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Review

Phenyliodine(III)diacetate (PIDA): Applications in Organic Synthesis

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Abstract: One of the hypervalent iodines most widely used as an oxidizing agent in organic chemistry is (diacetoxyiodo)benzene ($PhI(OAc)_2$), also known as (DAIB), phenyliodine(III) diacetate (PIDA). In this septennial mini-review, the authors have concisely and systematically presented representative applications of PIDA in organic synthesis involving C-H functionalization, hetero-hetero bond formations, heterocyclic ring construction, rearrangements or migrations and miscellaneous reactions along with their interesting mechanistic aspects starting from the summer of 2015 to the present.

Keywords: phenyliodine(III) diacetate (PIDA); C-H functionalization; hetero-hetero bond formations; heterocyclic ring construction; rearrangements or migrations; miscellaneous reactions

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1. Introduction

In comparison to conventional heavy-metal oxidants, hypervalent iodine (III) reagents, also known as "3-iodanes", have attracted a lot of attention over the past three decades because they are plentiful, stable, non-toxic, environmentally friendly, and mild $2e^-$ oxidants with a variety of applications [1–6]. They consistently support distorted trigonal bipyramidal geometry with the electronegative ligands in the axial positions and the less electronegative aryl ring and two lone pairs of electrons in the equatorial positions. Hypervalent iodine (III) reagents are electrophilic in nature due to the node in a hypervalent nonbonding orbital, a 3-center-4-electron (3c-4e) bond (L-I-L), which is created by the overlap of the iodine atom's 5p orbital with the orbitals of two ligands [7].

Many new heterocyclic compounds have been created as a result of the extensive usage of hypervalent iodine (III) reagents to generate carbon-carbon, carbon-hetero atom, and hetero-hetero atom bonds, such as phenyliodine(III) bis(trifluoroacetate), phenyliodine(III) diacetate, iodosobenzene (PhIO). The hypervalent iodine compound (diacetoxyiodo)benzene ($PhI(OAc)_2$), commonly abbreviated as (DAIB) or phenyliodine(III) diacetate (PIDA), is widely utilized as an oxidizing agent in organic chemistry (Figure 1) [8–10]. In addition, (diacetoxyiodo)benzene is utilized in a wide range of pharmaceutical intermediates, liquid crystal display (LCD) polarizing films, industrial, human, and animal nutrition products [https://seemafinechem.com/iodobenzene-diacetate/, accessed on 10 December 2022].

The original PIDA was synthesized by Willgerodt in 1886 by reacting iodobenzene with a solution of acetic and peracetic acid [11]. Current methodologies use a variant of this process that entails the oxidative diacetoxylation of iodoarenes in acetic or trifluoroacetic acid with suitable oxidants such as periodates, *m*-chloroperoxybenzoic acid, potassium peroxodisulfate, H_2O_2-urea, selectfluor, and sodium perborate [12–14]. The applications of PIDA in relation to a few illustrative organic syntheses are the main subject of this brief review, which spans the summer of 2015 to the present.

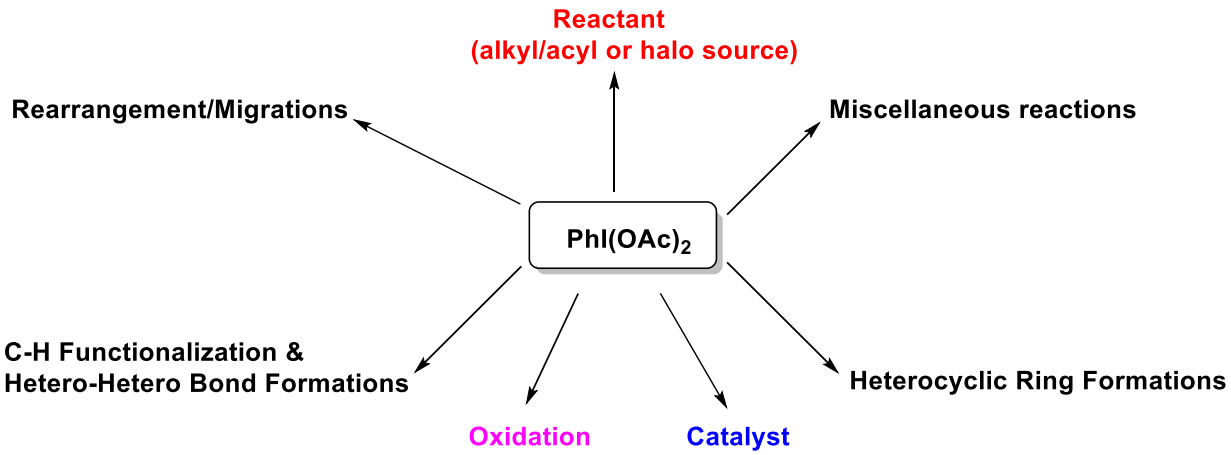


Figure 1. Structure of phenyliodine(III) diacetate (PIDA, **1**).

2. Recent Applications of PIDA (from 2015)

2.1. C-H Functionalization and Hetero-Hetero Bond Formations

2.1.1. C-C Bond Formation

(a) C-Alkylation reaction

Due to the importance of alkyl groups in the life and material sciences, alkylation reactions to create alkylated heterocycles have garnered the attention of chemists as a key area of research. On the other hand, quinoxalin-2(1*H*)-ones are widely present in a variety of pharmacologically active molecules and naturally occurring chemicals, making them a valuable class of heterocycles. The decarboxylative alkylation of quinoxalin-2(1*H*)-ones (**2**) with phenyliodine(III) dicarboxylates under visible light was established by He and co-workers, as an effective and sustainable method for producing 3-alkylquinoxalin-2(1*H*)-ones (**3** and **4**) in the presence of PIDA (**1**) and PEG-200 as solvent (Scheme 1) [15].

The current ruthenium(II) catalytic system, which could be successfully recycled five times without major decrease in its effectiveness, made it simple to create various 3-alkylquinoxalin-2(1*H*)-ones. The optimized reaction parameters are: PIDA (1 equiv.), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1 mol%) in PEG-200 and 3W Blue LED. Additionally, $PhI(OTfa)_2$ was employed in place of $PhI(OAc)_2$ without causing any reaction. In general, the synthesis of quinoxalin-2(1*H*)-ones with phenyl rings carrying electron-withdrawing and electron-donating substituents went without a hitch, yielding the intended products in good to exceptional amounts. Notably, this methylation process also demonstrated high compatibility with functionalities, and some functional groups, such as halogen, acyl, nitro, and ester groups, were tolerated to produce compounds that can be used for additional synthesis.

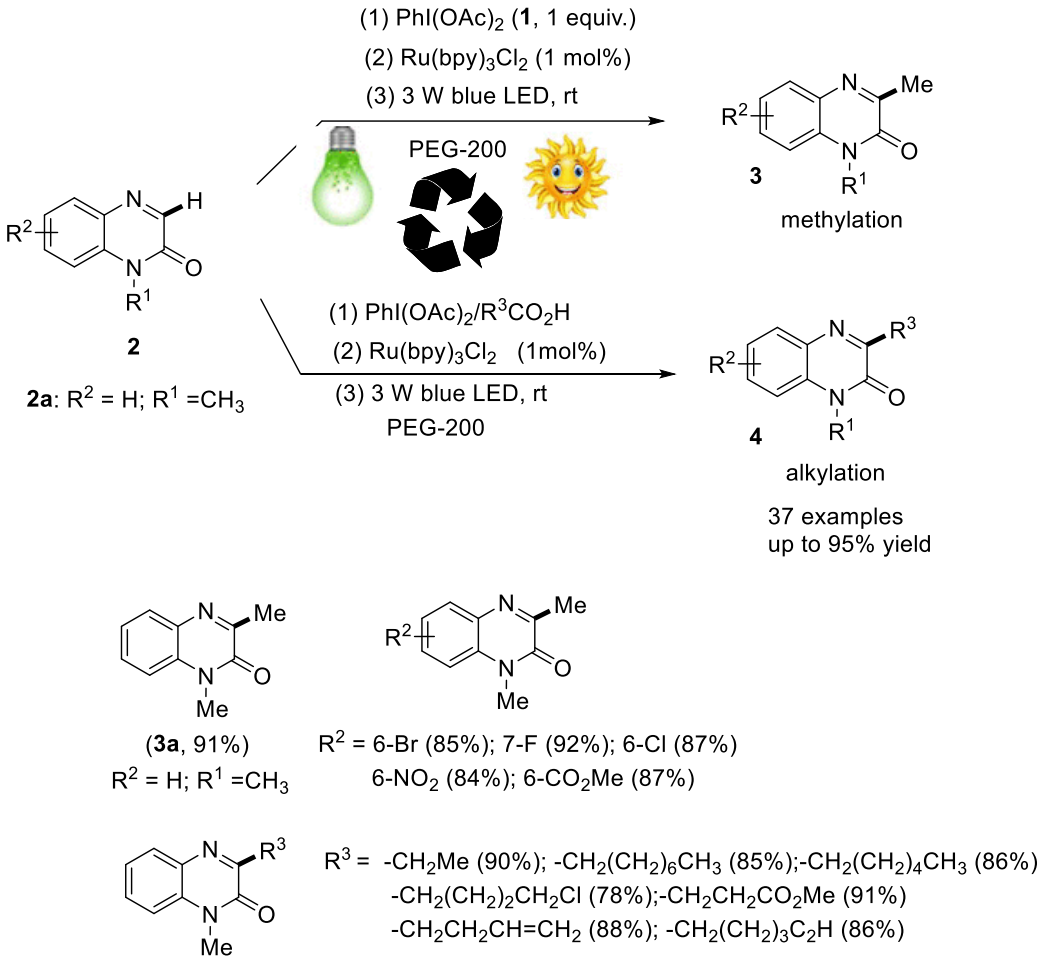
As shown in Figure 2, a potential reaction pathway was suggested. Initial visible light exposure produces the excited-state $*Ru(ppy)_3^{2+}$. After this, a single electron transfer (SET) process occurs. Radical **5** and $Ru(ppy)_3^{3+}$ are produced between the reaction of $PhI(OAc)_2$ (**1**) and $*Ru(ppy)_3^{2+}$. The radical **5**'s I-O link is then broken, resulting in an acyloxy radical, which is then converted to a different compound by decarboxylation to produce the methyl radical **6**. Next, the resulting methyl radical **6** is added to **2a**, which results in the formation of the nitrogen radical **7**. This nitrogen radical **7** is then oxidized by $Ru(ppy)_3^{3+}$, which results in the formation of the nitrogen cation **8**. In conclusion, the creation of product **3a** will take place as a consequence of the abstraction of β-H from **8** by carboxylic anion.

(b) C-C bond formation reaction on alkenes

Fluorinated substances have a significant role in the creation of pharmaceuticals. The difluoro-methyl group (CF2H) stands out among them as a physiologically stable lipophilic bioisostere of weak hydrogen bond donors such as alcohols, anilines, amines, or thiophenols and has been used in a variety of medicinal compounds as a result. Terminal alkenes (**9**) were hydrodifluoromethylated (**11**) regioselectively in the presence of PIDA,

in accordance with a protocol devised by Gouverneur and his group (Scheme 2) [16]. By adopting this metal-free method, it was possible to obtain bio-relevant building blocks that would have otherwise required many deoxyfluorination-based processes in synthetic chemistry. It is photocatalyst-free, exhibits broad functional group tolerance, and employs inexpensive reagents.

