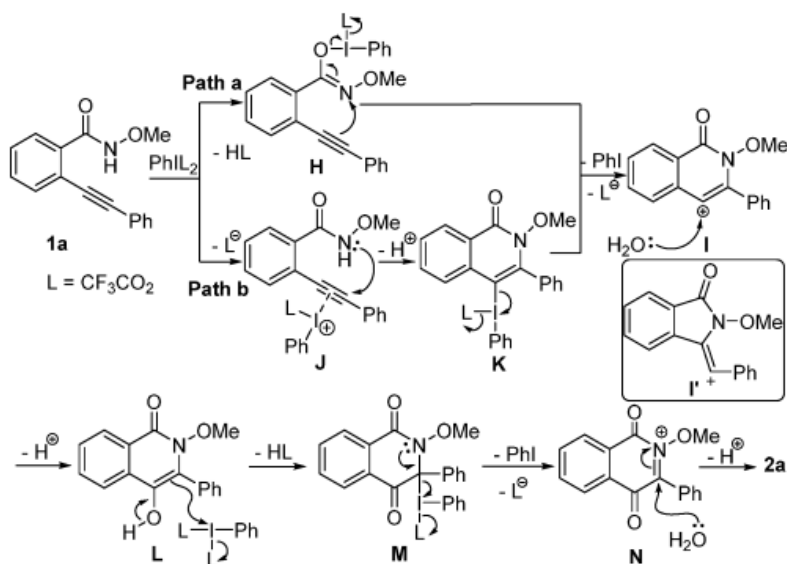


Mechanism Envisioned.

In path a, the N-methoxyamide moiety, as the nucleophile, reacts with PIFA and gave intermediate H, accompanied by the loss of one molecule of trifluoroacetic acid. After the intramolecular cyclization the cationic intermediate is formed. One molecule of iodobenzene and trifluoroacetate is formed.

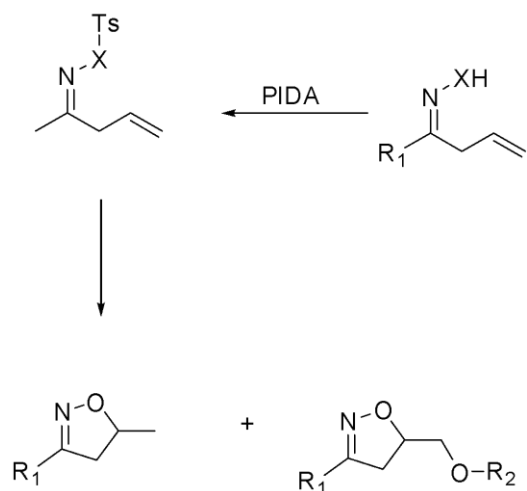
In path b, it was the triple bond instead that serves as a nucleophile and initially activated by PIFA and forms the electrophilic intermediate J, which reacts with the nucleophilic N-methoxyamide moiety to produce intermediate K. The elimination of the iodobenzene and trifluoroacetate anion from K leads to the same cationic intermediate I.

Conversion to the iminium salt intermediate N after releasing an iodobenzene molecule and a trifluoroacetate anion, followed by the nucleophilic attack of water and the removal of one proton furnishes the title product.



2.1.3 Synthesis of pyrazoline and isoxazoline derivatives.

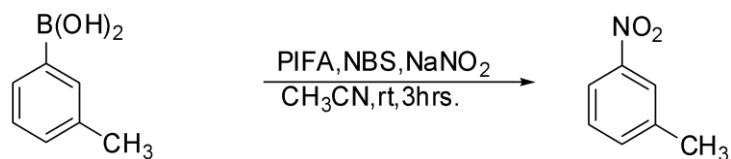
Xiao-Qiang Hu et al have made this work. The functionalisation of unactivated alkenes represents one of the most powerful approaches for carbon–carbon and carbon–heteroatom bonds formation. Not surprisingly, over the past decades, considerable research efforts have been devoted into this field. Particularly, remarkable advances have been achieved in transition-metal-mediated (Pd, Ni, Cu, Au, Ti, Pt etc.) hydroamination, hydroxylation, oxyamination, diamination and dioxygenation of alkenes.



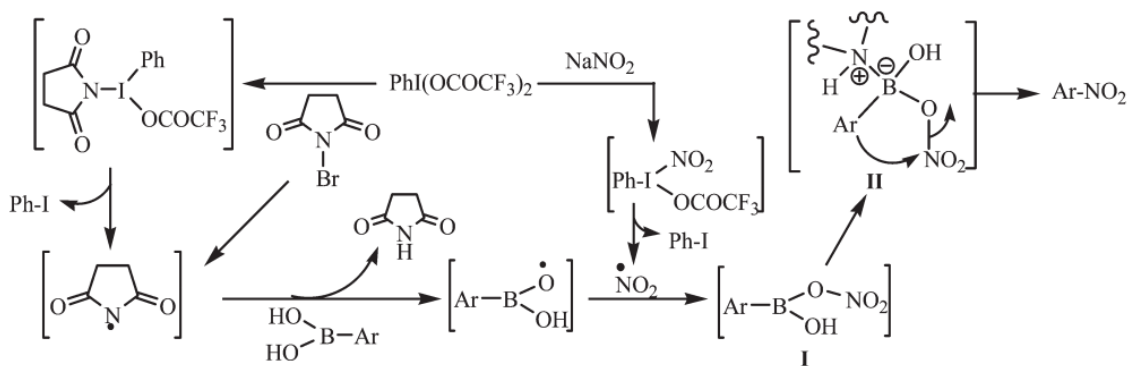
2.1.4. Oxidative ipso nitration of organoboronic acids.

A mild, convenient and transition metal free methodology for oxidative ipso nitration of diversely functionalized organoboronic acids, including heteroaryl- and alkylboronic acids, has been developed at ambient temperature using a combination of [bis(trifluoroacetoxy)]iodobenzene (PIFA) – N-bromosuccinimide (NBS) and sodium nitrite as the nitro source. It is anticipated that the reaction proceeds through in situ generation of NO₂ and O-centred organoboronic acid radicals followed by the formation of an O–N bond via combination of the said radicals. Finally transfer of the NO₂ group to the aryl moiety occurs through 1,3-aryl migration to provide the nitroarenes.

This work is done by Nachiketa Chatterjee et al.



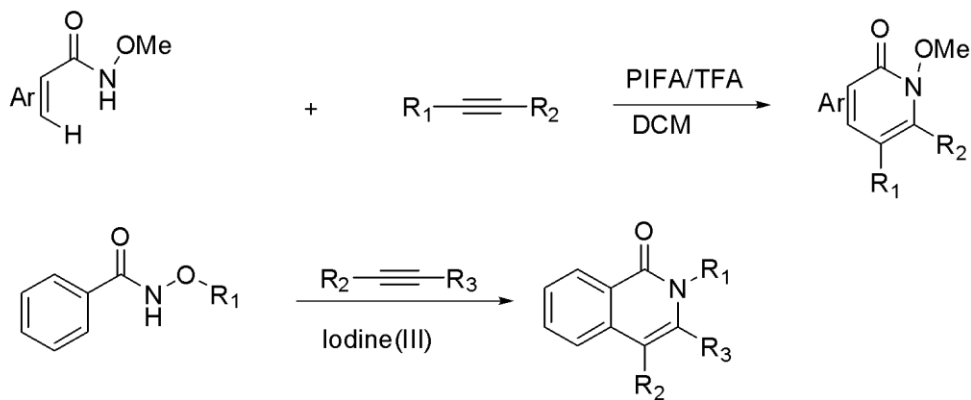
Envisioned Mechanism



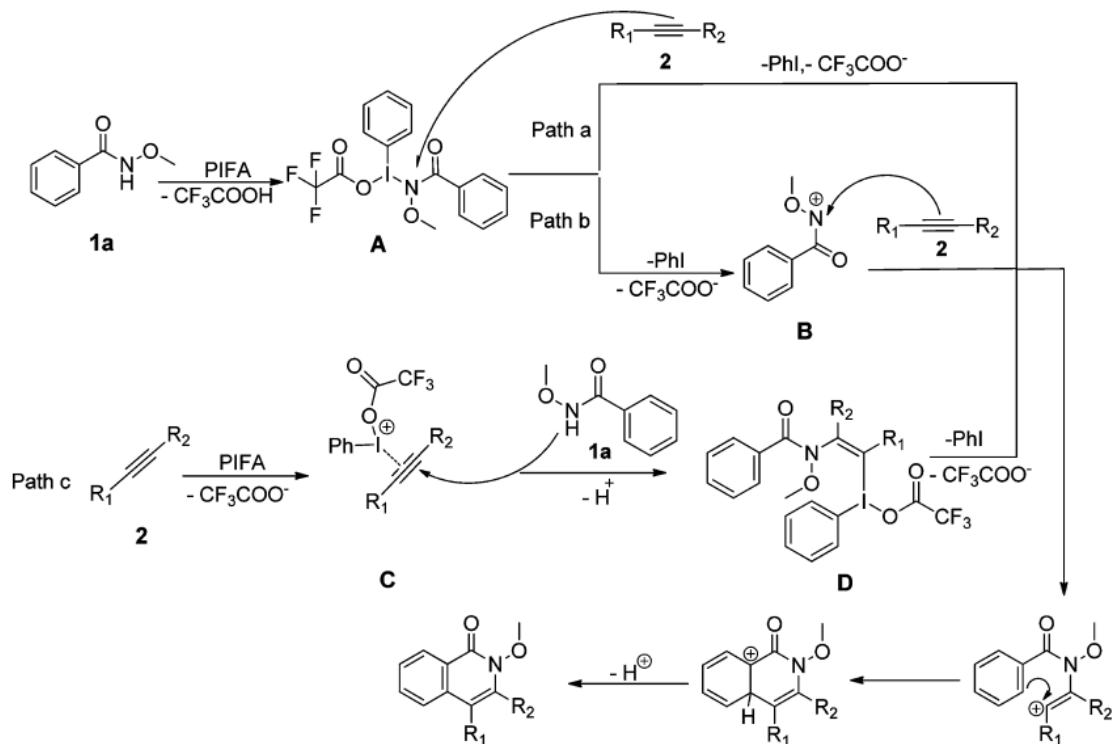
2.1.5 Synthesis of Isoquinolones

Isoquinolones are unique because they form an important molecular skeleton in natural alkaloids. After many years of efforts to synthesize the Isoquinolones Zhi-Wei Chen et al have successfully synthesized it with the help of hypervalent iodine. A wide variety of isoquinolones were easily prepared using PIFA in the presence of TFA.

Compared to transition metal catalysed methods the oxidation ability of hypervalent iodine has proved a boon to chemists to prepare these compounds.

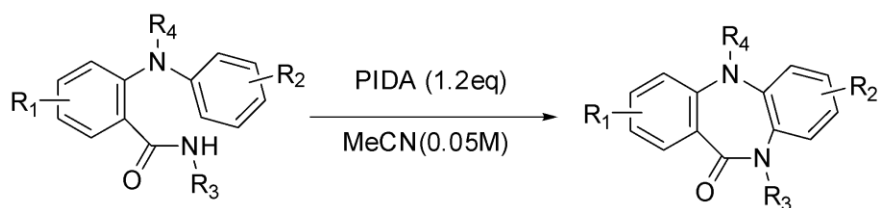


ENVISIONED MECHANISM



2.1.6. Construction of 1,4-Benzodiazepine Skeleton from 2-(Arylamino)benzamides.

1,4 Benzodiazepine structure is a key heterocyclic structure in the medicinal chemistry and it is also a very good pharmaceutical agent. Because of this many synthetic strategies have been developed to synthesize the benzodiazepine.



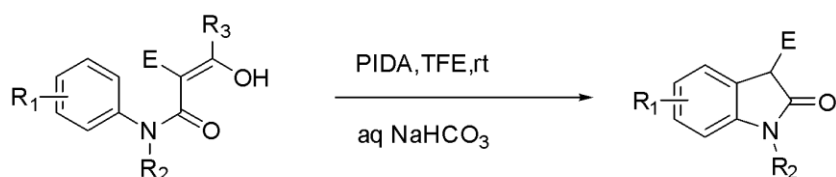
Here Xuming Li et al have designed this way of construction of benzodiazepine skeleton.

The appealing features of this research is the environmental benign feature of hypervalent iodine reagents.

2.1.8 Synthesis of 2-Oxindoles via PIDA reagent.

Oxindoles are building blocks for the synthesis of various natural products. They are also biologically active molecules. Enthused by the previous work of preparing the oxindoles via PIDA reagent Jinglei Lv et al have prepared a new strategy of preparing the oxindoles by functionalized anilide derivatives.

To the great delight of chemists when PIDA was used with MeCN then the intramolecular oxidative cyclization occurred and gave the oxindole product.



E=CN,CO₂Et,COMe

R₂=Me,Ph,Bn

R₁=F,Cl,Br

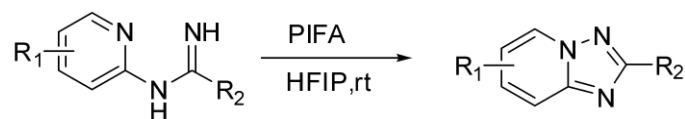
R₃=mE,Ph

2.1.9 Synthesis of 1,2,4-Triazolo[1,5-a]pyridines.

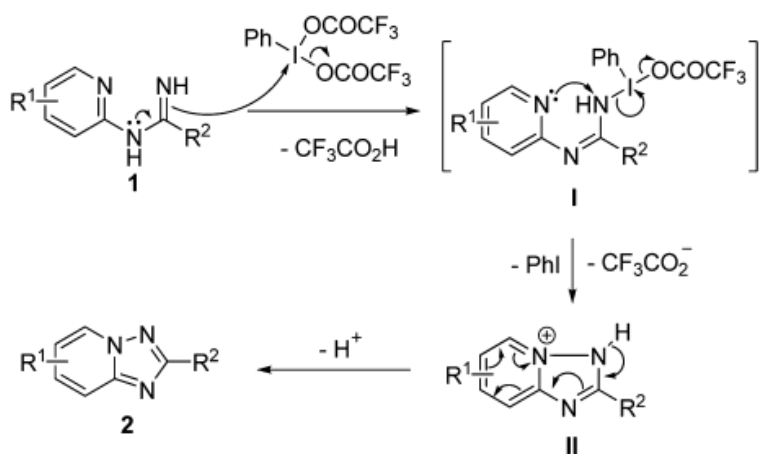
This work is done by Zisheng Zheng et al. They have prepared the pyridine compound by using PIFA reagent.

They have mentioned that Kotali, Dong, Tellitu and Dominguez have done many promising works in this field.

Disadvantages of earlier methods was the low yield. Chemists were hence encouraged by these limitations to develop methods which are devoid of transition metals and could proceed at ambient temperatures.



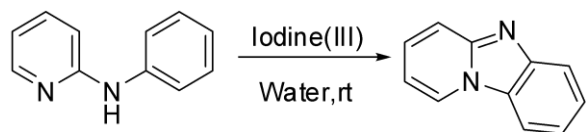
Envisioned Mechanism



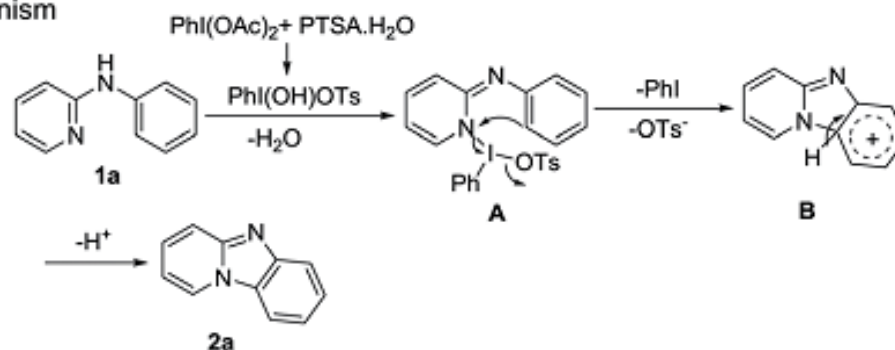
2.1.10 Synthesis of benzimidazole fused heterocycles .

The benzimidazole fused heterocyclic scaffold exists as a wide range of biologically active compounds.

D.Nageswar Rao et al have reported this work. This work is a regioselective one and is utilized in synthesizing medicinally important heterocycles.



Mechanism



2.1.12 C–H cycloamination of N-aryl-2-aminopyridines and N-arylamidines.

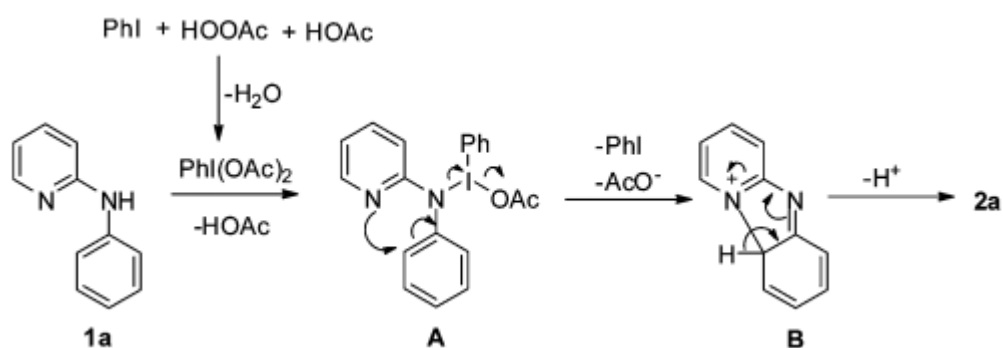
Over the past decade, intramolecular C–N bond formation through

direct C–H functionalization catalyzed by transition metals such as Pd, Rh, Ru, and Cu complexes has emerged as a step-efficient and atom-economic alternative to traditional methods for the synthesis of N-heterocycles.¹ However, these transition-metal-catalyzed reactions generally suffer from high reaction temperature, narrow substrate scope, and the use of stoichiometric or even excess amounts of metal salts as oxidants.² In large scale synthesis, these metal-based methods are not only costly, but also problematic to remove heavy metal contaminants from products. As a result, they are less applicable to drug synthesis especially at a late stage, despite their virtue of step-efficiency and atom-economy. Therefore, the development of alternative metal-free (for both catalysts and oxidants) reactions that can be performed at ambient temperature starting from unprefunctionalized precursors is highly desirable.

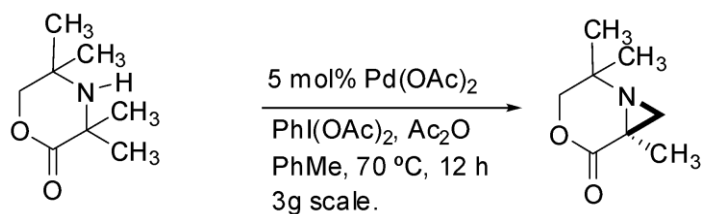
Recently, significant achievements have been made in hypervalent iodine(III)-mediated C–H amination, amidation, and imidation reactions under mild metal-free conditions.³ For instance, Chang et al. and DeBoef et al. reported elegant research on PIDA-mediated intermolecular C–H imidation of both aryl sp^2 and benzylic sp^3 C–H bonds.⁴ Hypervalent

iodine(III)-promoted intramolecular oxidative C–N formation was also realized, and thus provided an efficient approach to the construction of N-heterocycles.⁵ However, these reactions are hard to scale up unless the hypervalent iodine reagents are used in catalytic amounts.⁶ In this context, studies on in situ generated hypervalent iodine(III)-catalyzed C–C,⁷ C–O,⁸ and C–N⁹ bond-forming reactions grow rapidly. For example, Antonchick et al. reported an efficient intramolecular C(sp²)–H amidation reaction using biaryliodide as a precatalyst in the presence of peracetic acid as a stoichiometric oxidant at room temperature.

Envisioned Mechanism.

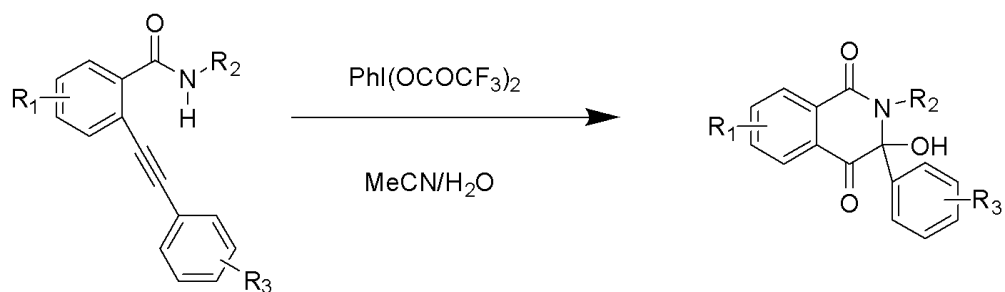


2.1.13 Hypervalent Iodine-catalysed C–H activation of aliphatic amines to give strained nitrogen heterocycles.



Chemists probed the reactivity of the strained cyclopalladation complexes; they thought whether mild chemical oxidants, such as the hypervalent iodine compound $\text{PhI}(\text{OAc})_2$, might allow access to C–H functionalization pathways proceeding through highvalentPd(IV) cyclometallated intermediates, as well as formulating the basis of a catalytic transformation. When they treated a cyclopalladation complex with $\text{PhI}(\text{OAc})_2$ they were surprised to discover raziridine, presumably formed via C–N bond forming reductive elimination from a high oxidation state Pd(IV) intermediate.

2.1.14 $\text{PhI}(\text{OCOCF}_3)_2$ -Mediated Cyclization of o-(1-Alkyl)benzamides: Metal-Free Synthesis of 3-Hydroxy-2,3-dihydroisoquinoline-1,4-dione.



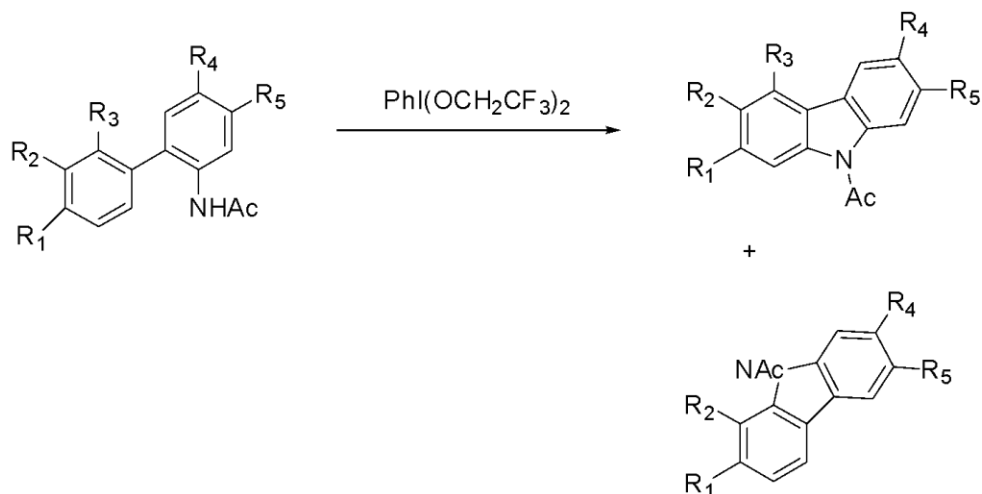
R1=H, Me, OMe
 R2=OMe, alkyl
 R3=H, F, Cl, NO₂, CF₃

The above reaction is a splendid discovery report by **Kang Zhao in 2015**. It is the synthesis of 3-hydroxy-2,3-dihydroisoquinoline-1,4-diones.

After performing intramolecular cyclization of o-(1-alkynyl)benzamides in MeCN/H₂O, mediated by metal-free, hypervalent reagent of $\text{PhI}(\text{OCOCF}_3)_2$, followed by an oxidative hydroxylation reaction the researchers are able to derive 3-hydroxy-2,3-dihydroisoquinoline-1,4-diones.

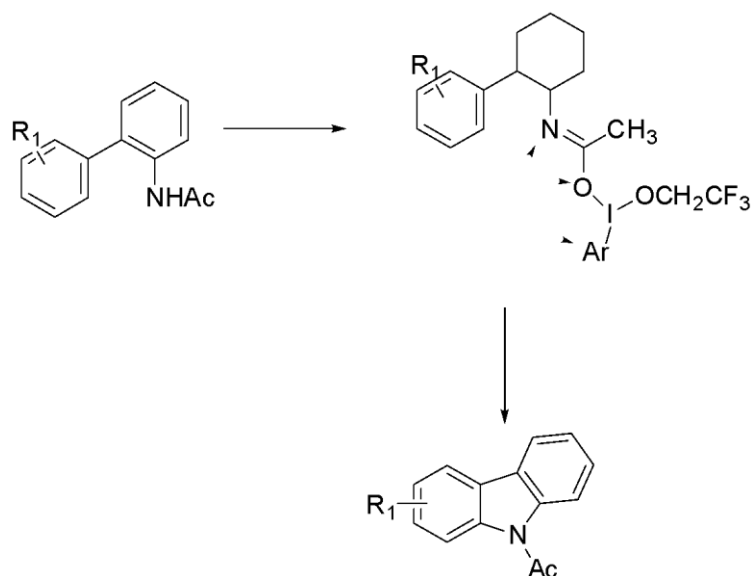
2.1.15 Oxidative Cyclisation of diaryl derivatives by electrochemically generated hypervalent iodine oxidant.