The optimized reaction parameters are: PIDA (3 equiv.), CF2HCO2H (**10**, 6 equiv.) in THF under visible light (λ = 450 nm). Esters, amides, alcohols, aldehydes, halides, and nitriles were all tolerated, and yields ranging from moderate to good were obtained when separating the necessary products. The intended compounds were effectively produced from alkenes containing carboxylic acids or aldehydes in modest yields; however, such functional groups would need to be protected using deoxyfluorination chemistry. Heteroarenes survived the reaction conditions well and did not compete with other heteroarenes for heteroaryl C-H difluoromethylation. The reaction mechanism was claimed to proceed via radical pathway. Difluoroacetic acid **10** is exchanged for the acetate group on **1** to produce **12**. When exposed to blue light, photolysis produces **14** that can be decarboxylated to produce •CF_2H (Figure 3). The alkene substrate would benefit from the regioselective addition of this radical. The net hydrodifluoromethylation product would then be produced by the further reaction of the resulting carbon radical **15** with THF. Tetrahydrofuran's hydrogen atom can be extracted to release the THF α-radical **16**, which can then undergo a single electron transfer to the third dimension while simultaneously releasing the oxonium ion **17**, iodobenzene, difluoroacetate, and radical **14** for additional alkene functionalization. Given the greater stability of CF_2H than CH_3, hydromethylation was not seen as predicted.



Scheme 1. PIDA-mediated synthesis of 3-alkylquinoxalin-2(1*H*)-ones.

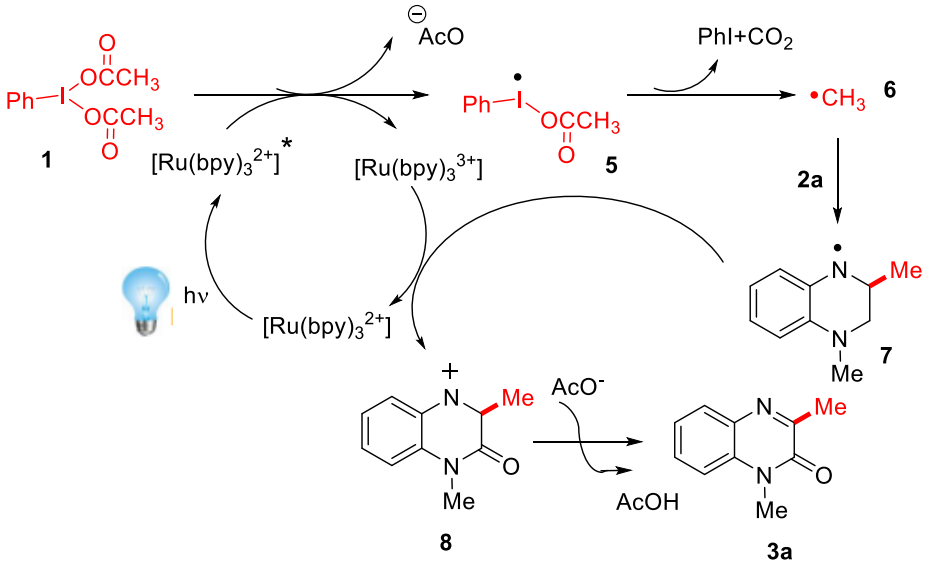
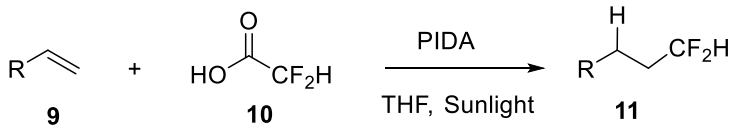


Figure 2. PIDA-mediated radical pathway for the synthesis of 3-alkylquinoxalin-2(1*H*)-ones.



Scheme 2. PIDA-mediated synthesis of hydrodifluoromethylation of terminal alkenes.

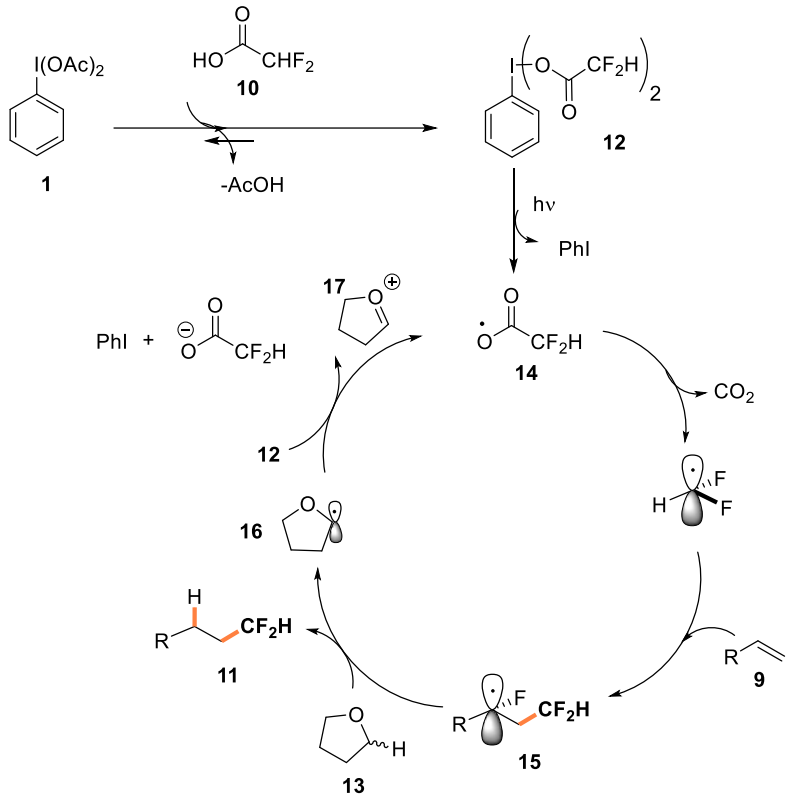
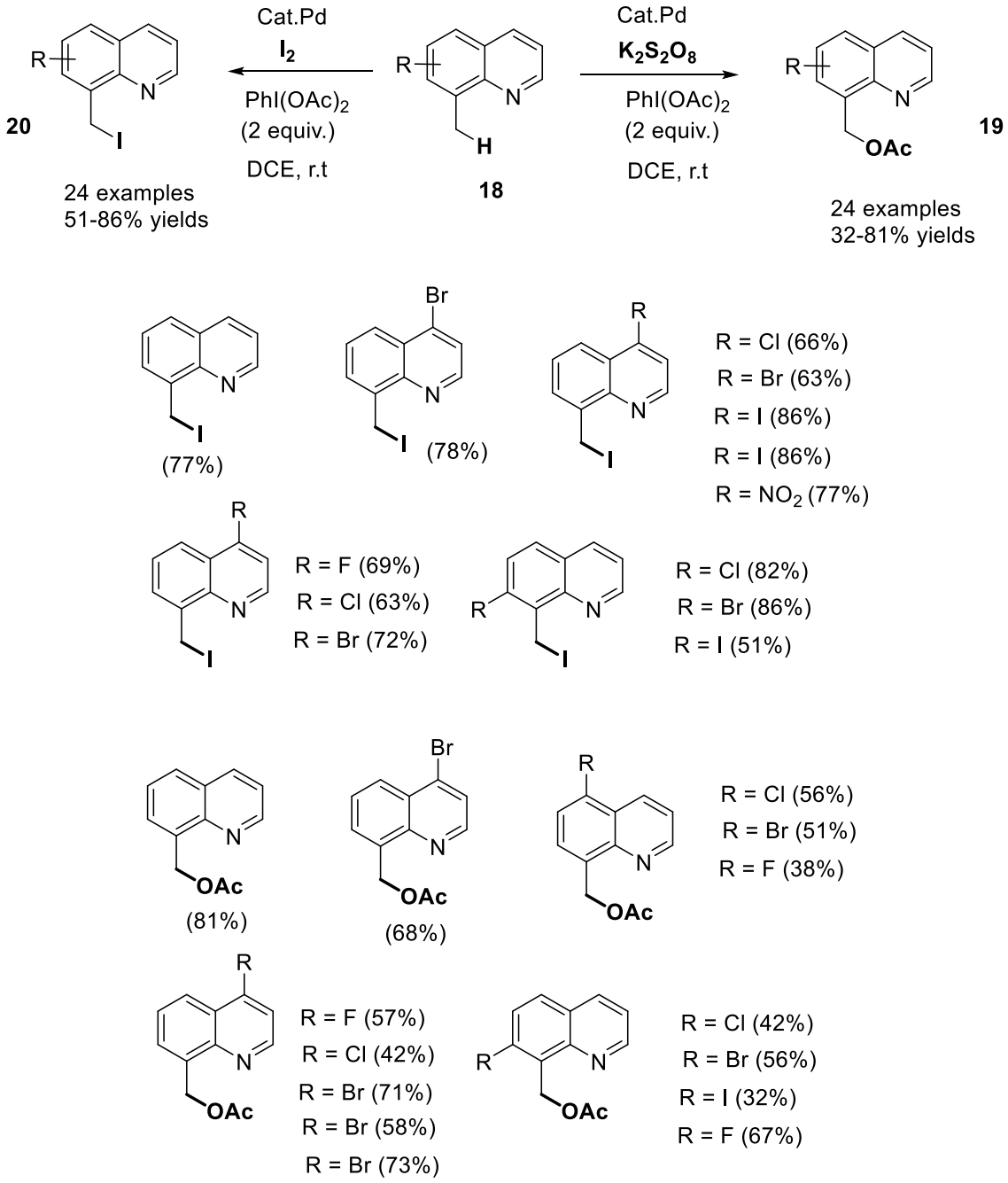


Figure 3. PhI(OAc)$_2$-mediated radical pathway for the hydrodifluoromethylation of terminal alkenes.

2.1.2. C-O and C-X Bond Formation

Quinoline is a flexible *N*-based heterocyclic system that is well-known for being present in a wide range of natural products, agrochemicals, medicines, functional materials,

and ligands for transition-metal catalysis. Therefore, it is important to create effective synthetic processes for substituted quinolines. The more difficult site-selective C(sp^3)-H activation/functionalization of 8-methylquinoline is particularly noteworthy in this domain. A report was developed by Jia et al. on an effective Pd-catalyzed C(sp^3)-H selective iodination of 8-methylquinolines (**18**) [17]. The method provided simple access to a variety of C8-substituted quinolines due to the adaptability of organic iodides (Scheme 3). The effective C(sp^3)-H acetoxylation of 8-methylquinolines was also made possible by slightly altering the reaction conditions.



Scheme 3. PIDA-mediated formation of C-X and C-O bonds.

Both strategies had a wide range of substrates, gentle reaction conditions, and strong functional group tolerance. The optimized reaction parameters are: $PhI(OAc)_2$ (2.0 equiv.), I_2 (1 equiv.), $Pd(dba)_2$ (10 mol%) in DCE at RT (for C(sp^3)-H iodination, **20**) and $PhI(OAc)_2$ (2.0

equiv.), $K_2S_2O_8$ (2 equiv.), $Pd(dba)_2$ (10 mol%) in DCE at RT (for C(sp^3)-H acetoxylation, **19**). It is important to note that the halides F, Cl, Br, and I were all well tolerated at the reaction conditions utilized at the time. These halides were also useful synthetic handles that could be used in additional transformations with ease. The reactivity was essentially unaffected by the position of the substituent on the aromatic rings. The acetoxylation procedure demonstrated excellent functional group compatibility, much like the iodination process mentioned above. Sequential transformations were made possible because a variety of electron-withdrawing and electron-donating groups, at various positions of the quinoline ring, were all well tolerated under the reaction circumstances. It should be noted that substrates having substituents at the C7 position produced lower yields, which was likely due to the steric hindrance of substituent groups at the *ortho*-position.

According to Figure 4, a possible mechanism for the Pd-catalyzed C(sp^3)-H iodization and acetoxylation of 8-methylquinoline (**18**) was proposed. $PhI(OAc)_2$ oxidizes $Pd_2(dba)_3$ to produce a Pd(II) species, which is then palladium-directed by quinoline to produce cyclopalladated complex **21**. It should be noted that Pd(II) compounds, such as $Pd(OAc)_2$ and $Pd(PPh_3)_2Cl_2$, produced worse results, which can likely be attributed to newly formed Pd(II) species that were produced in situ and had higher catalytic activity. I_2 is added oxidatively to produce Pd(IV) intermediate **22**, which is subsequently eliminated reductively to produce iodide **20** and regenerate Pd(II) catalyst. As opposed to this, the oxidative addition of cyclometalated Pd(II) complex **21** with IOAc, which can be produced in situ by the reaction of I_2 with $PhI(OAc)_2$, results in Pd(IV) species **23**, which then produces the acetoxylation product **19** and the Pd(II) catalyst through a subsequent reductive elimination.