This is a report from Shigeru Nishiyama and co workers in 2010. An oxidant solution is produced from oxidizing the iodobenzene in $\text{CF}_3\text{CH}_2\text{OH}$ where the oxidant : substrate is in 3:1 ratio. It was treated with substrates for oxidative cyclization. 0-91% of carbazoles was recorded.



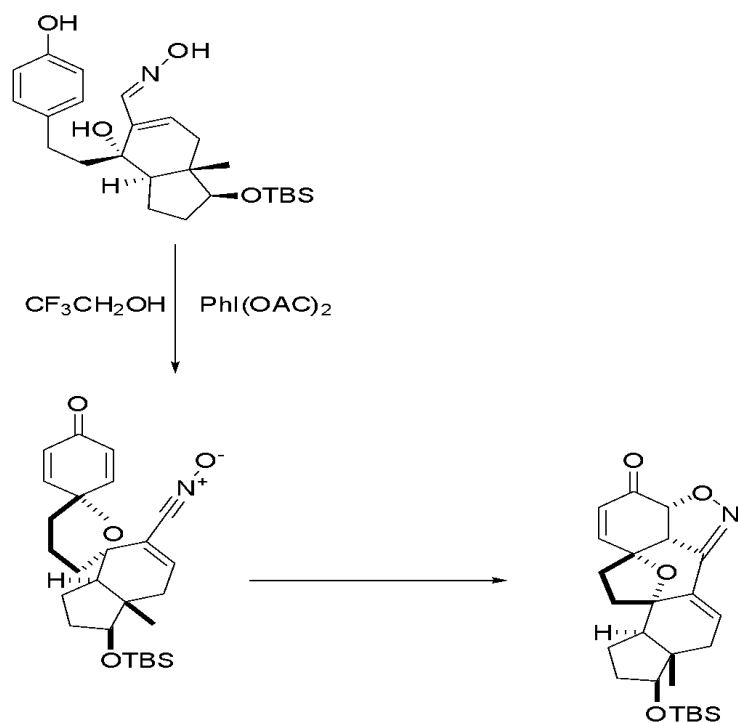
PLAUSIBLE MECHANISM

In the first step there is an $\text{S}_{\text{N}}2$ attack of amide oxygen to the oxidant. Imidate type intermediate is produced. An attack from the adjacent aromatic ring gave the cyclized product. When compared with the PIFA, electrochemically generated oxidant proved to have clear reactions at ambient temperatures, but in those conditions the PIFA gave a complex mixture.



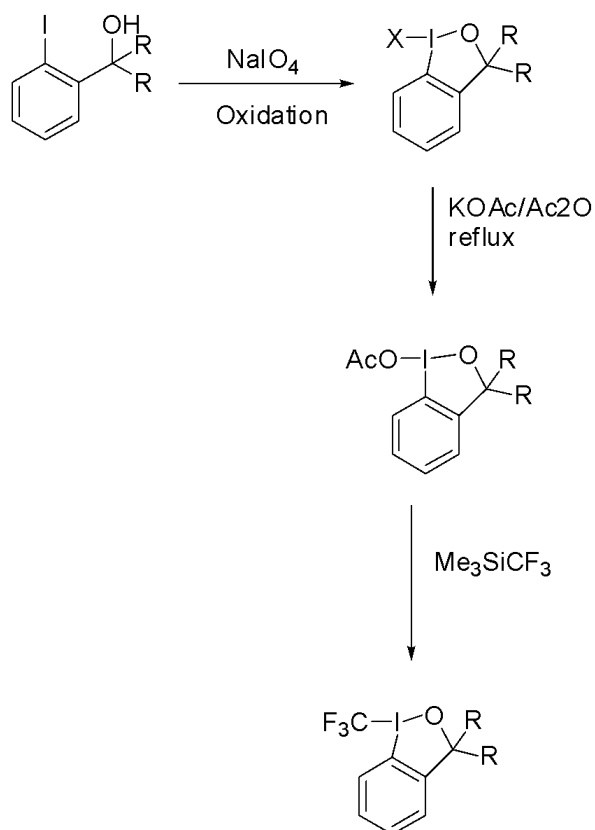
2.1.16 Tandem oxidative reactions by hypervalent iodine.

Here the chemists have done the synthesis of bioactive polyspirocyclohexa-2,5 dienones. Due to the challenging polyspirolyic structure and cytotoxic activity of this compound chemists have been synthesizing various derivatives of this compound. The important functional group is cyclohexa-2,5-dienone for the biological activity of this compound. Here the chemists have aimed to keep the cyclohexa-2,5-dienone moiety (pharmacophore) intact. Another aim was to trigger the polyspiroannulation process initiated by phenolic oxidation.

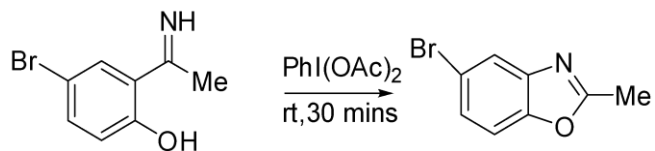


2.1.17 Trifluoromethylation by Hypervalent Iodine reagents.

Here NaIO_4 plays an important role by oxidizing the reactant. This is reported by Antonio Togni and co workers in 2010.



2.1.18 Synthesis of benzoxazoles and benzimidazoles mediated by hypervalent iodine.



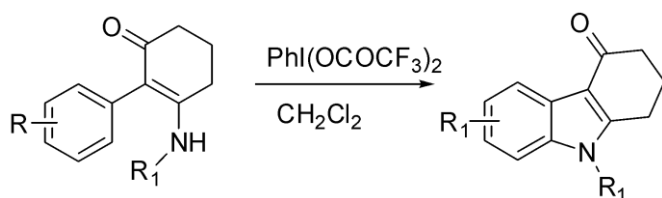
Here intramolecular cyclizations take place under oxidative conditions of hypervalent iodine.

Yan Xiong and co workers have used the technique of triggering Beckmann type rearrangements for benzoxazole and benzimidazole motifs formation by hypervalent iodine reagents.

By using various solvents the maximum yield of 82% was obtained at 1.5 eq of $\text{PhI}(\text{OAc})_2$

2.1.19 Oxidative C-N bond formation through PIFA –mediated annulation of 2-aryl enaminones

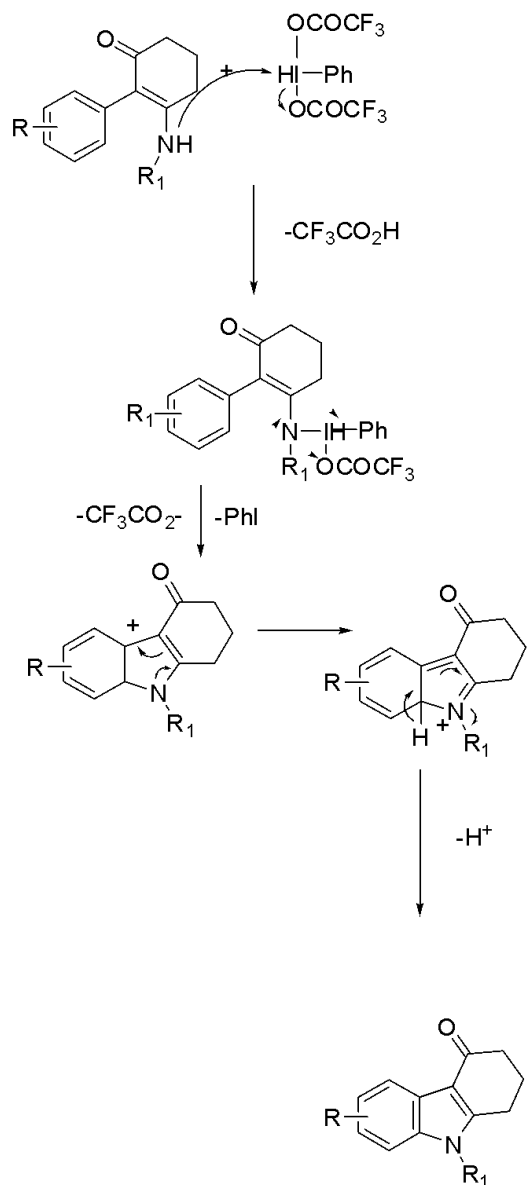
In this article the PIFA reacted with a compound to give a cyclized product.



A PLAUSIBLE MECHANISTIC SEQUENCE.

The N-iodo intermediate is formed from enaminone and PIFA. Loss of a molecule of trifluoroacetic acid occurs. Then a Wheland intermediate is formed as the N-centre on the Phenyl ring gets attacked thereby simultaneously releasing the PhI and $\text{CF}_3\text{CO}_2\text{H}$.

Then it is proposed that the carbon cation is stabilized by lone pair on nitrogen through conjugation to give iminium salt. Finally a proton is eliminated and aromatic system is regenerated to form carbazolone.



2.1.20 One pot synthesis of benzoxazol-2'-yl bicyclo[2.2.2]octen -2-one derivatives.

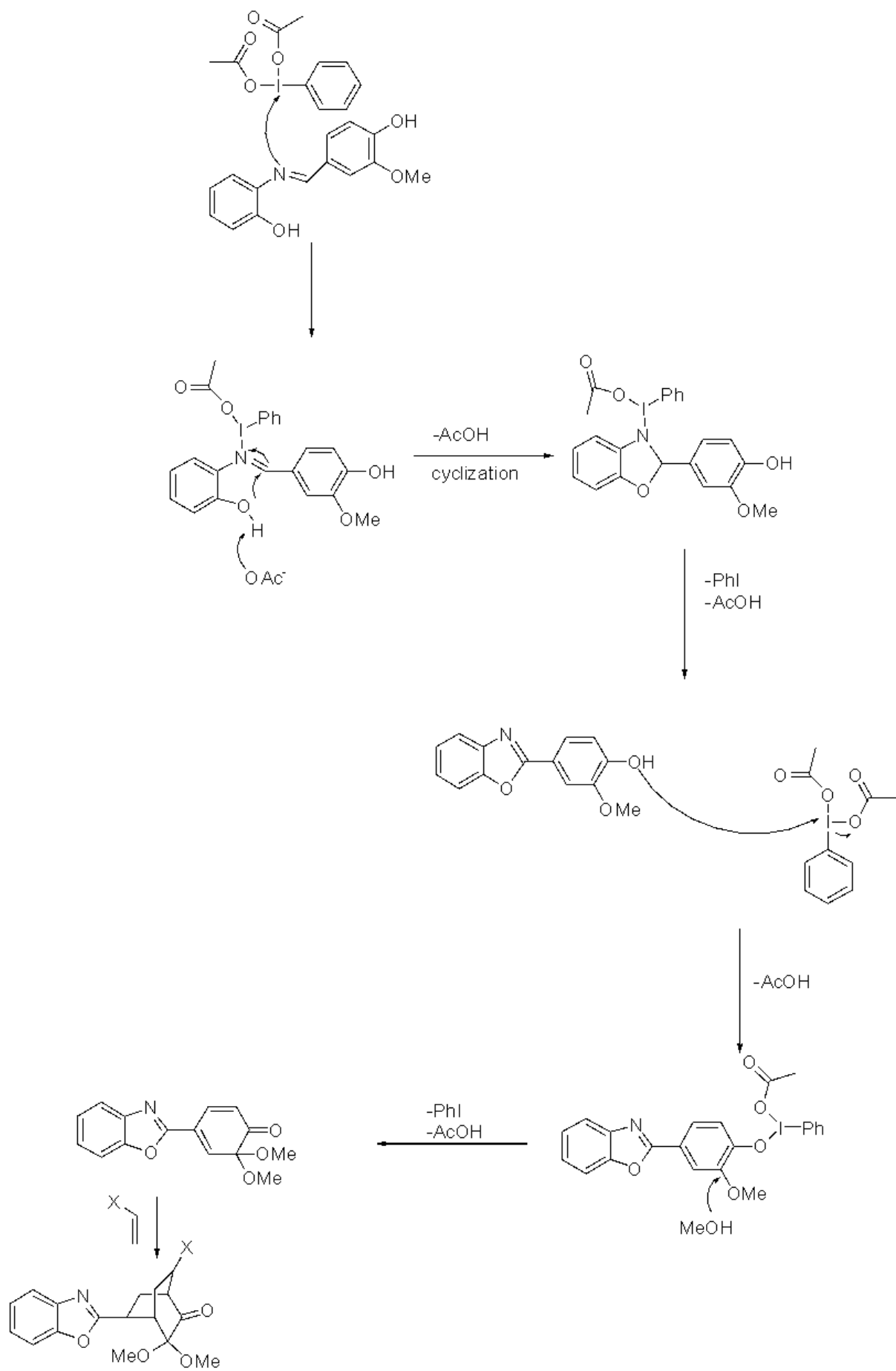
The aldimine got oxidized with DIB at room temperature. The MOB generated underwent dimerization. Chemists obtained a single isomer out of 8 possible isomers of MOB.

PLAUSIBLE MECHANISM BY CHEMISTS:

The lone pair electrons on N atom attacks the HI giving cyclized product.

On elimination of PhI and AcOH the compound produced underwent associative pathway mechanism, underwent further

Elimination of PhI and AcOH to have DIEL ALDER reaction with alkene to give cyclo adduct.

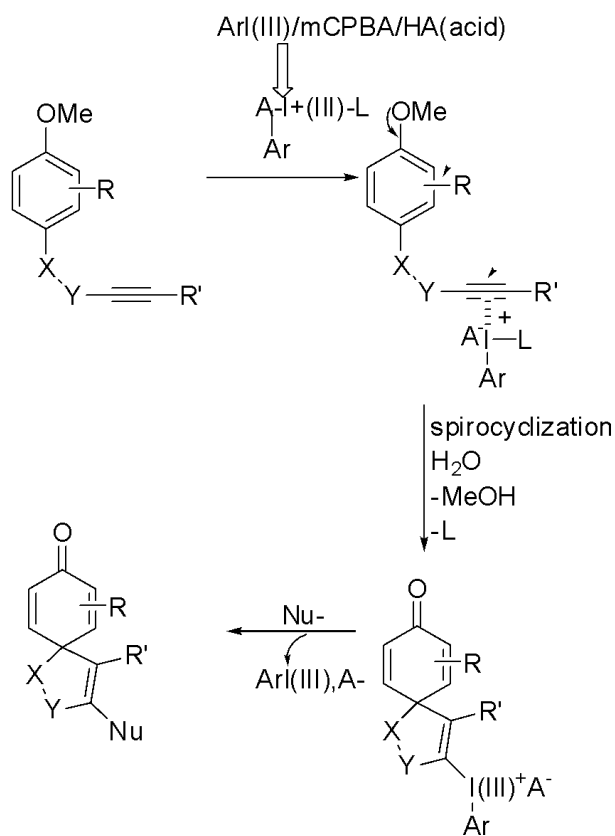


2.1.21. Hypervalent iodine in the synthesis of spirocycles

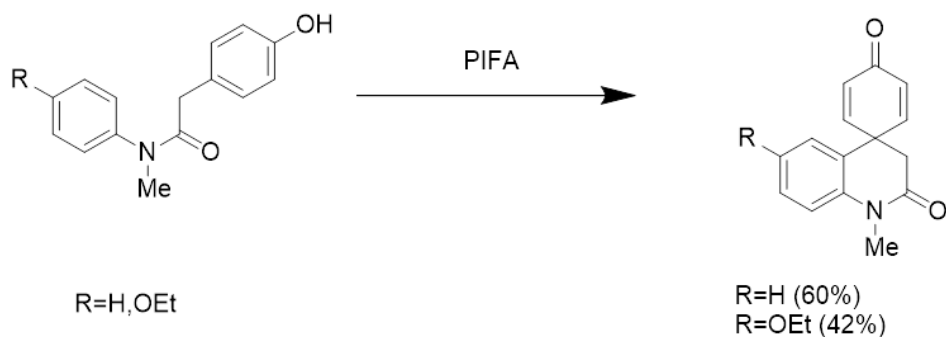
In this article the chemists have spirocyclized the aryl alkynes .

In the PLAUSIBLE MECHANISM they have performed the in situ generation of cationic hypervalent iodine species from iodo arene using mCPBA in the presence of HA .Then for inducing ipsocyclization of aryl alkynes the electrophilic iodines have activated the alkynes.

Finally by the reductive coupling the nucleophiles are attached to the formed compound thereby forming the spirocyclic compounds.



2122 Hypervalent iodine –mediated oxidative cyclization of p- hydroxy acetanilides to 1, 2 – dispirodienones.

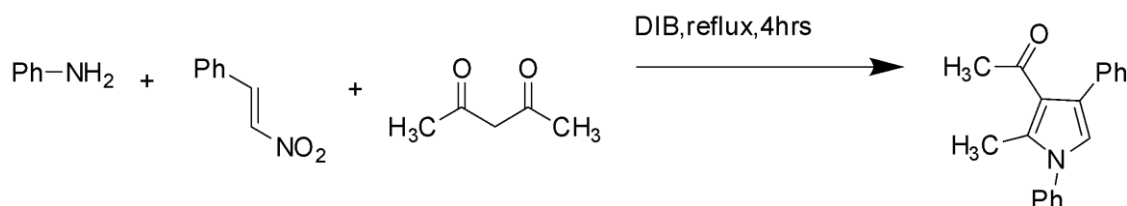


Here the 1,2Dispirodienones are synthesized by Hypervalent Iodine.

As already stated ,since a few years ,Hypervalent Iodine reagents like PIDA ,PIFA are used in oxidative phenolic coupling reactions and in preparing natural alkaloids. When it came to the spirocyclohexadienones and spirodienone lactams chemists preferred the Hypervalent Iodine as it is non toxic.

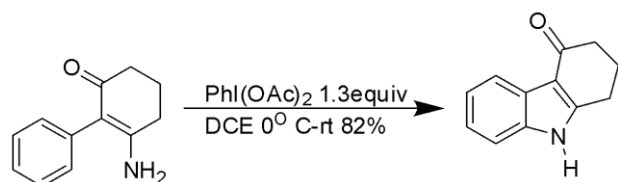
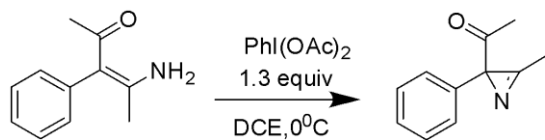
A spirodienone is synthesized in this reaction.

2.1.23 Three component direct synthesis of substituted pyrroles from easily accessible chemical moities using hypervalent iodine reagent

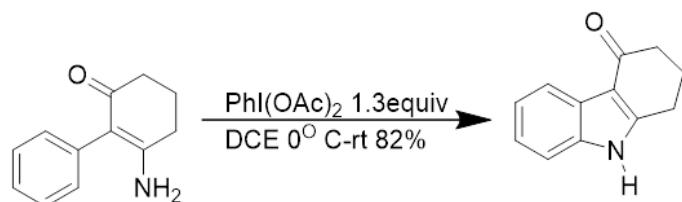
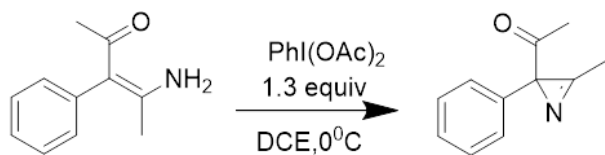


Pyrroles belong to an important class of heterocyclic compounds which are found in many pharmaceuticals .These are anti bacterial reagents. Chemists had many strategies for preparing the pyrrole moieties

but they have chosen Hypervalent Iodine because of its non-toxic character. Previous methods did not work well because there are difficulties in purifying the metals and thereafter removing them. Some reaction conditions are very harsh when metals are used.



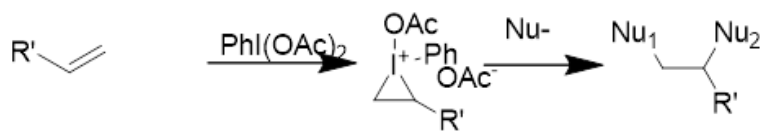
2.1.24 Synthesis of carbazoles and 3-acetylimidoles via oxidative C-N bond formation through PIFA mediated annulation of 2-aryl enaminones



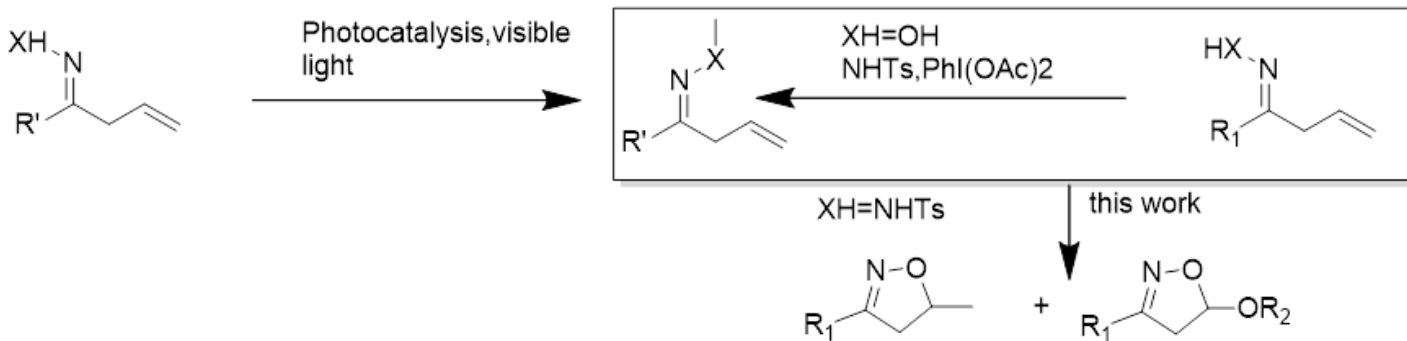
In this article the chemists have synthesized carbazolones and 3-acetyl indoles by PIFA mediated annulations of enaminones. In this process there is metal free oxidative aromatic bond formation. When the cyclic enaminone was treated with PIFA carbazolone was obtained. PIFA was also tested as it is more potent than the PIDA with excellent yield.

2.1.25 PhI(OAc)_2 -mediated functionalization of unactivated alkenes for the synthesis of pyralozine and isoxazoline derivatives.

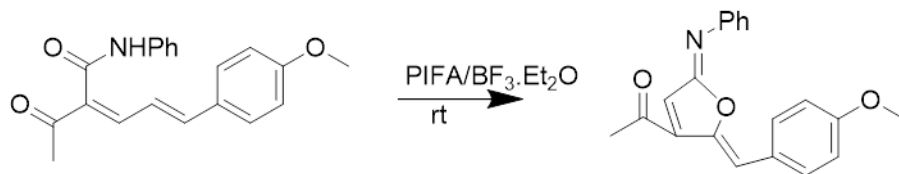
alkene oxidation strategy



reaction design radical process



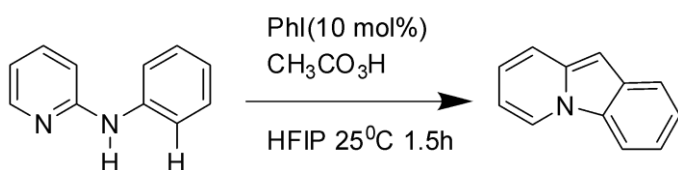
2.13 One-pot synthesis of substituted 2,5-dihydrofurans from β -oxo amides and cinnamaldehydes.



Here the chemists have reported the efficient synthesis of substituted Isothiazol-3(2H)one pyrrolin-4-one, spiro fused cycloalkano-(C₄)-

Pyrazolin-5-one-oxides from various enaminones, thioamides in presence of PIFA. Here an C-S, N-C bond is formed. Here the new bond of C-O is reported (as a result of one pot synthesis of substituted 2,5 dihydrofurans from beta oxo amides and cinnamaldehydes) using PIFA.

2.1.25 C-H cycloamination of N-aryl-2-amino pyridines and N-aryl amidines catalyzed by an in situ generated hypervalent iodine(3) reagent.

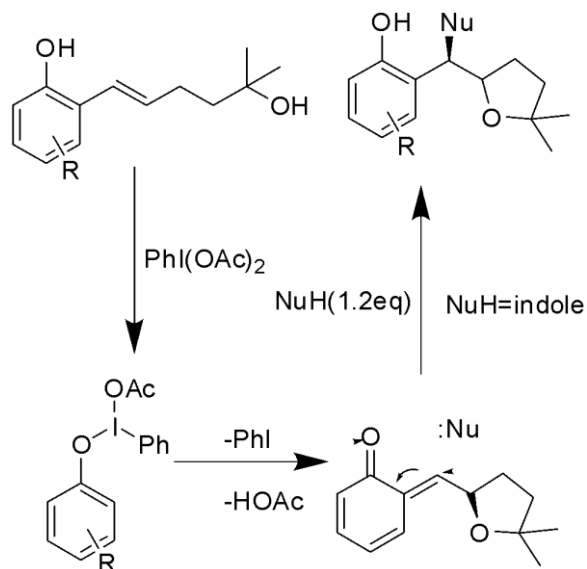


Here the chemists have used hypervalent iodine instead of Pd, Cu complexes for their cycloamination reactions.