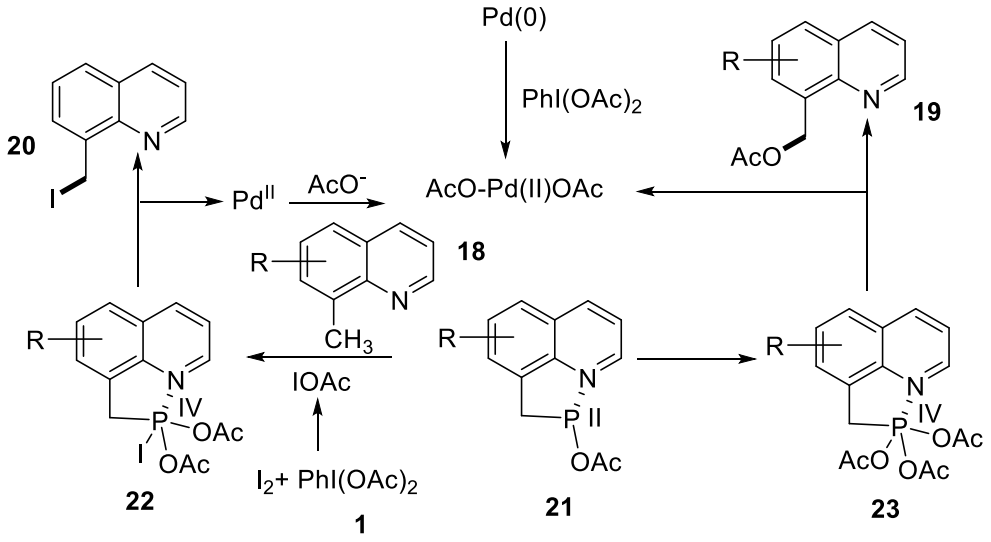


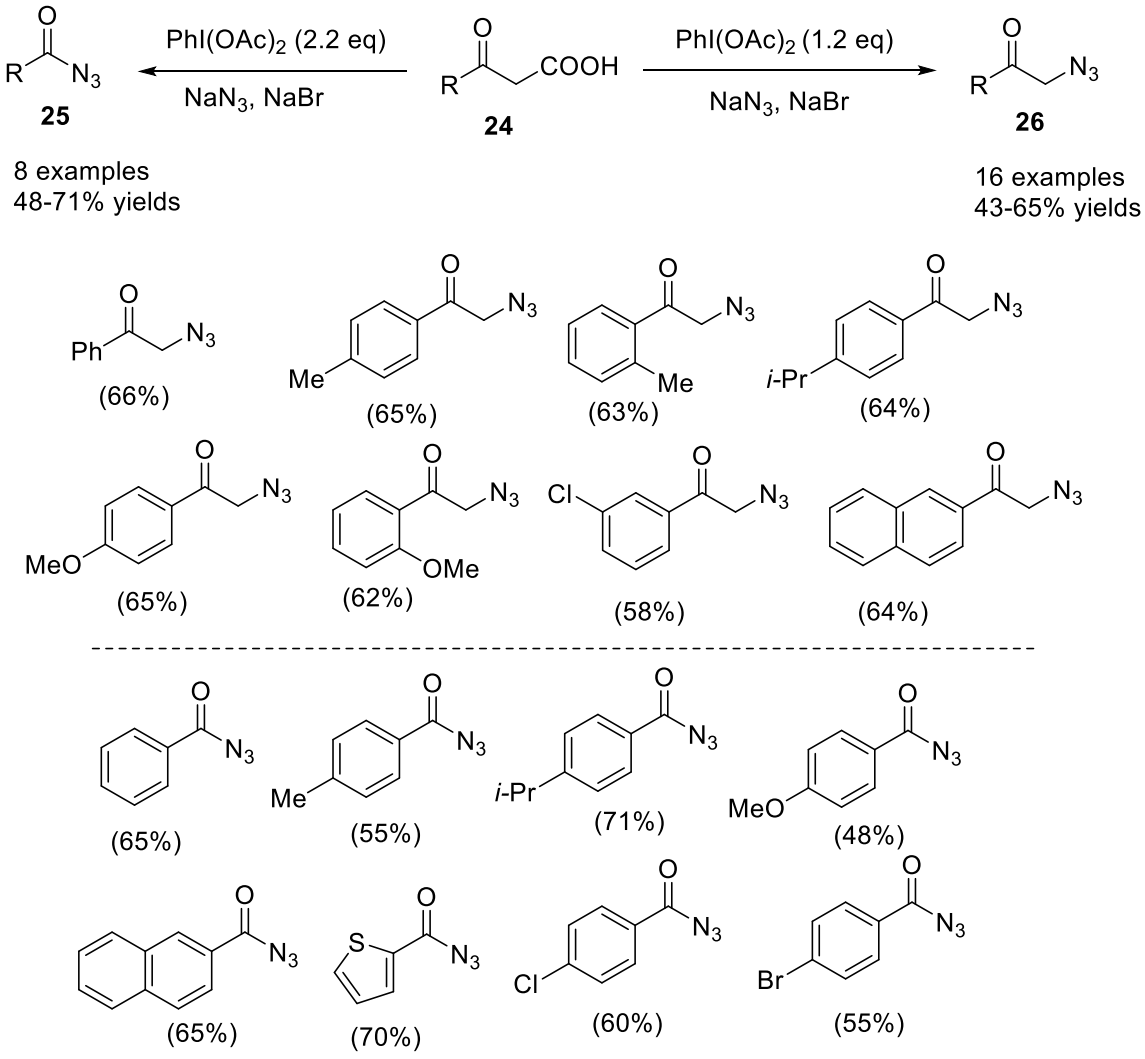
Figure 4. Proposed mechanism for selective iodination/acetoxylation.

2.1.3. C-N Bond Formation

Organoazide compounds are important synthetic building blocks and intermediates in organic chemistry. In addition, the azido moiety is added to lead compounds in drug discovery to boost biological activity. The reasons β-keto acids are often employed as raw materials in organic synthesis include stability, operability, accessibility, and low cost. Selective synthesis of acyl azides (**25**) or α-azido ketones (**26**) from keto acids (**24**) using PIDA(**1**) was developed by the research group of Xu and Wei [18].

The quantity of reagents used affects selectivity. When 1.2 or 2.2 equiv. of (diacetoxyiodo)benzene were added to derivatives of β-keto acids, the resulting products were α-azido ketone or acyl azide, respectively (Scheme 4). The optimized reaction parameters for obtaining α-azido ketone are: PIDA (1.2 equiv.), NaN_3 (3 equiv.) and NaBr (1.1 equiv.) in acetone: H_2O (5/1, v/v) at RT-Condition A. The optimized reaction parameters for obtaining acyl azide are: PIDA (2.2 equiv.), NaN_3 (6 equiv.) and NaBr (2.5 equiv.)

in acetone: H_2O at RT-Condition B. Other hypervalent iodine(III) reagents were found to be less successful in this transformation, including [bis(trifluoroacetoxy)iodo]benzene (PIFA) and (dichloroiodo)benzene. In order to produce the appropriate α-azido ketones in moderate to good yields, authors subjected a variety of different β-keto acids to the optimal reaction conditions. At room temperature, these reactions moved quickly, and utilizing Condition A, quantitative conversion was attained in less than two hours. The reaction conditions were consistent with a variety of substitution patterns, including *ortho-*, *para-*, and *meta*-substituted aromatic rings, naphthyl, and heterocycles (thiophene and furan). As anticipated, benzyl, as well as primary, secondary, tertiary, and cyclic alkyl groups, were all well tolerated.



Scheme 4. PIDA-mediated formation of C-N bonds.

The authors also examined how various β-keto acids reacted when exposed to Conditions B. It was possible to easily convert both electron-rich and electron-deficient aryl-substituted β-keto acids into the necessary compounds. The fact that halo-substituted aryl ketones survived the reaction well and produced halo-substituted compounds, which may be useful for subsequent transformations, was also remarkable. Additionally, this transformation was tolerable to the substituted naphthyl and heteroaryl (thiophene) keto acids, which produced the respective products in good yields.

Following the findings of the control experiments, it can be said that the decarboxylation step precedes the ligand exchange between the β-keto acid and the hypervalent iodine reagent and that the carboxyl group is crucial to these processes. Keto acid **24** would react

with PIDA and sodium bromide under Condition A to produce intermediate **27**, which would then undergo decarboxylation to produce compound **28** (Figure 5). The introduction of azide would then cause compound **28** to produce the observed product **26**. There are two alternative paths under Condition B. To create enolate intermediate **29**, which would then combine with PIDA and sodium bromide to produce dibromo compound **31**, intermediate **27** may undergo decarboxylation in Path A. Dibromide intermediate **30** would be decarboxylated in process B to produce **31**. Following nucleophilic substitution, an unstable diazido molecule **32** would be created, which would then go through rearrangement to produce product **25** (Figure 4).

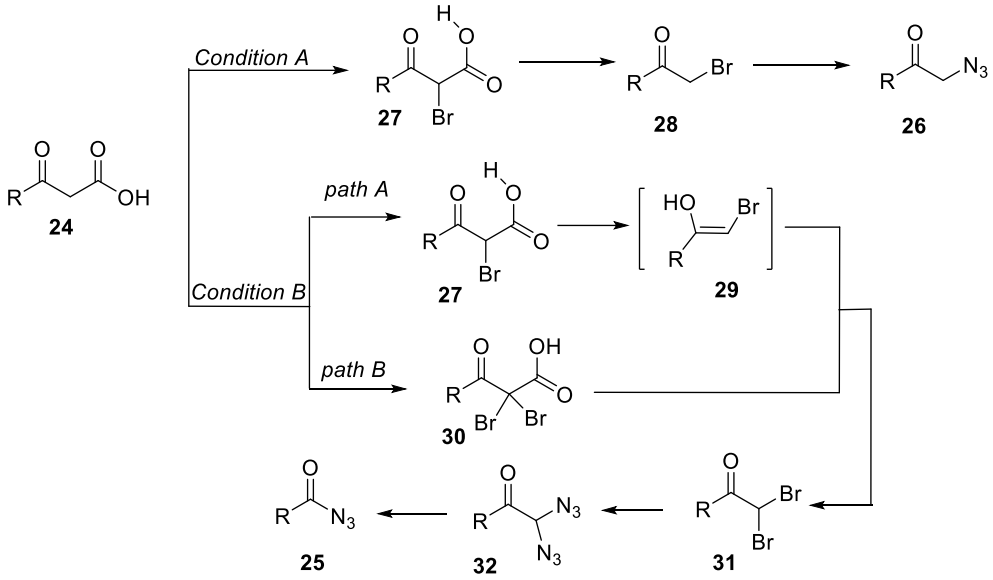


Figure 5. Possible pathways for the synthesis of acyl azides or α-azido ketones.

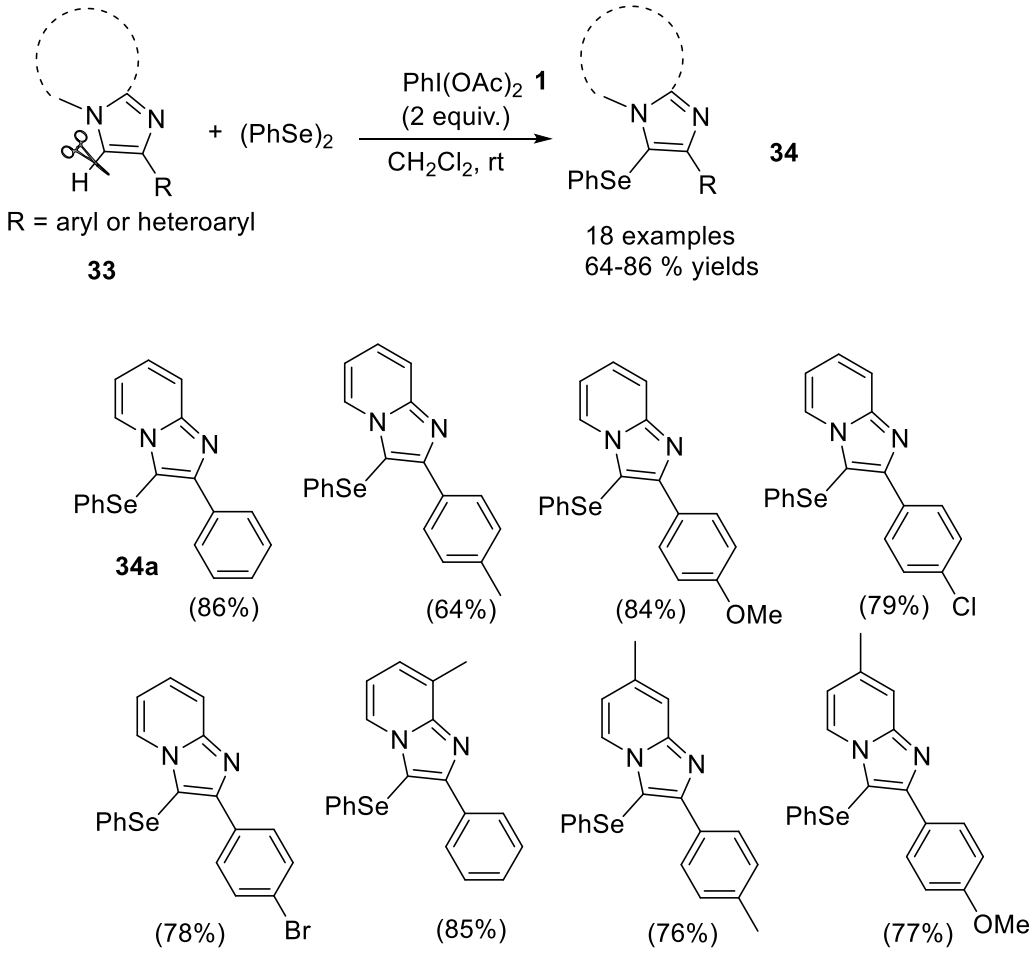
2.1.4. C-Se Bond Formation

Organoselenium compounds serve as crucial building blocks in the synthesis of organic molecules. The derivatives of organoselenium compounds are also used as fluorescence probes in the study of materials. More recently, organic and medicinal chemists have paid close attention to organoselenium compounds and subsequent studies of their biological activities. Numerous aryl-Se-heteroaryl compounds that are unsymmetrical exhibit a variety of pharmacological traits, including anticancer, antioxidant, antiproliferative, antibacterial, and anticholinesterase actions. Diphenyl diselenide was used by Karade et al. to enable metal-free (diacetoxy)iodobenzene-mediated C(sp^2)-H phenylselenation of imidazo[1,2-*a*]pyridines and imidazo[2,1-*b*]thiazoles (**33**) in the presence of PIDA [19]. The imidazoheterocycle phenyl selenation product (**34**) of this procedure demonstrated broad substrate scope, good to outstanding yields, and rapid reaction times (Scheme 5).

The optimized reaction parameters are: PIDA (2 equiv.) in DCM at RT. Numerous imidazo[1,2-*a*]pyridines with electron-donating and electron-withdrawing groups at aryl or pyridine moieties can be synthesized using this approach. The electronic effect of the substituents does not proportionally affect the yield of the reactions. The steric barrier had no impact either.

In Figure 6, a possible process for phenylselenating imidazo[1,2-*a*]pyridines using 1,2-diphenyldiselane is depicted. PhI(OAc)SePh **35** is a potential intermediate that can be produced by the ligand exchange reaction between **1** and PhSeSePh. Electrophilic benzeneselenyl acetate **37** may be produced as a result of intermediate **35**'s tendency for the reductive elimination of iodobenzene. Through its C3 position, the electrophilic benzeneselenenyl acetate **37** is attacked by the imidazo[1,2-*a*]pyridines **33** to create the complex **38**, which then undergoes aromatization to produce the 3-phenylseleno imidazo[1,2-*a*]pyridines

34. The use of DIB and PhSeSePh for phenylselenation of imidazo[1,2-*a*]pyridines cannot, however, completely rule out the possibility of a free radical process.



Scheme 5. PIDA-mediated formation of C-Se bonds.

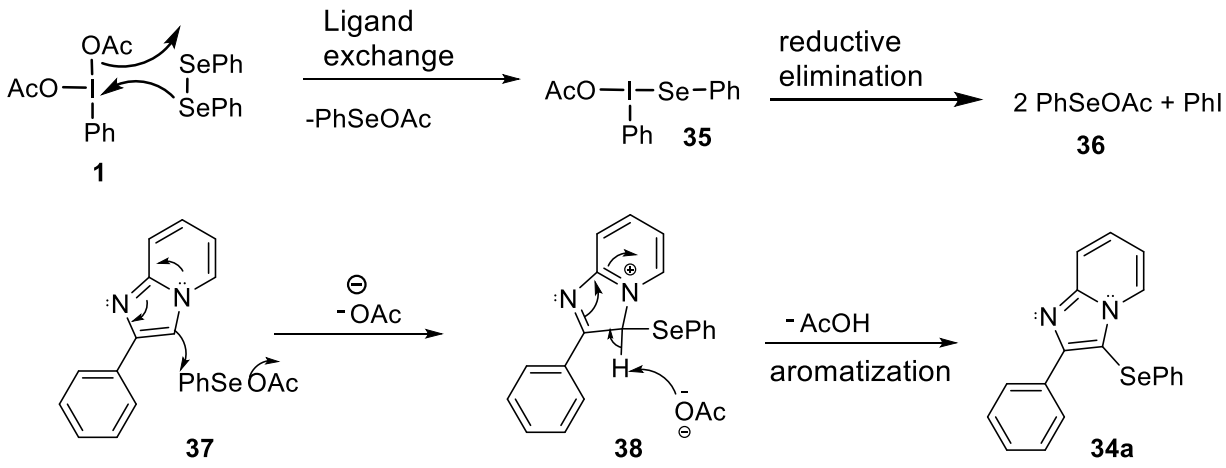
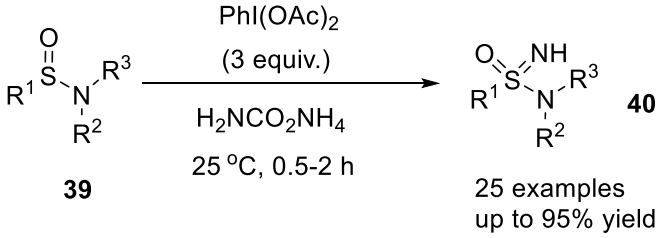


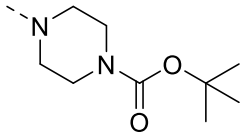
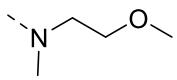
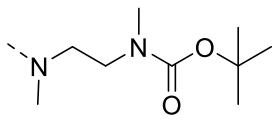
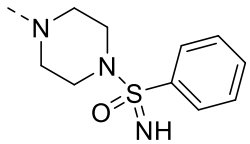
Figure 6. PIDA-mediated plausible mechanism for the phenylselenation.

2.1.5. Hetero-Hetero Bond Formation

With its widespread use in anticancer, anti-inflammatory, and antiviral drugs, the sulfonamide group has long been a very significant pharmacophore in drug discovery. Sulfonimidamides, the mono-aza analogues of sulfonamides, on the other hand, have

received relatively little attention in the life sciences up to this point despite having some very intriguing properties such as high stability, advantageous physicochemical characteristics, numerous hydrogen-bond acceptor/donor functionalities, and structural diversity. Through NH transfer, unprotected tertiary sulfonimidamides (**40**) have been produced in one-pot in good to outstanding yields from tertiary sulfonamides (**39**). Commercially accessible PIDA and ammonium carbamate in methanol were used by Stockman et al. to conveniently facilitate the reaction (Scheme 6) [20].



Sulfonimidamide	NR^2R^3	Yield (%)
39a	1-piperidinnyl	94
39b	NMe_2	72
39c	NEt_2	77
39d	$NiPr_2$	17
39e	1-Azedinyl	71
39f	1-Pyrrodinyl	77
39g	4-morphonyl	77
39h		65
39i		67
39j		78
39k		50

Scheme 6. PIDA-mediated formation of hetero-hetero bonds.

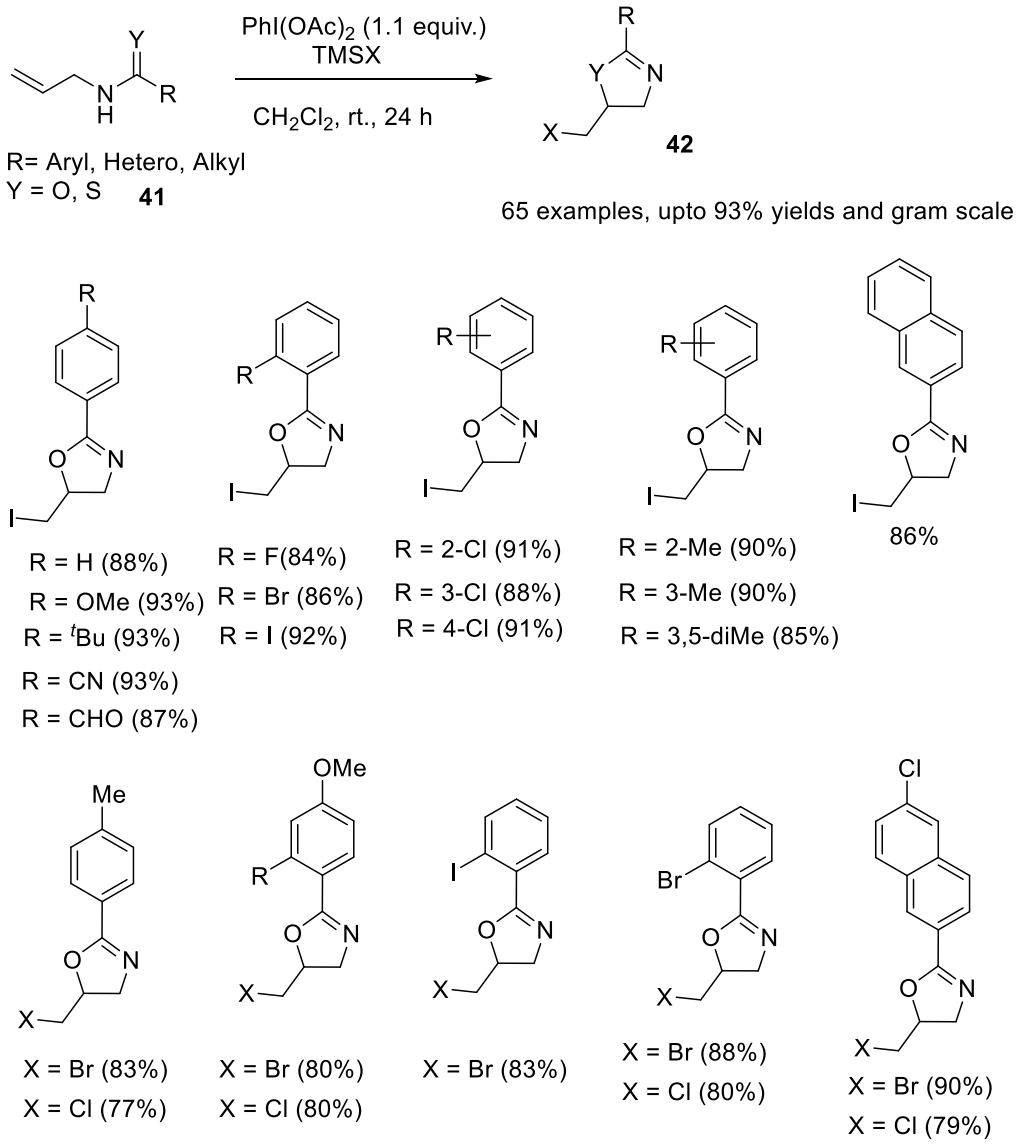
Numerous functional groups were tolerated, and preliminary findings showed that the N-H transfer was stereospecific. A recent, expanding area of interest in the life sciences, sulfonimidamides, can now be approached safely, quickly, and effectively thanks to this novel reaction. The optimized reaction parameters are: $H_2NCO_2NH_4$ (4 equiv.), PIDA (3 equiv.) in MeOH at room temperature. However, the authors discovered that the reaction was only

possible when tertiary sulfinamides were used. The equivalent sulfonimidamide was not formed when the commercial, primary sulfinamide was subjected to the normal conditions; instead, sulfonimidate was separated in a moderate yield along with sulfonamide in low yield. The secondary ethyl sulfinamide reacted to produce a variety of compounds, the main one being sulfonimidate.