The hypervalent iodine reagents are used in catalytic amounts. The in situ generated hypervalent iodine catalyzed intramolecular

C(sp²)-H amination of N-aryl-2-amino pyridines paved the path for the synthesis of 1H-benzo [d] imidazoles.

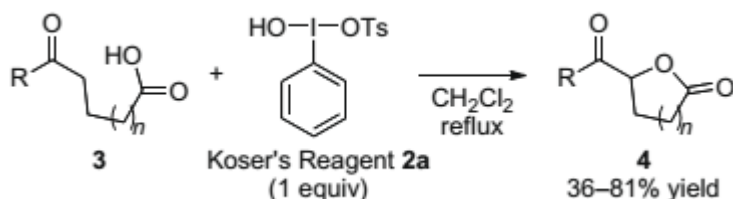
2.1.26 Hypervalent iodine mediated alkene difunctionalization of vinyl phenols: diastereoselective synthesis of substituted indoles and indolizines.



Here the chemists have reported the I(III) mediated alkene

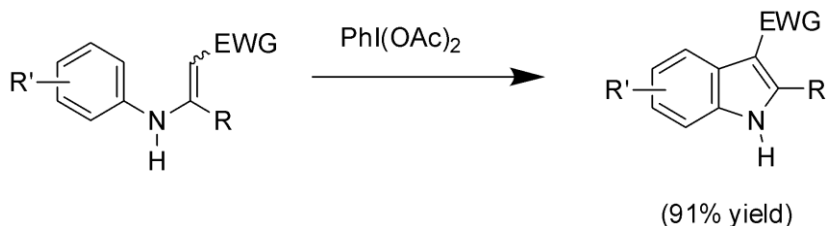
difunctionalization on the reactions of vinyl phenols which resulted in the efficient synthesis of indoles.

2.16 Hypervalent iodine-catalyzed oxylactonization of ketocarboxylic acids to ketolactones



Along with the role of lactones in the organic chemistry the report of hypervalent iodine (III) mediated oxylactonization is reported in this paper. Here the researchers have thoroughly examined TOGO and MORIARTYS paper of oxylactonization and based on it they have prepared the ketolactones from ketocarboxylic acids.

2.17 PIDA-Mediated Oxidative C-C Bond Formation: Novel Synthesis of Indoles from N-Aryl Enamines

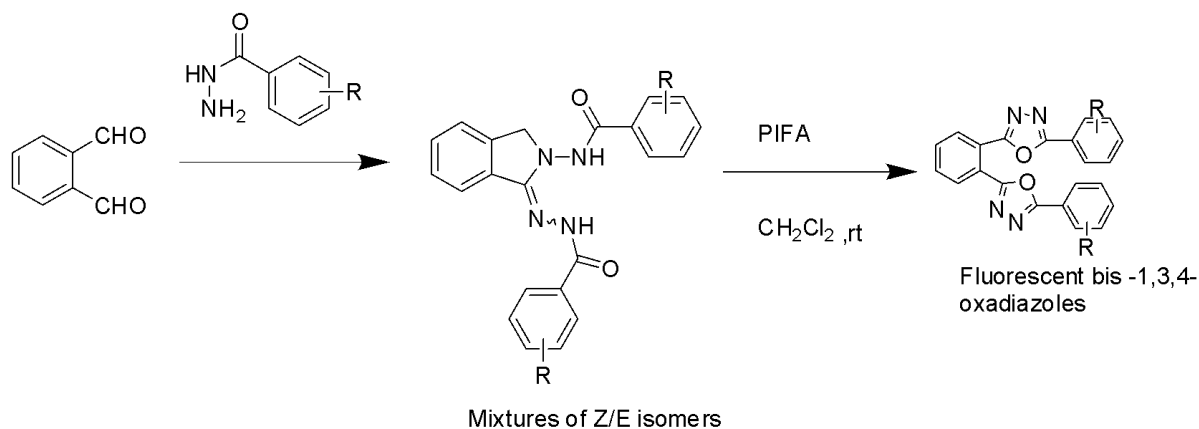


Considering C-C bond construction as the essence of organic synthesis and the foundation of many complex molecular structures the researchers have avoided metals and have involved the PIFA, PIDA for the above works.

Metal catalysed reactions involve a lot of capital investment and carefully monitored conditions.

Here a novel C-C bond formation strategy for indole synthesis via PIDA mediated oxidation of N-aryl enamine is reported. This method also involves good functional group tolerance.

2.18 Unexpected Formation of N-(1-(2-Aryl-hydrazono)isoindolin-2-yl)benzamides and Their Conversion into 1,2-(Bis-1,3,4-oxadiazol-2-yl)benzenes.



This report is given by Niculina D. Hädade in 2013.

When ortho-phthalaldehyde reacts with aryl hydrazines N-(1-(2-arylhyaazono)isoindolin-2-yl)benzamide is formed as the major product. Generally various geometrical isomers are also formed. Oxidation of these isomers with PIFA forms the fluorescent 1,2-bis(5-aryl-1,3,4-oxadiazol-2-yl)benzenes.

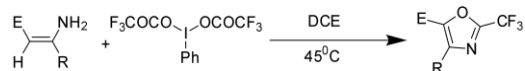
2.19 Synthesis of 2-(Trifluoromethyl) oxazoles from β -Monosubstituted Enamines via $\text{PhI}(\text{OCOCF}_3)_2$ -Mediated Trifluoroacetoxylation and cyclization.

When the β -monosubstituted enamines are treated with PIFA then it yielded a variety of 4,5-disubstituted 2-(trifluoromethyl)oxazoles.

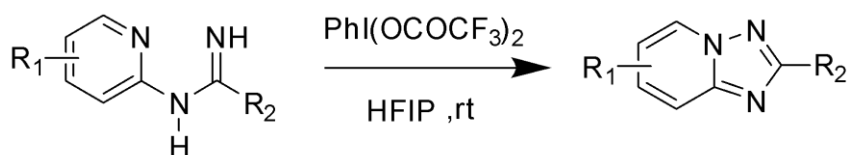
By β -trifluoroacetoxylation of enamines followed by intramolecular cyclization the final products are formed.

Here the researchers have reported novel formation of 2-(trifluoromethyl)oxazole derivatives from the reactions of β -monosubstituted enamines with PIFA.

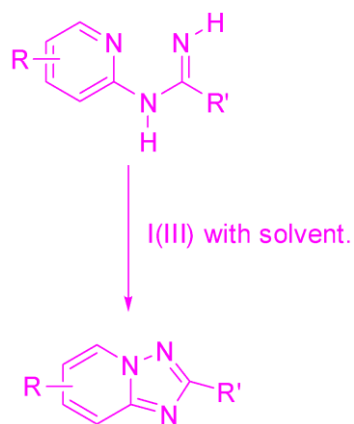
Here the PIFA is behaving as a fluorinating agent for the introduction of trifluoromethyl moiety which is a biologically important functional group.



2.20 $\text{PhI}(\text{OCOCF}_3)_2$ -Mediated Intramolecular Oxidative N-N bond formation :metal free synthesis of 1,2,4-Triazolo[1,5-a]pyridines



R1=H,Me, Halogens
R2=aryl, alkyl

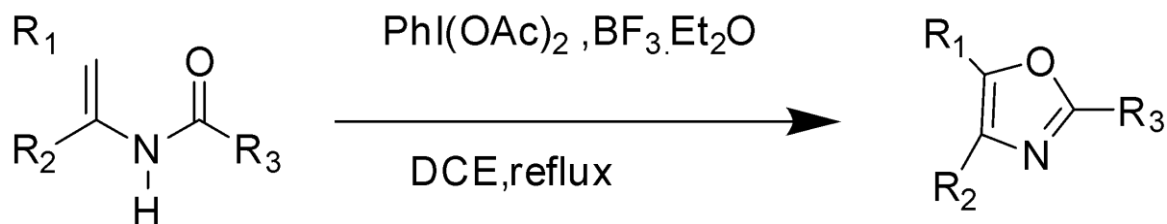


Using the superb oxidizing power of PIDA and PIFA the chemists are now constructing various heterocyclic compounds .

Investigations are carried out on C-heteroatom and C-C bond formations.

In 1996 Kotali et al reported PIDA mediated oxidative cyclization of o-amino aryl ketone acyl hydrazones to form the amino indazoles by removing the 2 Hydrogens from the aryl amine moiety.

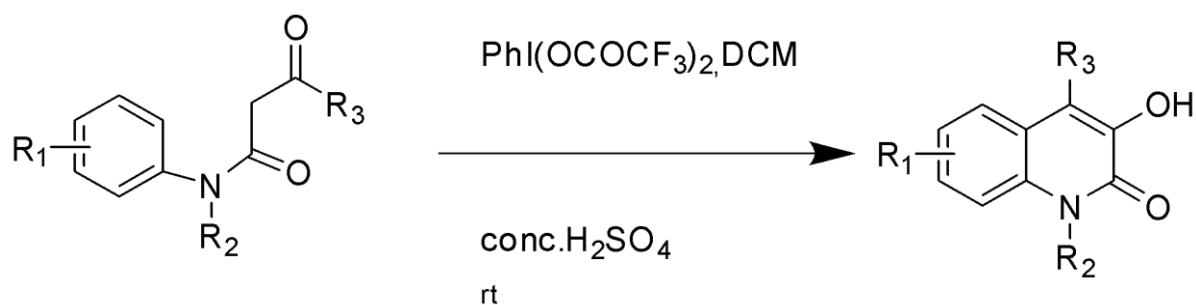
2.21 Synthesis of Oxazoles from Enamides via Phenyliodide Diacetate – Mediated Intramolecular Oxidative Cyclization.



Oxazole skeleton is the structural backbone of many biologically active natural products and pharmaceutical agents.

After the intramolecular cyclization of various enamides by PIDA the Oxazole formation is reported here by **Kang Zhao in 2012**.

2.22 One pot Synthesis of 3-Hydroxyquinolin-2(1H)-ones from N-Phenylacetacetamide via $\text{PhI}(\text{OCOCF}_3)_2$ -Mediated α -Hydroxylation and H_2SO_4 -Promoted Intramolecular Cyclization.

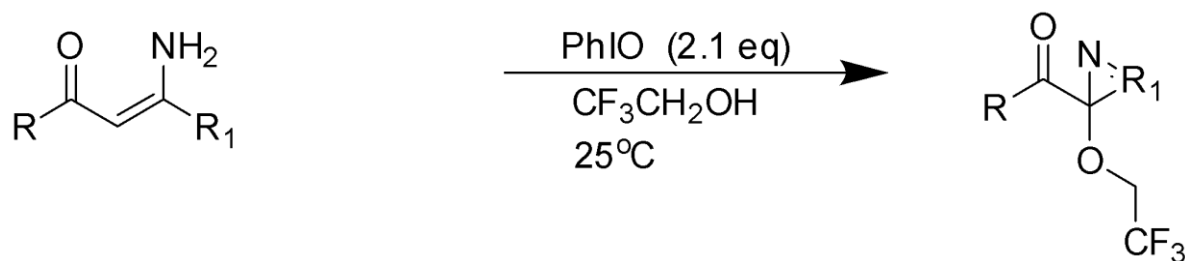


PIFA mediated synthesis of biologically important 3-hydroxyquinolin-2(1H)-one compounds is a clean one pot synthesis process.

Yunfei Du and co workers have used the readily available N-phenyl acetoacetamide derivatives, by PIFA mediated α -hydroxylation and a H_2SO_4 -promoted

reaction particularly intramolecular condensation the 3-hydroxyquinolin-2(1H)-one is synthesized.