2.2. Heterocyclic Ring Formations

2.2.1. Synthesis of Oxazoline and Thiazoline Derivatives

The creation of the oxazoline moiety via a novel methodology was described by Li et al. [21]. Intramolecular halooxygenation and halothionation of *N*-allylcarboxamides/*N*-allylcarbothioamides (**41**) proceeded easily, producing the corresponding 5-halomethyloxazolines/5-halomethylthiazolines (**42**) in good to excellent isolated yields, using PIDA as the reaction promoter and halotrimethylsilane as the halogen source (Scheme 7).



Scheme 7. PIDA-mediated formation of oxazoline and thiazoline derivatives.

The 5-halomethyl compounds could be modified using conventional nucleophilic substitution patterns to create various derivatives. The reactions did not require harsh reaction conditions and were carried out utilizing readily available starting ingredients. The optimized reaction conditions for the synthetic protocol are: TMSI (1.1 equiv.), PIDA

(1.1 equiv.) in DCM at RT. Substrates with either electron-donating or electron-withdrawing groups on aromatic rings could all be cyclized in good isolated yields despite the electronic effects of the substituents on the aryl groups, which had less of an impact on the reactions. Scale up was also performed satisfactorily using the present optimized reaction parameters.

A tentative chemical route was suggested as illustrated in Figure 7. When the substrate (**41a**) and TMSI interacted, intermediate **43** was silylated and could then be further tautomerized to become intermediate **44**. In the interim, $PhI(OAc)_2$ activated the C=C double bond in the substrate, and the intramolecular oxygen nucleophilic attack on the iodinium three-membered ring (**45**) formed the intermediate **46**, which ultimately gave rise to the halooxygenation product (**42a**) after workup.

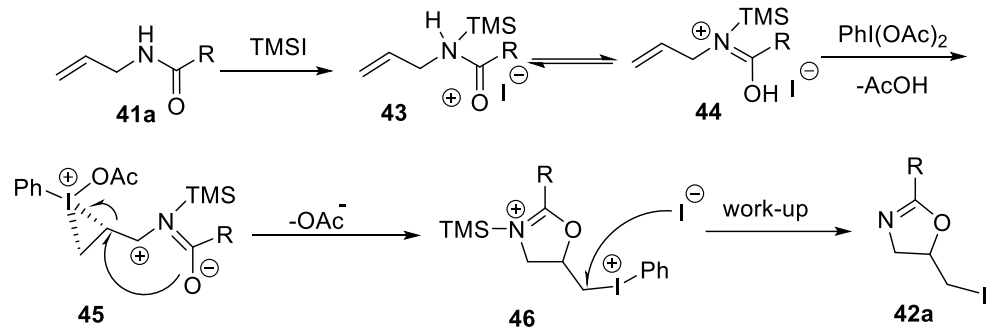


Figure 7. Proposed mechanism for the formation of 5-halomethyloxazolines/thiazolines.

2.2.2. Synthesis of Quinoxaline Derivatives

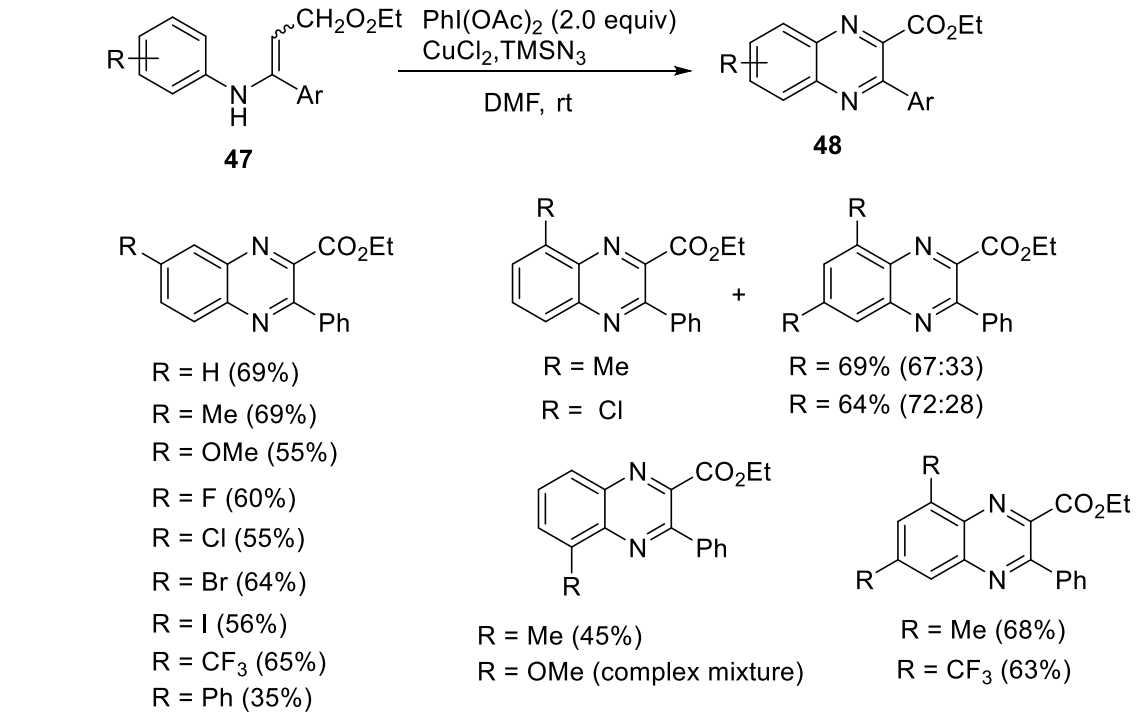
Quinoxaline is a major heterocyclic skeleton that is present in a variety of compounds with biological and pharmacological importance. Quinoxaline (**48**) synthesis was developed using a novel methodology by Yu and co-workers in which *N*-arylenamines (**47**) and $TMSN_3$ as the nitrogen source were used as the starting materials, and (diacetoxyiodo)benzene was used as the common oxidant to implement two oxidative C-N bond-forming processes in a tandem pattern (Scheme 8) [22].

When (ditrifluoroacetoxyiodo)benzene was employed in place of DIB, comparable yields were achieved. The optimized reaction conditions for the present synthetic methodology are: $TMSN_3$ (2 equiv.), PIDA (2 equiv.), $CuCl_2$ (10 mol%) in DMF at RT. Finding that compounds with an *ortho*-substituent at the *N*-phenyl ring also interacted to produce quinoxalines is fascinating. When *meta*-substituted substrates were utilized, the mixture of two regioisomers was produced, with the sterically hindered ones making up the majority of the mixture.

It is possible that the nonradical process depicted in Figure 8 is used to change **47a** into final product **48**. The oxidation of component **47a** must be a fast process because it could never be isolated from the reaction mixture, even though we are unable to determine which mechanism is more likely at this time.

2.2.3. Synthesis of Imidazolidinones

1,4-imidazolidinones and their derivatives have been employed as organocatalysts. Additionally, this heterocycle is a key component of antipsychotic, antibacterial, anti-inflammatory, and antineuropathic drugs due to its potent therapeutic qualities. Hulme and co-workers synthesized imidazolidinones (**53**) by using 5-*endo trig* oxidative radical cyclization strategy via benzylamine-derived Ugi three-component reaction (**52**) with three diversity elements (Scheme 9) [23].



Scheme 8. PIDA-mediated formation of quinoxalines.

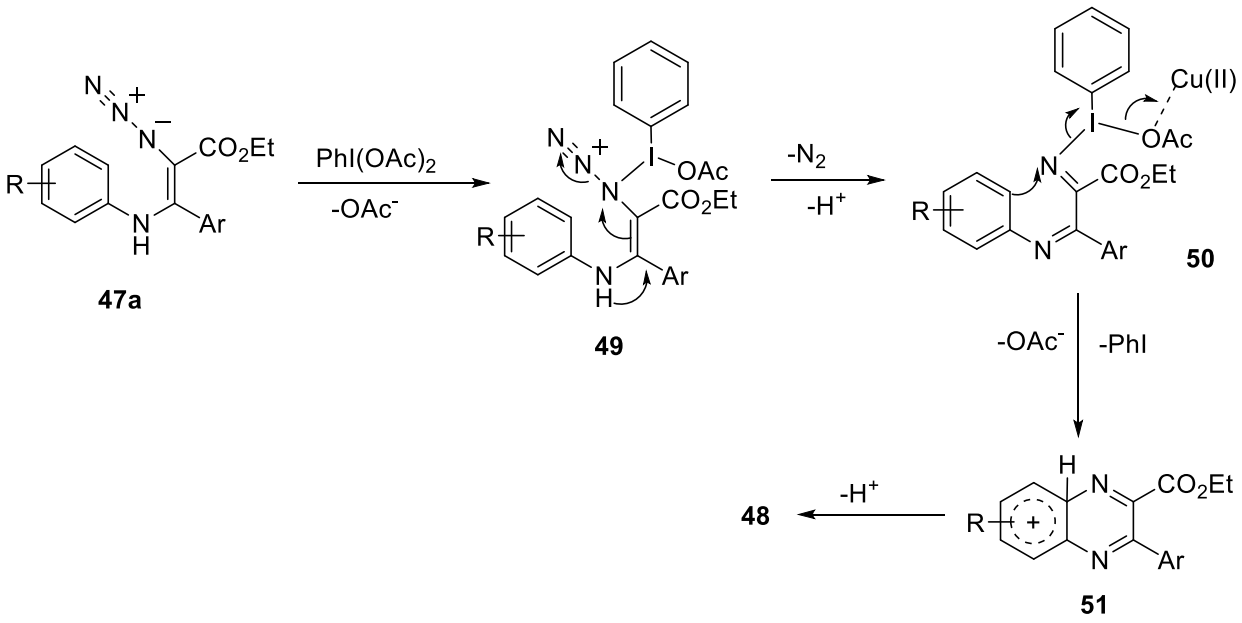
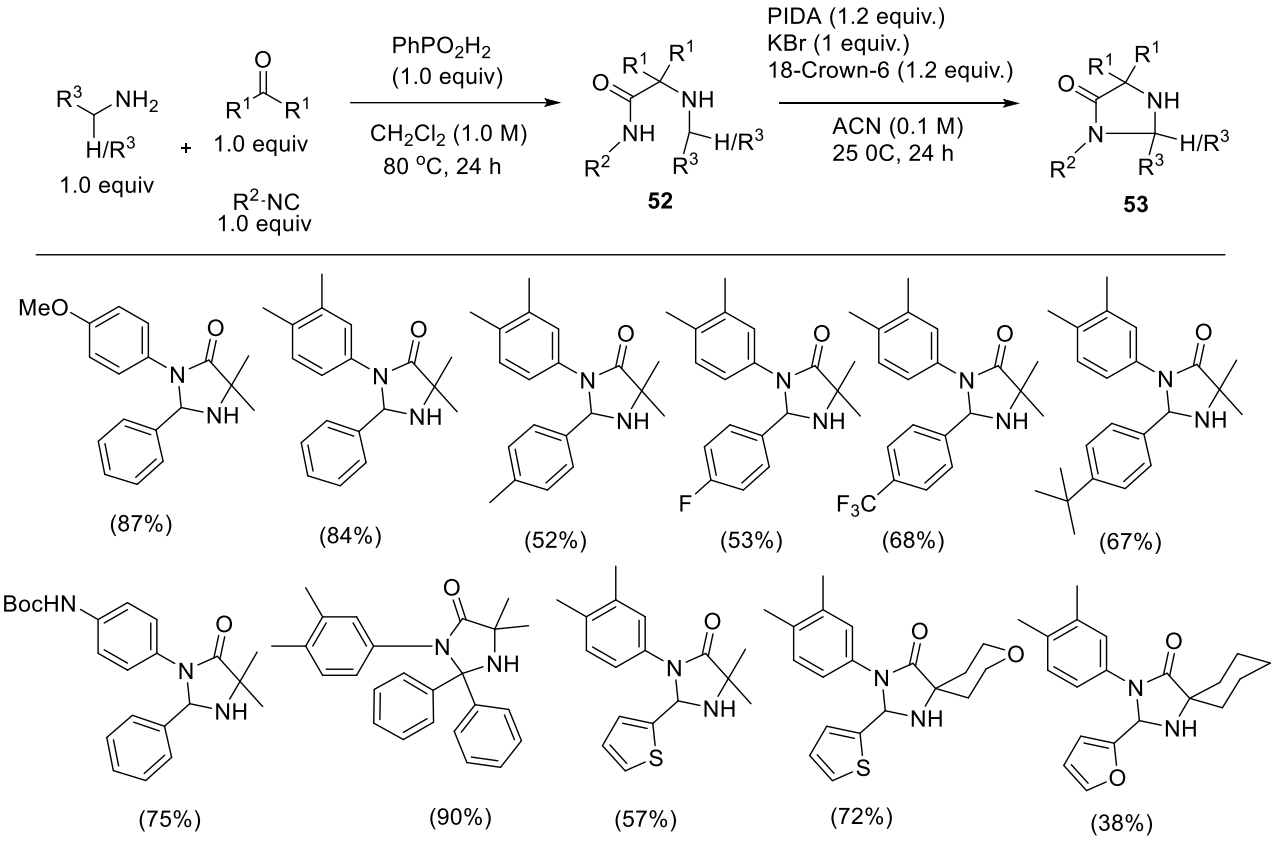