2.23 Formation of functionalized 2H-Azirines through PhIO-Mediated Trifluoroethoxylation and Azirination of Enamines

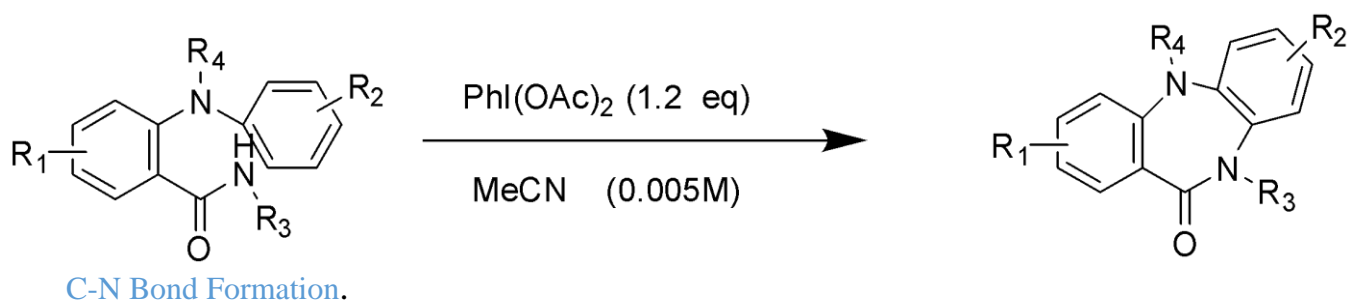


By using a variety of enaminones and enamine carboxylic esters **Kang Zhao and co workers** have converted them into trifluoroethoxylated 2H-azirines

By reacting them with PhIO in TFE which is postulated to have proceeded

Via the PhIO-mediated oxidative trifluoroethoxylation and a subsequent azirination of the R-trifluoroethoxylated enamine intermediates.

2.24 Construction of 1,4-Benzo diazepine Skeleton from 2-(Arylamino)benzamides through PhI(OAc)₂-Mediated Oxidative

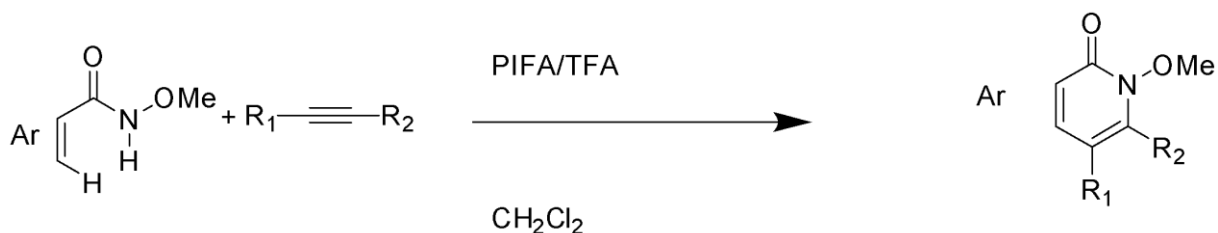


Kang Zhao and co workers in 2014 have reported the development of novel methods for preparing the heterocycles which is an unavoidable hot topic in the Medicinal chemistry.

1,4 benzodiazepine skeleton, which is one of the key heterocyclic structures, is an important pharmaceutical reagent. It is also biologically active. It is now reported to have been constructed by 2-(arylamino)benzamides and PIFA

Mediated oxidative C-N bond formation . Attractive features of this strategy are mild reaction conditions, the heavy-metal-free characteristic of the oxidative coupling process, and the flexibility to tolerate a broad scope of substrates.

2.25 Metal-Free Iodine (III)-Promoted Synthesis of Isoquinolines.



Here the isoquinolones are synthesized by using the PIFA and TFA .Isoquinolones are important molecular skeleton in natural alkaloids .

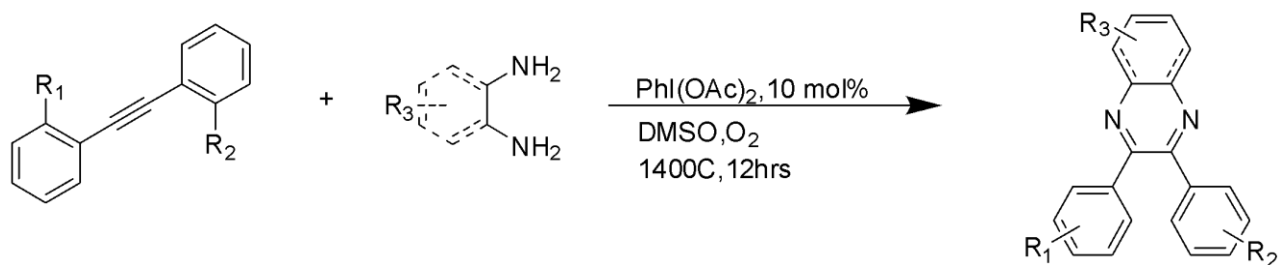
Unique chemical activities are shown by molecules which have them.

Recently Antonchick and coworkers reported annulations of N –alkoxybenzamide derivatives with alkynes by the Hypervalent Iodine derivatives.

Here in another intermolecular oxidative annulation is done from simple

N-methoxybenzamide derivatives and disubstituted acetylene which is reported by Jian-Yu Zheng and co workers in2014.

2.26 Efficient synthesis of quinoxalines with hypervalent iodine as a catalyst.



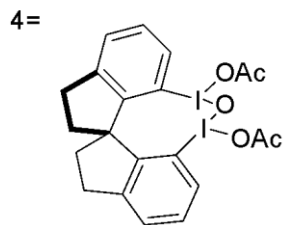
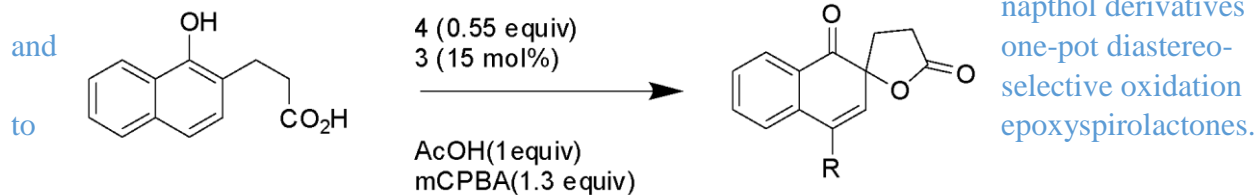
Quinoxaline is an antileukemia cancer reagent. Various biologically active and

Important quinoxalines are synthesized in excellent yields via one-pot reaction between 1,2-diaminobenzenes and internal alkynes.

Mei-Ing Chung and co workers have used PIDA as an alternative to other metals.

QUINOXALINES are also anti viral, anti tuberculatory reagents.

2.27 Chiral hypervalent iodine –catalysed enantioselective oxidative Kita spirolactonization of 1-



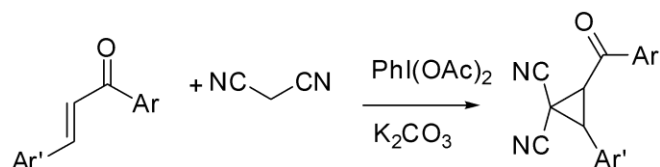
Iodosyl arenes are here generated in situ from iodosrenes and mCPBA. Here Kazuaki Ishihara and co workers have demonstrated the C2-symmetric iodosyl arene which is based on the hydrogen bonding interactions for the Kita oxidative spirocyclizations of 1-Naphthol derivatives. This is reported in 2010.

3. INTERMOLECULAR OXIDATIVE ANNULATIONS BY HYPERVALENT IODINE.

Oxidative annulations in between two separate molecules is termed as intermolecular oxidative annulations.

Regarding intermolecular oxidative annulations also the hypervalent iodine compounds have shown miraculous effects. When metallic compounds and reagents failed to achieve their target molecules the less toxic character and other valuable properties of hypervalent iodine helped many chemists to do their reactions. Following are the list of reactions which can be performed by hypervalent iodine regarding the intermolecular oxidative annulations.

3.1 Cyclopropana(e)tion of alkenes/alkynes by Hypervalent iodine(III).



The chemists have reported the suppression and production of

Cyclopropane derivatives when hypervalent iodine is used in the reaction.

THE PLAUSIBLE MECHANISM:

A plausible mechanism of iodo(III)cyclopropanation is proposed here.

The first step is ring opening by the carbon nucleophile, then there is the recyclization for trans alkene substrates.

The plausible steps are:-

(I)Iodo(III)cyclopropanation.

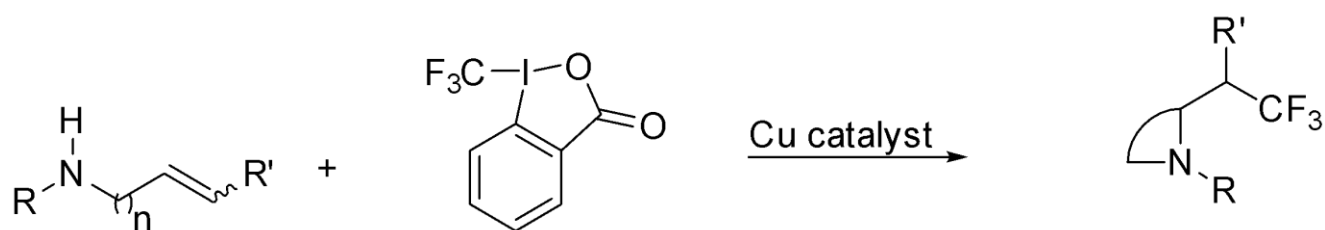
(II)Ring opening attack by the carbon nucleophile.

(III)Recyclization into a 4 membered iodo(III)cyclobutene.

(IV)Reductive elimination.

3.2 Synthesis of trifluoromethylated pyrrolidines by hypervalent iodine.

Trifluoromethylated compound is a good reagent in agrochemical industry. In this article the chemists have used Togni reagent. According to the results, the hypervalent iodine moiety of the Togni reagent is activated by Cu(II) compound which behaves as a Lewis acid.



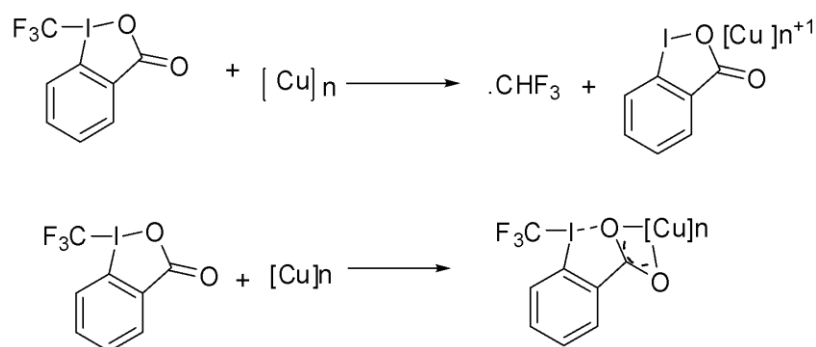
PLAUSIBLE MECHANISM STEPS:

Two types of key reactive species have been proposed.

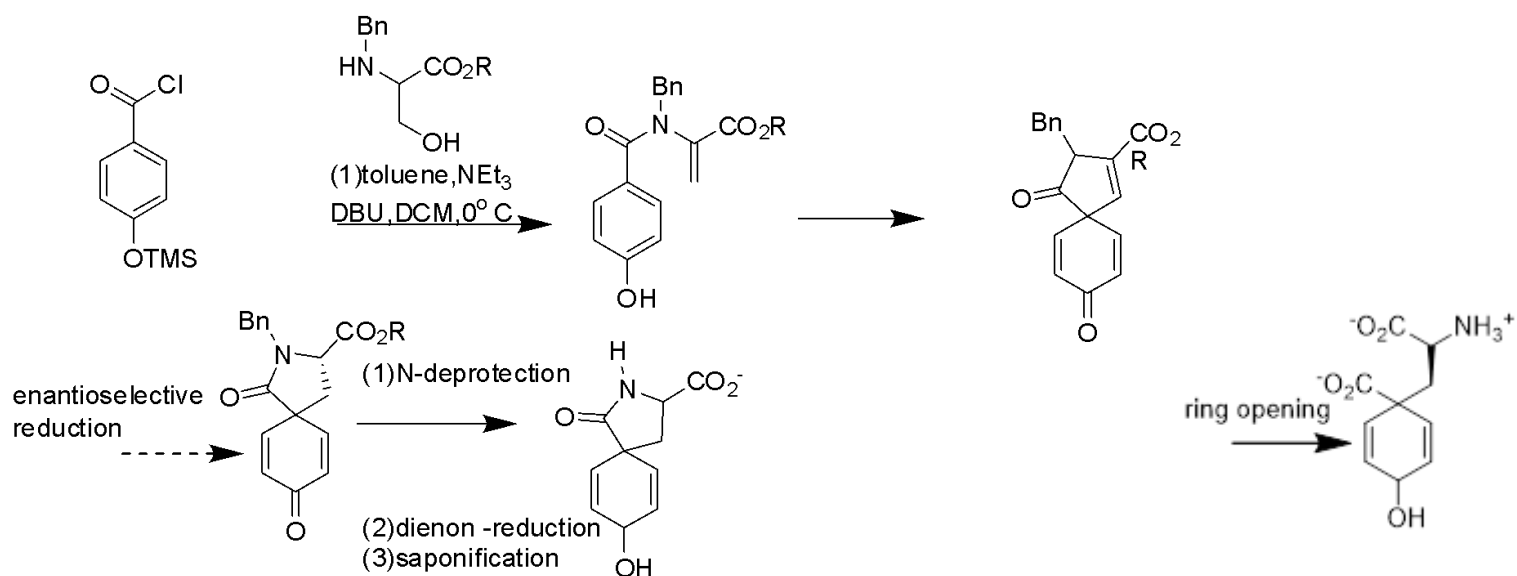
In one mechanism generation of a trifluoromethyl radical is proposed which is a precursor for Cu-CF₃ species.