Figure 8. Proposed mechanism for the formation of quinoxalines.



Scheme 9. PIDA-mediated synthesis of substituted imidazolidinones.

Low yields and a range of side products that frequently co-eluted with the product were produced when IBX was used. Other oxidants with lower yields and a smaller range of substrates included PIFA, DMP, iodobenzene, and TBHP. The optimized conditions for this methodology are: PIDA (1.2 equiv.), KBr (1 equiv.) and 18-crown-6 (1.2 equiv.) in acetonitrile at RT. The authors used 18-crown-6 to coordinate potassium in order to increase the solubility after observing that KBr was poorly soluble in acetonitrile. To prevent the development of mixtures of diastereomers during 5-*endo-trig* oxidative cyclization, symmetrical ketones were utilized throughout. Because the resultant C-H is vulnerable to oxidation and can produce cleavage products, aldehydes from the Ugi-3CR were not tolerated in the oxidation. Additionally, under these oxidative circumstances, Cbz- and Boc-protected Ugi-3CR products remained stable, showing that a variety of components suitable to further functionalization were present. Additionally, the synthesis was carried out on a gram scale with no yield loss. The aliphatic amine-containing Ugi-3CR product produced nothing.

Figure 9 shows a possible mechanism for this oxidative cyclization. The Br anion activates PIDA to produce **54**, which, along with **55a**, produces N-I complex **56b**. The generation of the numerous radical species throughout this hypothesized pathway may be attributed to the weak I-Br bond, which is susceptible to homolytic cleavage in **56**. The α-amino radical **56**, is then oxidized to imine (**57**). Since the aryl amide is a bioisostere of carboxylic acids, the authors hypothesized that **57** undergoes N-H abstraction to generate radical **58a**, albeit a non-radical process cannot be completely ruled out. Following a 5-*endo-trig* radical cyclization, this amidic radical produces **59**, which can be easily quenched to produce product **53a**.

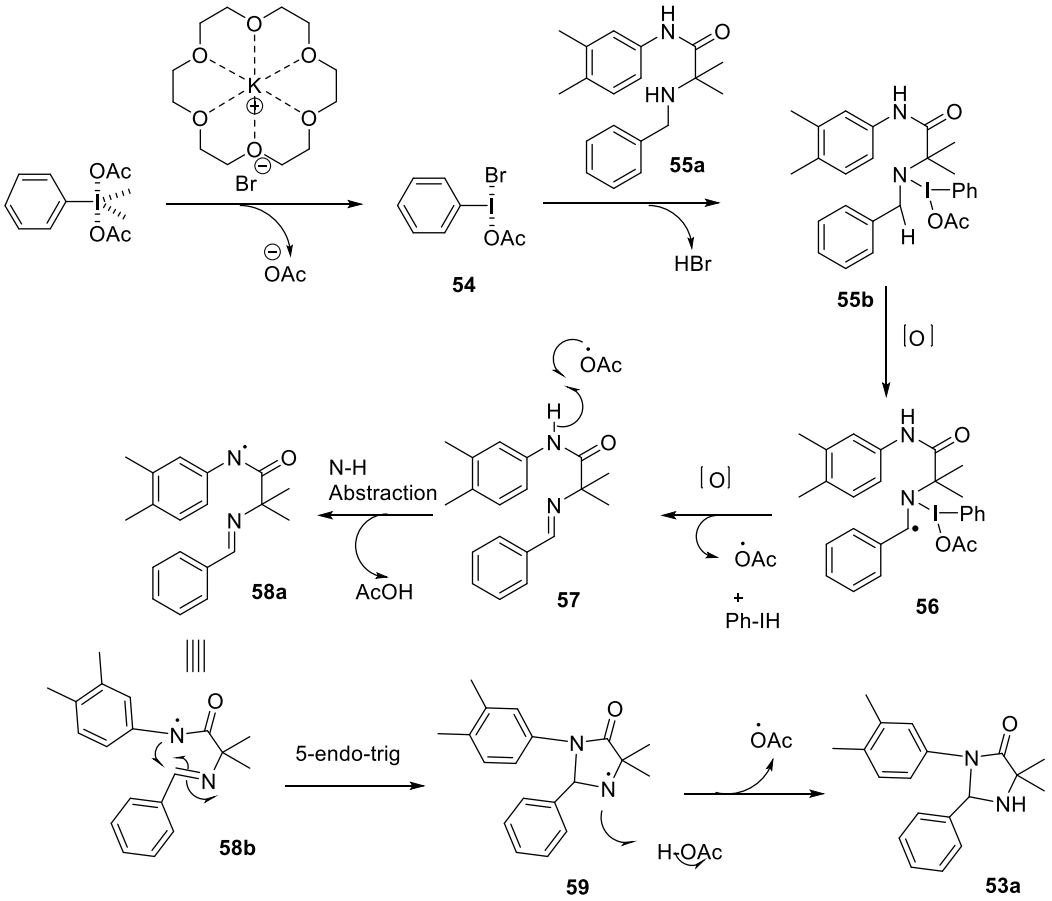


Figure 9. Proposed mechanism for the formation of 1,4-imidazolidinones.

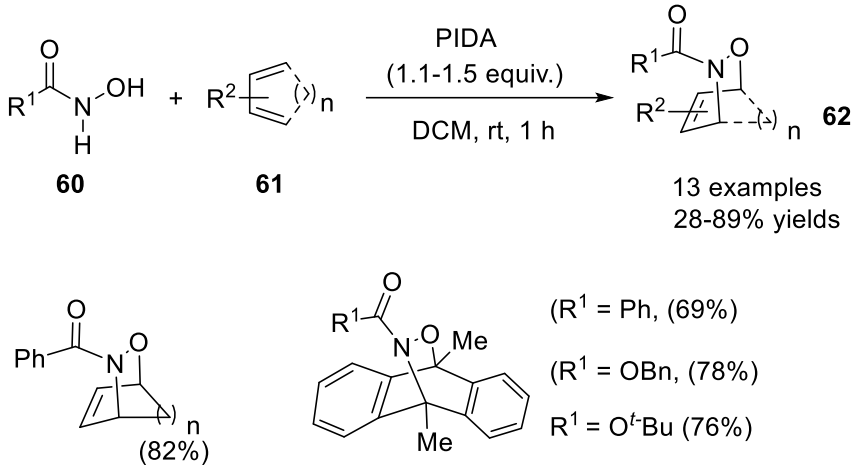
2.3. Rearrangement/Migration Reactions

2.3.1. Hetero Diels-Alder Addition

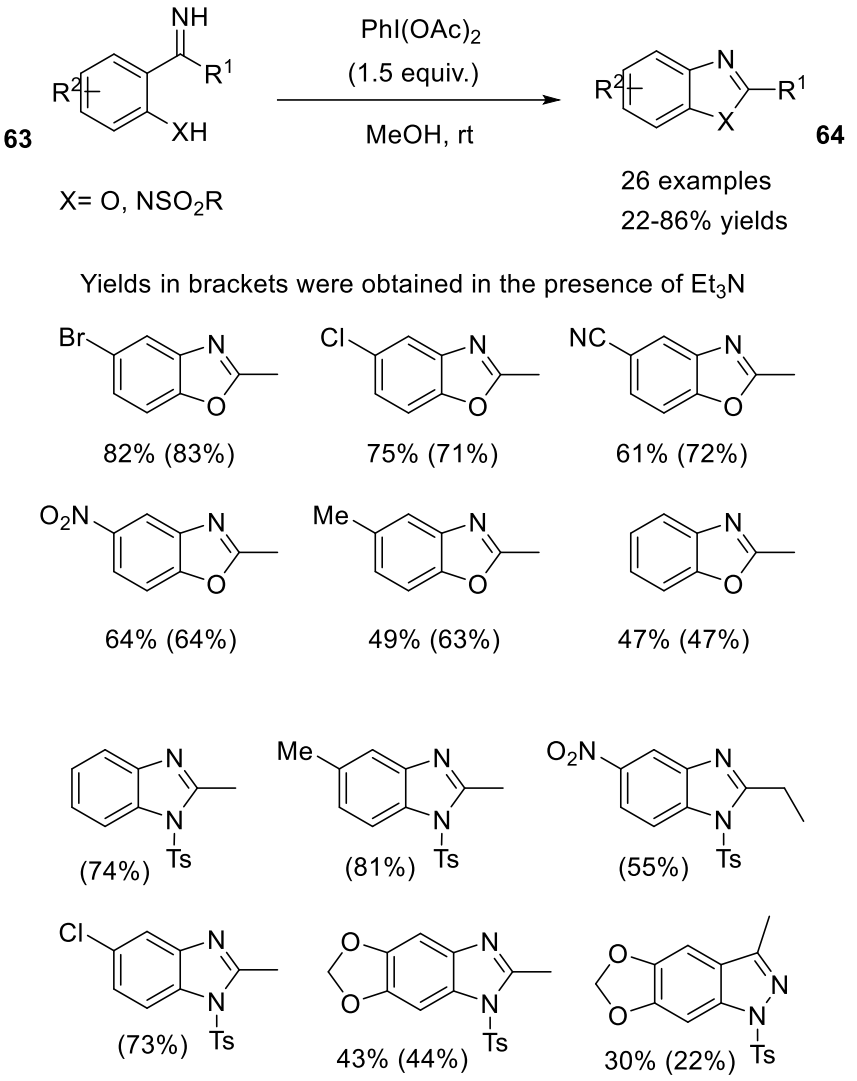
1,2-Oxazines are widely acknowledged as helpful synthons in the synthesis of biologically active natural compounds. 1,2-Oxazines can be easily and highly stereoselectively synthesized using the hetero-Diels–Alder (HDA) reaction between *N*-acylnitroso species and dienes. In the presence of different dienes (**61**), either PIDA or [bis(trifluoroacetoxy)iodo]benzene (BTI) effectively stimulated the production of acylnitroso species (**62**) from hydroxamic acids (**60**), yielding the required hetero-Diels–Alder (HDA) adducts in moderate to high yields, as reported by Saito and co-workers [24]. The current approach could be used in HDA reactions involving masked *o*-benzoquinones (MOBs), which are produced after the oxidative dearomatization of guaiacols, as well as simple dienes (Scheme 10).

2.3.2. Beckmann-Type Rearrangement

Despite significant progress in this area, the synthesis of benzoxazoles and benzimidazoles via hypervalent iodine-mediated Beckmann rearrangement is still uncharted ground. Many commercially available drugs and therapeutic prospects have these heterocycles as common structural components. Additionally, polymers, natural products, and diverse functional materials all contain benzoxazoles and benzimidazoles. Benzoxazoles and *N*-*T*s benzimidazoles (**64**) were synthesized by Xiong et al. using Beckmann-type rearrangements of the *o*-hydroxy and *o*-aminoaryl N-H ketimines (**63**), respectively (Scheme 11) [25].



Scheme 10. PIDA-mediated hetero Dields–Alder addition.



Scheme 11. PIDA-mediated Beckman-type rearrangement.

The necessary heterocycles were formed by condensation of ammonia with the appropriate ketones to produce the ketimine derivatives, and it was discovered that PIDA functions as an effective oxidant to initiate [1,2]-aryl migration. The benzoxazole was pro-

duced in good yields by the reaction of test imine with $PhI(OAc)_2$ or PhIO, but no reaction occurred when imine was combined with PhI(OH)(OTs) or $PhI(OTf)_2$. The optimized conditions for this methodology are: PIDA (1.5 equiv.) in MeOH at RT. It is important to note that the synthesis of corresponding product was not possible when *m*-chloroperbenzoic acid was used as a stoichiometric terminal oxidant together with a catalytic quantity of iodobenzene. Only degradation byproducts from imine were seen in these circumstances. The same reaction conditions were successfully applied for the synthesis of benzimidazole derivatives, as well. The outcomes showed another mechanistic route through which benzisoxazoles or 1*H*-indazoles could be produced, depending on the substitution pattern. The synthesis of benzimidazole-containing bio-relevant targets such as chlormidazole and clemizole used the Beckmann-type rearrangement strategy.

Based on the control experiments performed and information from the literature, a likely mechanism is shown below to explain how the various products are formed (Figure 10). The corresponding hypervalent iodine species **56** would be produced by the imine's reaction with $PhI(OAc)_2$. Following the path a, an aryl moiety would undergo a Beckmann-type [1,2]-migration to produce the intermediate **67**. This intermediate would then go through an intramolecular cyclization to produce either benzoxazole or benzimidazole (**64a**). The intramolecular cyclization of the phenol or amine onto the imine nitrogen following path b would result in the formation of the benzisoxazole and indazole (**64b**) through the intermediate **68**.

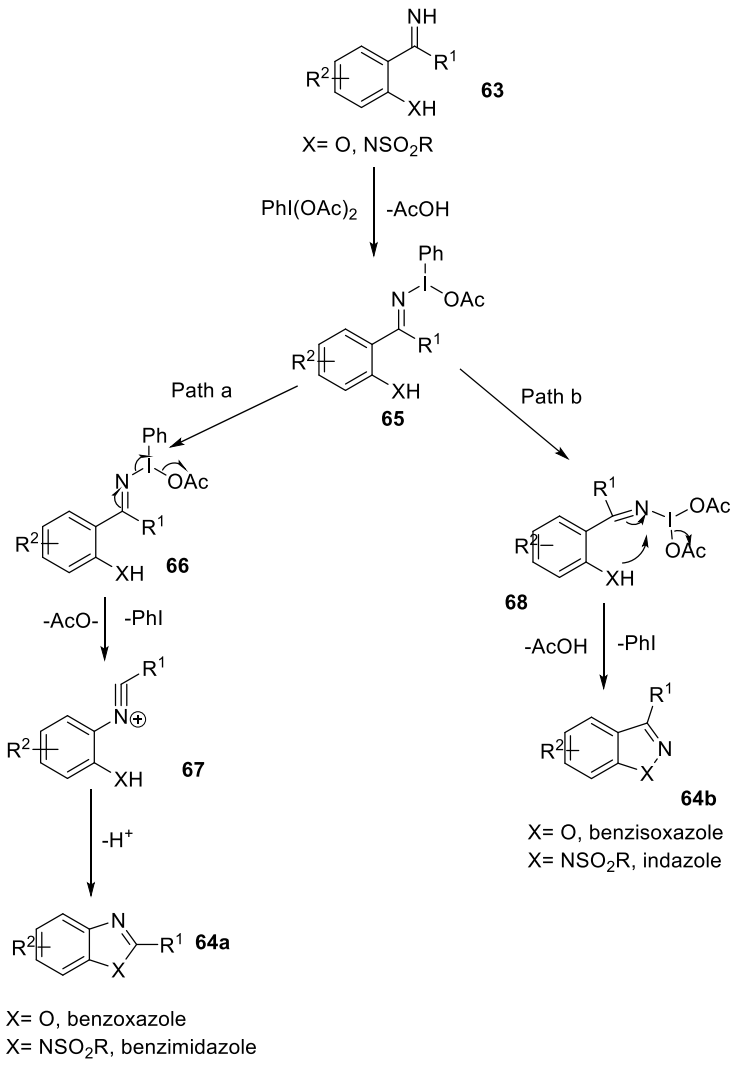
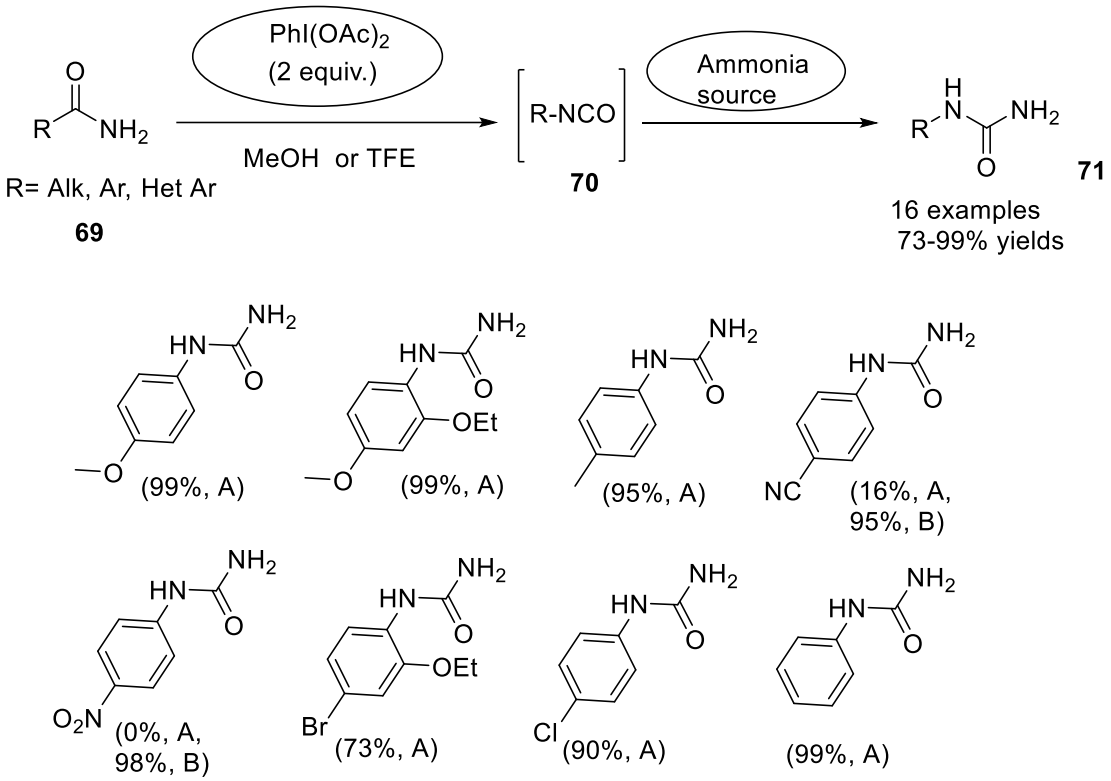


Figure 10. Plausible mechanism for synthesis of benzoxazoles and benzimidazoles.

2.3.3. Hofmann Rearrangement

Urea-containing compounds are increasingly utilized in many different research domains, including medicinal chemistry, agrochemistry, and petrochemistry, due to their intriguing physicochemical and biological features. The widespread use of such molecules as bioisosteres of peptide bonds in drug development is specifically due to their structural, biological, and electronic similarities. Reboul et al. reported that primary amides (**69**) when treated with PIDA in the presence of an ammonia source (NH_3 or ammonium carbamate) in MeOH produced *N*-substituted ureas (**71**) in a straightforward and practical manner (Scheme 12) [26]. The electrophilicity of the hypervalent iodine species is increased when 2,2,2-trifluoroethanol (TFE) is used as the solvent, which enables the synthesis of electron-poor carboxamides. The isocyanate intermediate (**70**) produced in situ by a Hofmann rearrangement of the initial amide which was nucleophilically added to by ammonia source throughout this transformation.



Scheme 12. PIDA-mediated Hofmann rearrangement.

The optimized conditions for this methodology are: Condition **A**: PIDA (2 equiv.) and NH_3 (17.5 equiv.) in MeOH (7 M) at 0 °C to RT and Condition **B**: PIDA (3 equiv.) and ammonium carbamate (AC) (2.5 equiv.) in TFE at 0 °C to RT. In addition to pyridyl-, phenyl-, and benzylureas, reactions involving aromatic amides bearing electron-donating or deactivating groups also produced the corresponding ureas in good to outstanding yields. Aliphatic amides were entirely converted into the desired ureas; however, because of their volatility, some of the products were lost during purification, which had an impact on the isolated yields. However, it appeared that the reaction yield of this transition was decreased by the presence of an electron-withdrawing group on the aromatic amide. While a substrate with a 2-OH group produced the isolated cyclic carbamate in a quantifiable yield, one with a 4-OH group failed to produce the required urea. However, under neither set of circumstances did 2-furamide react.

The authors believed that ammonia, which was more nucleophilic, trapped the isocyanate intermediate, which was generated in situ via a Hofmann-like rearrangement (**69**→**71**, Figure 11).