The other mechanism involves the activated Togni reagent .

Copper behaves as a Lewis acid and enhances the electrophilicity of hypervalent iodine.



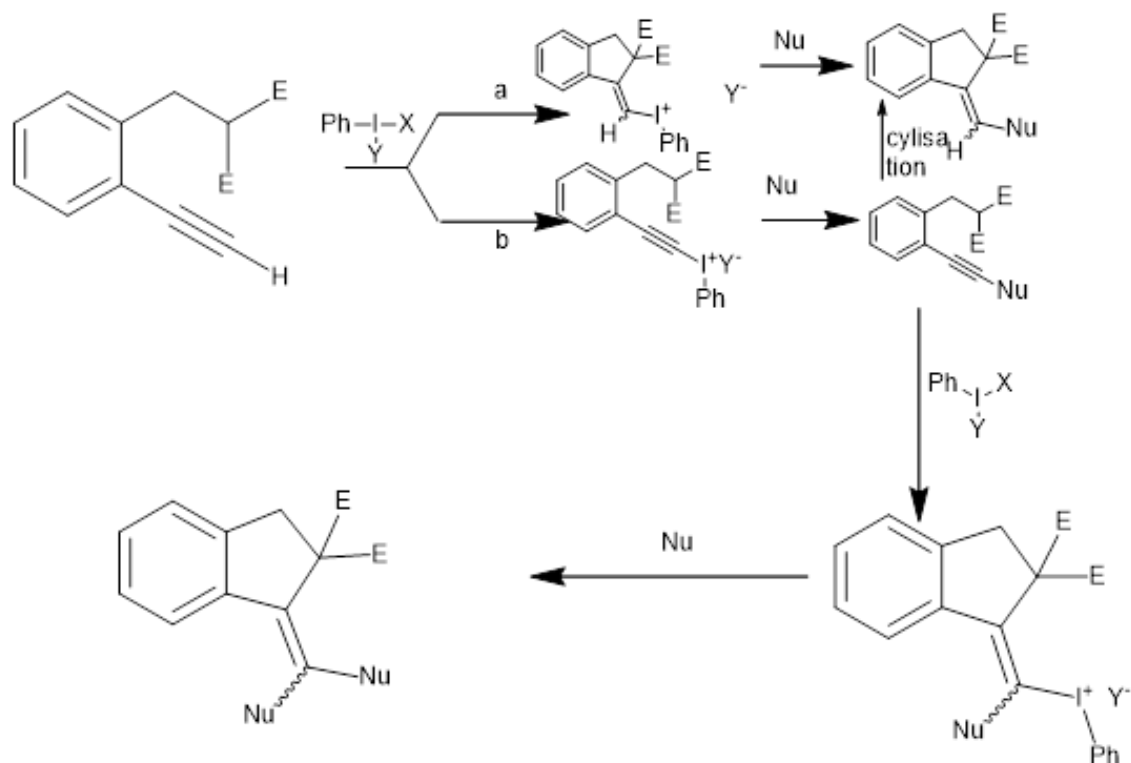
[3.3](#) A hypervalent iodine –mediated spirocyclisation of 2-(4-hydroxybenzamido)-acrylates-unexpected formation of delta- spiro lactones.



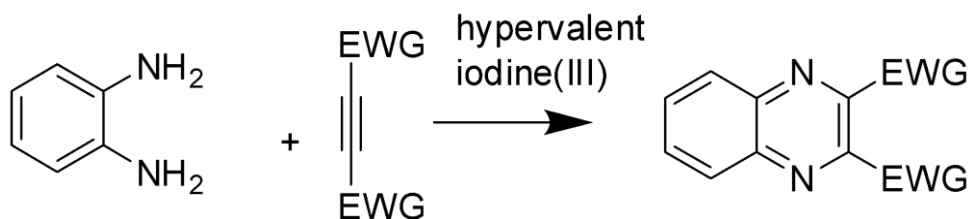
+

Here the chemists have constructed the spirocyclic compounds via dearomatization of Phenols .Oxidative spirocyclization of 2-(4-hydroxybenzamido)-acrylates is reported.A rare iodine(III)mediated spirocyclization resulting in novel delta Spirolactones is reported here.

3.4Hypervalent iodine –mediated regioselective cyclization of acetylenic malonates:facile synthesis of 1-diodomethylene indane and cyclopentane derivatives.



3.5 Hypervalent iodine(III) induced oxidative [4+2] annulation of o-phenylenediamines and electron deficient alkynes: direct synthesis of quinoxalines from alkynes substrates under metal free conditions.



Here the researchers have extensively used PIDA after screening the iodine compounds and various reagents. They have found PIDA to be highly effective for desired annulation.

PIDA and its consequent derivatives are used for synthesis of C-N

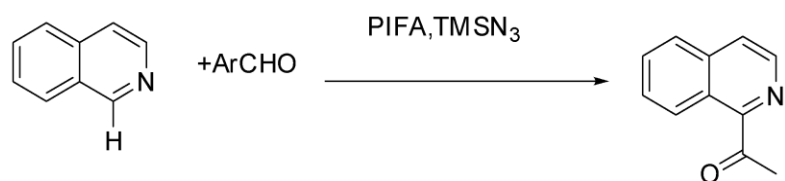
bond forming reactions. Here the quinoxalines have been prepared/synthesized from alkynes by using PIDA.

HYPERVALENT IODINE MEDIATED CROSS DEHYDROGENATIVE COUPLINGS.

When two molecules couple by liberating one hydrogen atom from each of them to form a complex it is termed as cross dehydrogenative coupling.

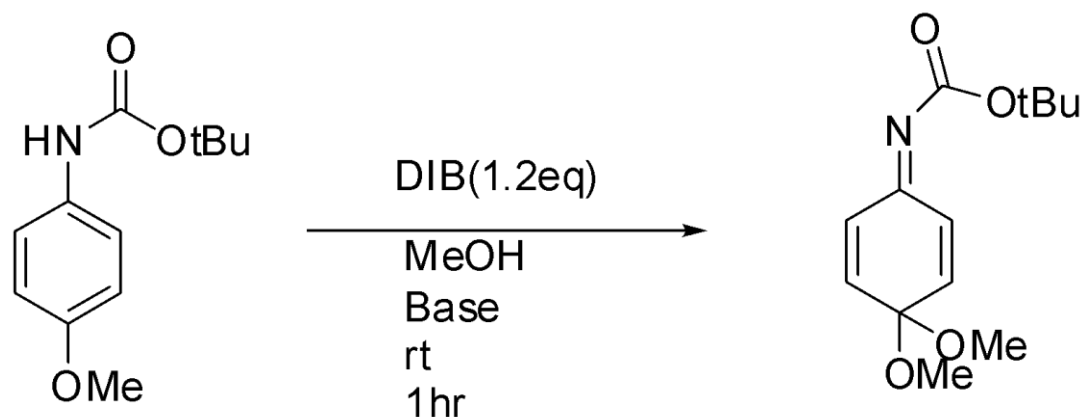
Even in the case of cross dehydrogenative couplings hypervalent iodine stands in front of metals. It has shown reactive pathways to chemists when it was tedious for them to prepare synthetic molecules by using metals and its derivatives.

1 .C1-Benzyl and benzoyl isoquinoline synthesis through direct oxidative CDC with methyl arenes.



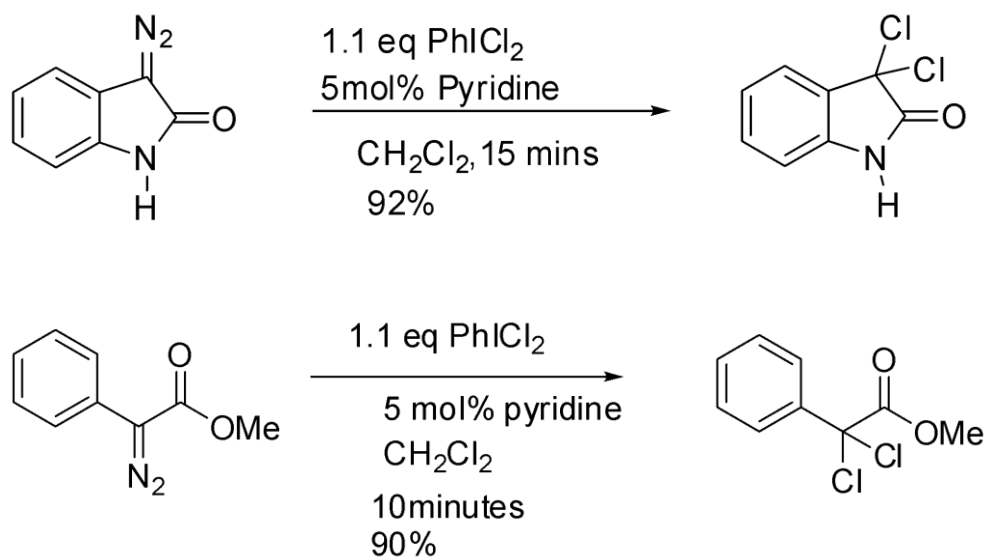
Under the supervision of Antonchick the chemists developed PIFA mediated benzoylation system, wherein the CDC OF ISOQUINOLINES with various aryl halides was done.

2. Hypervalent iodine mediated synthesis of carbamate protected p-quinone Monoamine ketals and p-benzoquinone monoketals.



The chemists have reported the development of a new, facile method to synthesize carbamate and acetyl protected quinone imine ketals from anilides.

4. Synthesis of 3,3-dichloroindolin-2-ones from isatin-3-hydrazone and (dichloroiodo)benzene.



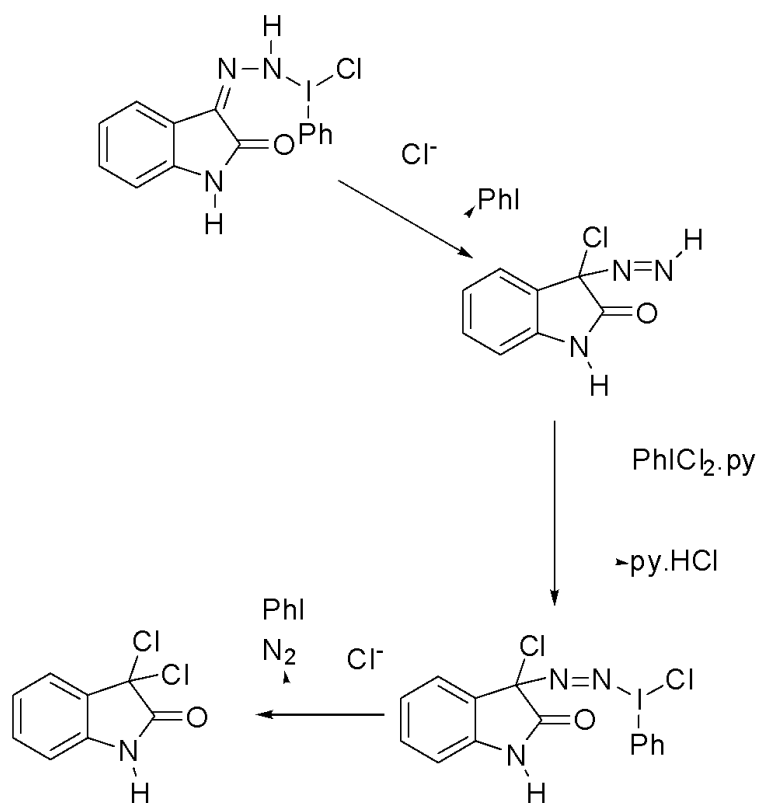
The Hypervalent Iodine (III) reagents have inherent ability of ligand transfer. Here the researchers have shown the strategy to transfer both the ligands from iodane into substrate by a leaving group.

This transformation is carried out by Lewis acid or Lewis base catalysed activation of iodane reagent enabling chemoselective conversion so as to produce the dihalogenated products.

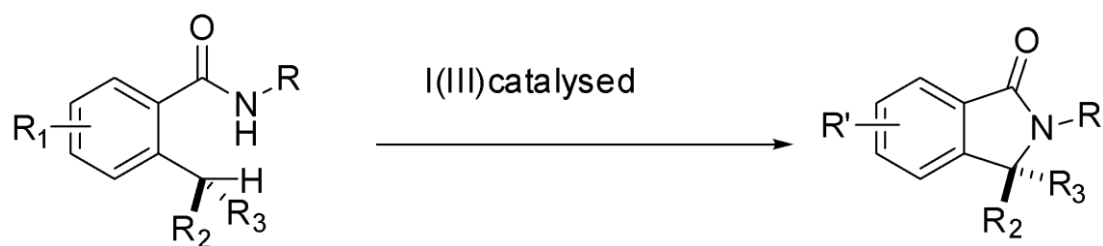
MECHANISM ENVISIONED

Adduct A is produced when the activated Iodane complex associates with the hydrazone. An azo intermediate B is formed when the chloride attacks A and removes PhI.

Association of B with 1 equivalent of Iodane complex gave C which when attacked by the chloride expels out the PhI and Nitrogen and gave the desired product.



5. Iodoarene-Catalyzed Stereospecific Intramolecular sp^3 C-H Amination: Reaction Development and Mechanistic Insights



The researchers have reported the first iodoarene –catalyzed intramolecular aliphatic C-H amination to synthesize lactams.

By DFT calculations the C-H bonding proceeds via concerted mechanism leading to stereospecific construction of chiral quaternary centres.

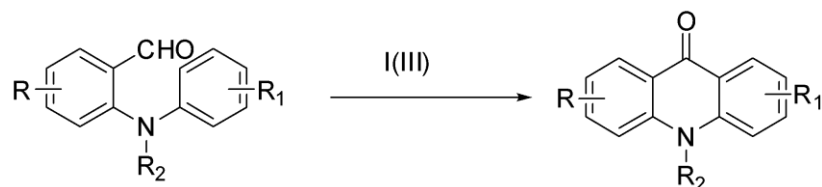
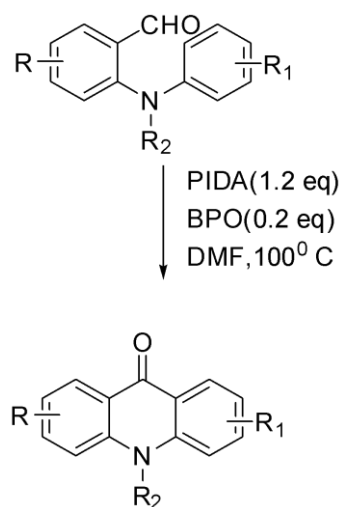
6. Hypervalent iodine(III)-mediated C(sp³)-H bond arylation, alkylation, and amidation of isothiochroman.



Report of developing a method for introducing the aryl, alkyl, amide

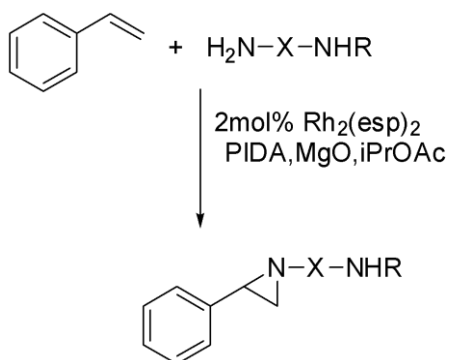
Groups at C(I) position of iso thiochroman by the use of hypervalent iodine reagents is given in this research article.

8. PhI(OAc)₂-Mediated Intramolecular Oxidative Aryl-Aldehyde Csp²-Csp² Bond Formation: Metal-Free Synthesis of Acridone Derivatives



Crossing the limitations of using the transition metals the chemists have used hypervalent iodine(III) in order to achieve intramolecular aryl aldehyde Csp²-Csp² formation.

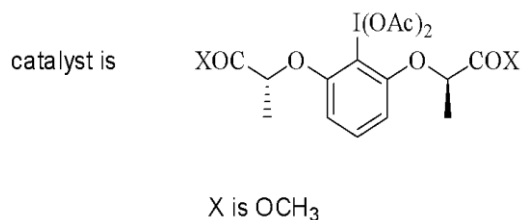
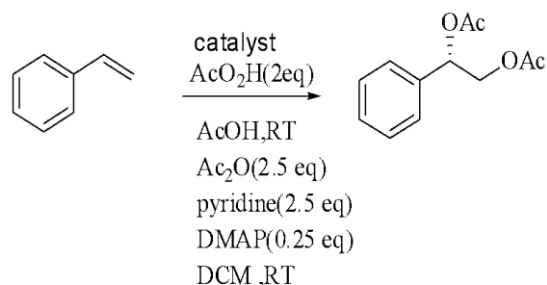
9.Hypervalent Iodine Mediated Vicinal Diamination Of Alkenes.



J.Du.Bois in the year 2014 has reported the formation of alkenes mediated by PIDA. In the presence of PhI(OAc)2, MgO, and 2 mol % Rh2(esp)2, reactions with H2NS(O)2NHBoc and the corresponding methylcarbamate derivative performed best and gave the desired aziridine products in yields exceeding 75%.

10. Structurally Defined Molecular Hypervalent Iodine Catalysts for Intermolecular Enantioselective Reactions.

A principle for a truly intermolecular asymmetric alkene oxidation under iodine(I/III) catalysis is now developed by Prof. Dr. Kilian Muñiz et al.



In the words of the authors

“A definite understanding of the mode of action of chiral hypervalent iodine reagents can form the basis to enlarge the differentiation of prochiral face recognition from the established intramolecular reaction control to more challenging topics, such as the asymmetric oxidation of prochiral substrates by intermolecular reaction control, and particularly in terms of catalysis.”

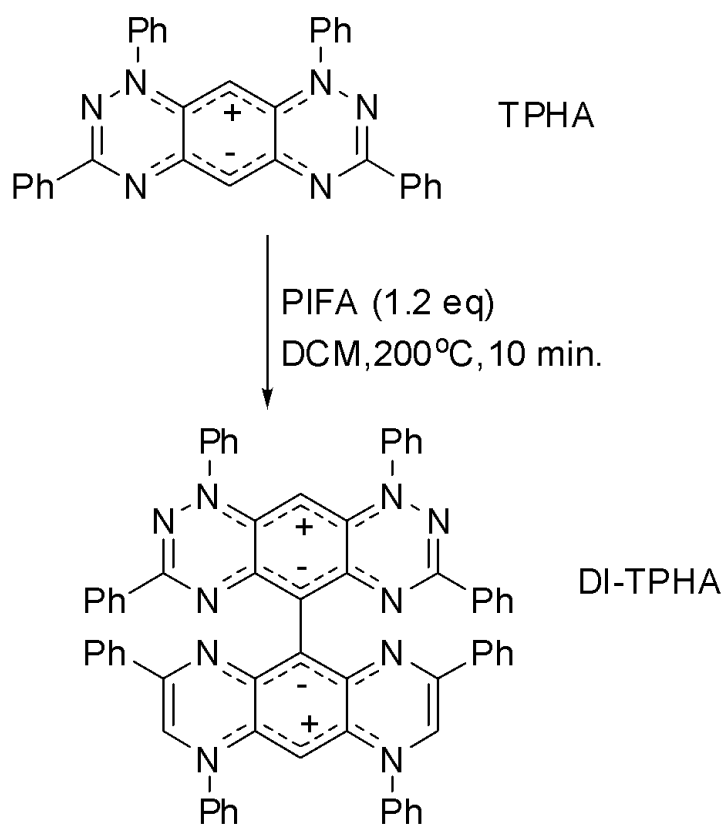
After such splendid report there is no doubt that hypervalent iodine has emerged as a ray of hope for chemists.

11.Oxidation of Tetraphenylhexaazaanthracene: Accessing a Scissor Dimer of a 16 π Biscyanine by PIFA.

Here Panayiotis A. Koutentis et al have again shown the excellent application of PIFA by converting TPHA to DI-TPHA.

The DI-TPHA has around zero dipole moment and is weakly fluorescent.

Cyclic voltammetry, electronic spectroscopy, and density functional theory (DFT) computational studies have proved the nature of DI-TPHA.

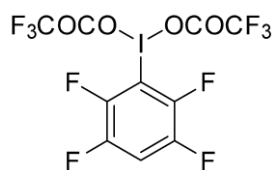


These are used as OFETs ,and as dyes in textile industries.

12. BTI-Mediated Syntheses of Heterocyclic Compounds



Numerous BTI-induced intramolecular amidation reactions of precursors give five-, six-, and seven-membered heterocycles have been reported by Tellitu and Dominguez. The key active species in these reactions, are N-acylnitrenium intermediates, are initially generated from amides and BTI, and the experimental evidence supports the ionic mechanism of these cyclization reactions.



BTI

Organo-
Iodine(III)-
Catalyzed
Oxidative
Phenol-

Arene and

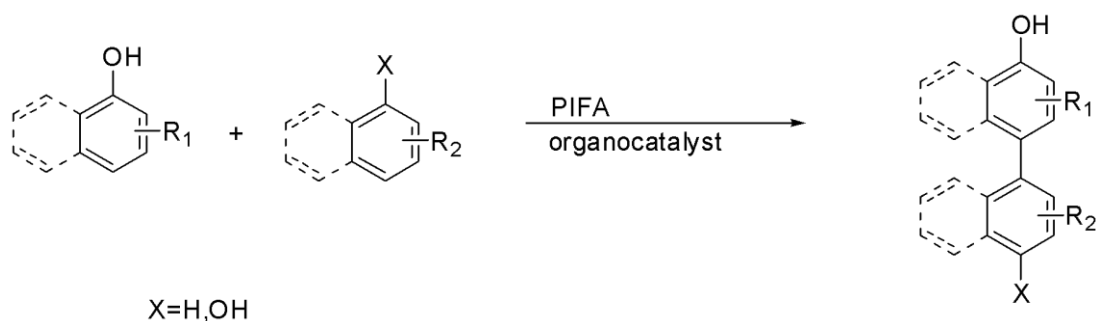
Phenol–

Phenol

Cross–

Coupling Reaction

13. Organo-Iodine(III)-Catalyzed Oxidative Phenol–Arene and Phenol–Phenol Cross-Coupling Reaction



The above reaction of hypervalent iodine was carried out by Koji Morimoto et al in 2016.

Features of this reaction: 1. atom economical.

2. environmentally friendly.

This reaction is
a challenge
because, when
simple phenols are
employed in
oxidative cross-
couplings, the

desired products are often concomitantly formed along with homocoupling by-products

This reaction is a challenge because, when simple phenols are employed in oxidative cross-couplings, the desired products are often concomitantly formed along with homocoupling by-products.

After using many reagents the chemists achieve success when they employed the hypervalent iodine.

CONCLUSION AND HIGHLIGHTS OF OUR REVIEW:-

1.EXAMINING THE ADVERSITY OF HEAVY METALS AND BENEFITS OF USING HYPERVALENT IODINE.

Hypervalent Iodine has tremendous potential in making various organic complexes. When metals take time and present various chemical adversities in preparing various molecules Hypervalent iodine compounds have practically helped the chemists in preparing them. Not only they are affordable but also they are environmentally benign. In this review we have shown many examples from various sources that how hypervalent iodine has gained importance over metals. Antonchik and others have contributed like pioneers in hypervalent iodine area.

2..COMPREHENSIVE VIEW OF THE APPLICATIONS OF HYPERVALENT IODINE.

From this review article we come to know that hypervalent iodine has applications in the following areas.

Hypervalent iodine has many applications like:

- Oxidation of alcohols
- Azidations ,Aminations,Thiocyanations
- Cross dehydrogenative couplings

- Oxidative annulations.
- Oxidative dearomatizations (e.g. Phenols)
- Group transfer reactions (eg.trifluoromethylations.)

Viktor V. Zhdankin has contributed a lot to show the comprehensive view of hypervalent iodine.

3.FINALLY THE VIEW OF CHEMISTS .

Various chemists have presented their views on hypervalent iodine and its applications in their articles/reviews. The major contribution of hypervalent iodine lies in the fact that it is environmentally benign .The potential of hypervalent iodine has been thoroughly explained by chemists in various articles For example ***Viktor V. Zhdankin has a pioneer contribution in explaining how hypervalent iodine. And compounds have started revolution in chemical world. In similar way Antonchik has also proved the potential of hypervalent iodine in his articles.***

Our view is in agreement with all the chemists.

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