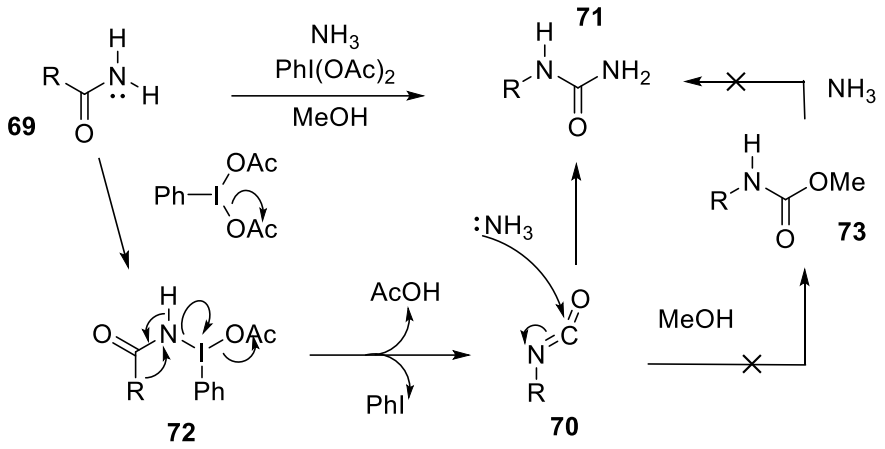
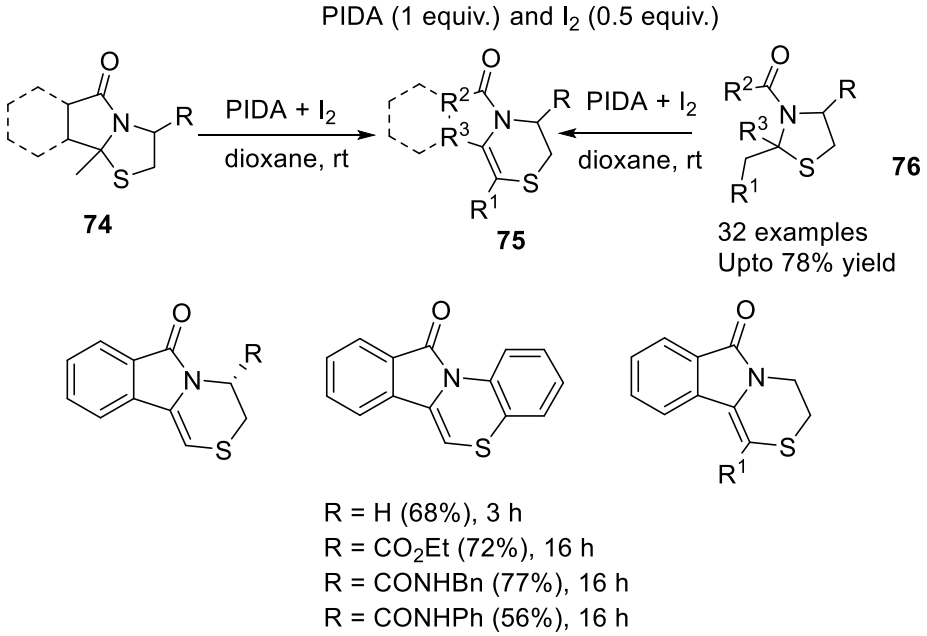


Figure 11. Proposed mechanism for PIDA-mediated Hofmann rearrangement.

2.3.4. Morin Rearrangement

In the weak chemical space being investigated at the moment, *N*,*S*-containing heterocyclic systems (such as 1,4-thiazines and benzo[1,4]thiazines) play a significant role as heterocyclic scaffolds. Various pigments and dyestuffs serve as examples of how these rings can be found in a variety of uncommon and fascinating natural and artificial items. They have several uses in pharmaceutical sciences and chemical manufacture. Particularly intriguing are the rare pyrrolo[1,4]thiazines, which can be represented with various degrees of biological relevance. Starting with *N*,*S*-acetals (**74**/**76**), an effective domino transformation using the PIDA/I_2 combination was developed by Daïch et al. [27]. for Morin 1,4-thiazine compounds (**75**). They achieved 'one-step' regioselective methylene insertion in good yields without the use of conventional sulfoxide intermediates (Scheme 13).



Scheme 13. PIDA-mediated Morin rearrangement.

The Morin product formed as the only reaction product in this instance when PIDA/I_2 was used. The optimized conditions for this methodology are: PIDA (1 equiv.) and I_2 (0.5 equiv.) in dioxane at RT. A vast assemblage of 1,4-thiazines that have been fused or not to pyrrolidones/isoindolones could be accessed quickly and effectively, with good yields and complete regioselectivity, where applicable. The predicted Morin products were formed in moderate to good yields along with the excessively oxidizing compounds when another proton is present at the endocyclic position of the sulphur atom, which is commonly in the pyrrolidone or piperidone family.

In terms of mechanism (Figure 12), the oxidation of sulphur would start the domino process, with PIDA producing the release of acetate and the sulfonium ion **77**. Both molecules underwent an acid-base reaction that produced the enamide **78** that was never isolated before the S-I bond broke down under the influence of acid to produce **79**. The medium then allowed **79** with PIDA to regenerate while providing the dimer **80** and iodobenzene. The latter, when combined with diiodide, can form the hypoiodothioite intermediate **81**, which can then provide the anticipated Morin product **75a** via the *N*-acyliminium ion **82**. Only 0.5 equivalents of I_2 are required in this case to produce the Morin product **75a**, suggesting that the dimer **80** is crucial for the domino process.

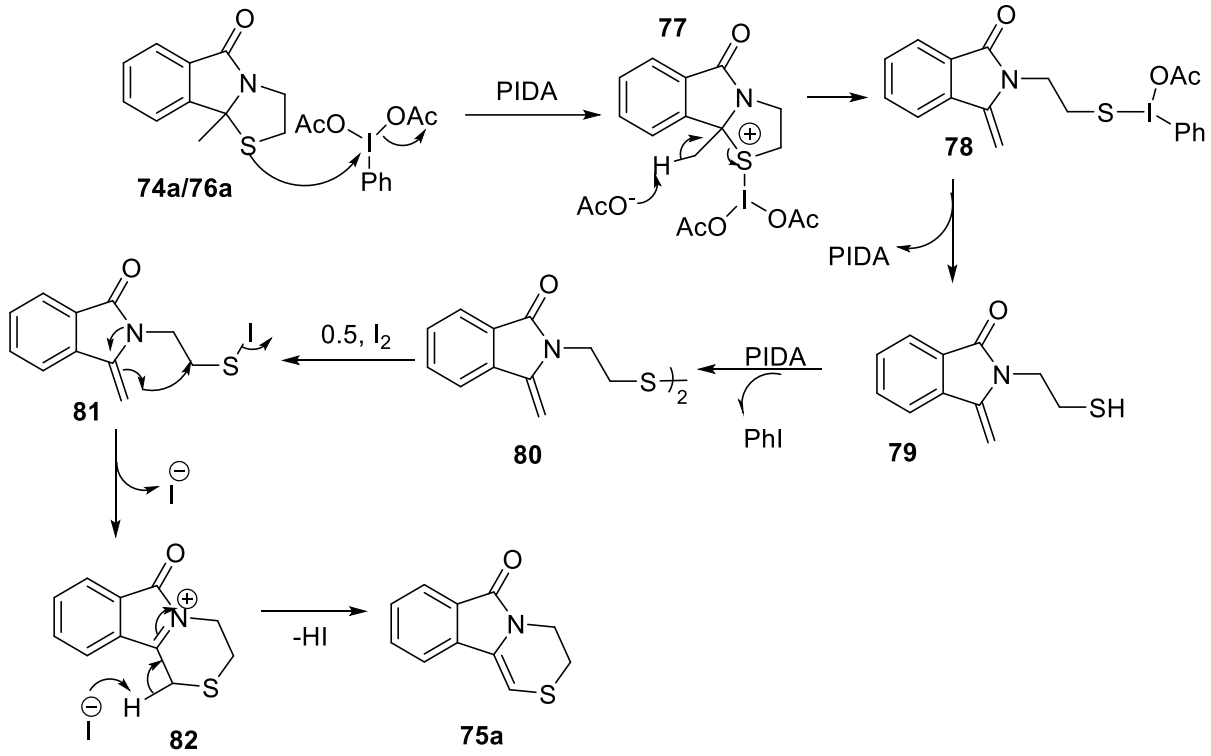
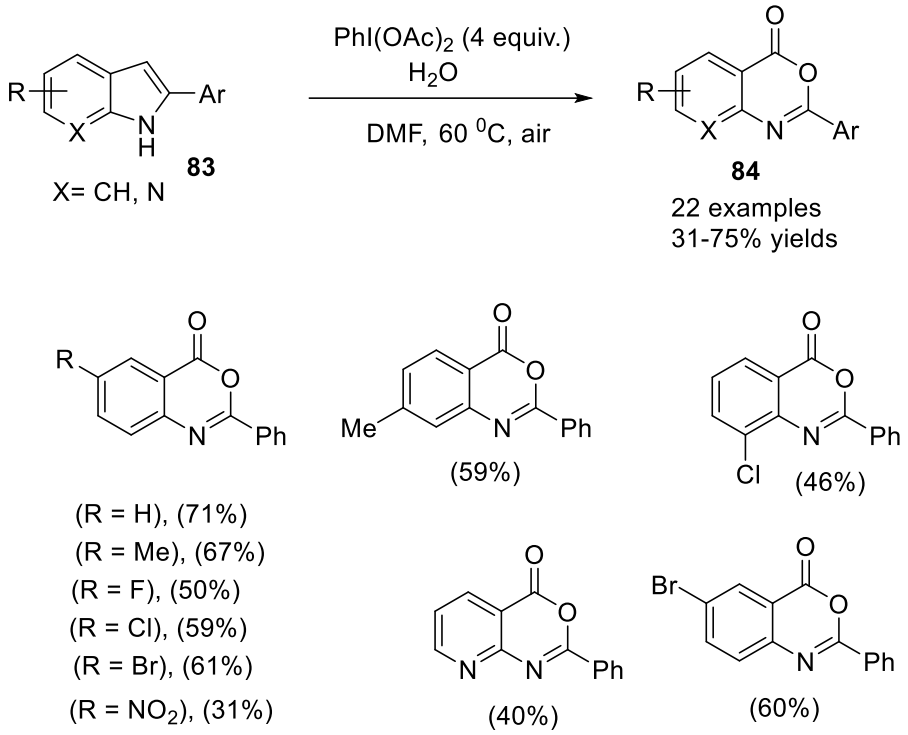


Figure 12. Proposed mechanism for ring expansion.

2.3.5. Grob-Type Fragmentation

The 4*H*-3,1-benzoxazin-4-one core is a crucial structural skeleton present in a variety of pharmaceuticals and bioactive substances. The 2-substituted 4*H*-3,1-benzoxazin-4-ones are also useful building blocks for the synthesis of molecules with medicinal activity, which is significant. A successful oxidative reaction conducted by PIDA and aided by water was used by Li and co-workers to produce a number of synthetically intriguing 2-arylbenzoxazinones (**84**) from 2-arylindoles (**83**). Water was a critical ingredient and the only oxidant used was PIDA (Scheme 14) [28].



Scheme 14. PIDA-mediated Grob-type fragmentation.

A number of iodine(III) oxidants with various oxy ligands, such as $PhI(OCOCF_3)_2$, $PhI(OPiv)_2$, $PhI(OCOPh)_2$, PhIO, PhI(OH)OTs, and iodosodilactone, were utilized in place of $PhI(OAc)_2$, although a negative impact on the reaction yield was noted in these instances. While IBX and DMP, two iodine (V) reagents, were also investigated as oxidants, the anticipated 2-arylbenzoxazinone was not identified. The optimized conditions for this methodology are: LiI (1 equiv.), PIDA (4 equiv.) in DMF (10 mL) and H_2O (10 equiv.) at 60 °C. The intended 2-phenylbenzoxazinones might be produced in fair to moderate yields by first using a succession of 2-phenylindoles with electronically distinct substituents (R=H, Me, F, Cl, Br, NO_2). Similar reactivity to that of the aforementioned 6-substituted indoles was displayed by the 7- and 8-substituted indoles as well.

Figure 13 suggested a possible mechanism for this reaction, and the conversion of **83a** to **84a** serves as an illustration. Initially, 3-acetoxy-substituted indole **86** was produced by electrophilic attack of $PhI(OAc)_2$ at the C-3 position of indole **83a** via intermediate **85**.

2.3.6. 1,2-Diaza-Cope Rearrangement

Hydrazones are a significant group of nitrogen-containing chemicals with exceptional biological properties that are found in both medicines and natural products. In organic chemistry, they are also useful synthetic intermediates for the Bamford–Stevens reaction, Shapiro reaction, Eschenmoser–Tanabe fragmentation, and Wolff–Kishner reduction. As a result, the synthesis of hydrazone compounds and the subsequent modification of hydrazones have drawn a lot of interest and prompted the creation of novel synthetic methodologies. Recently, radical tandem cyclization has made β,γ-unsaturated hydrazones into desirable substrates for the synthesis of pyrazoline derivatives, which are known to have strong biological activity. Based on the 1,2-diaza-cope rearrangement reaction of β,γ-unsaturated hydrazones (**81**) with acetate/H_2O, a novel metal-free methodology for the synthesis of diacyl/acyl *N*-allylhydrazines (**94**/**97**) was described by Qi, Wang and co-workers [29]. Under favorable conditions, this cascade reaction operated effectively (Scheme 15).

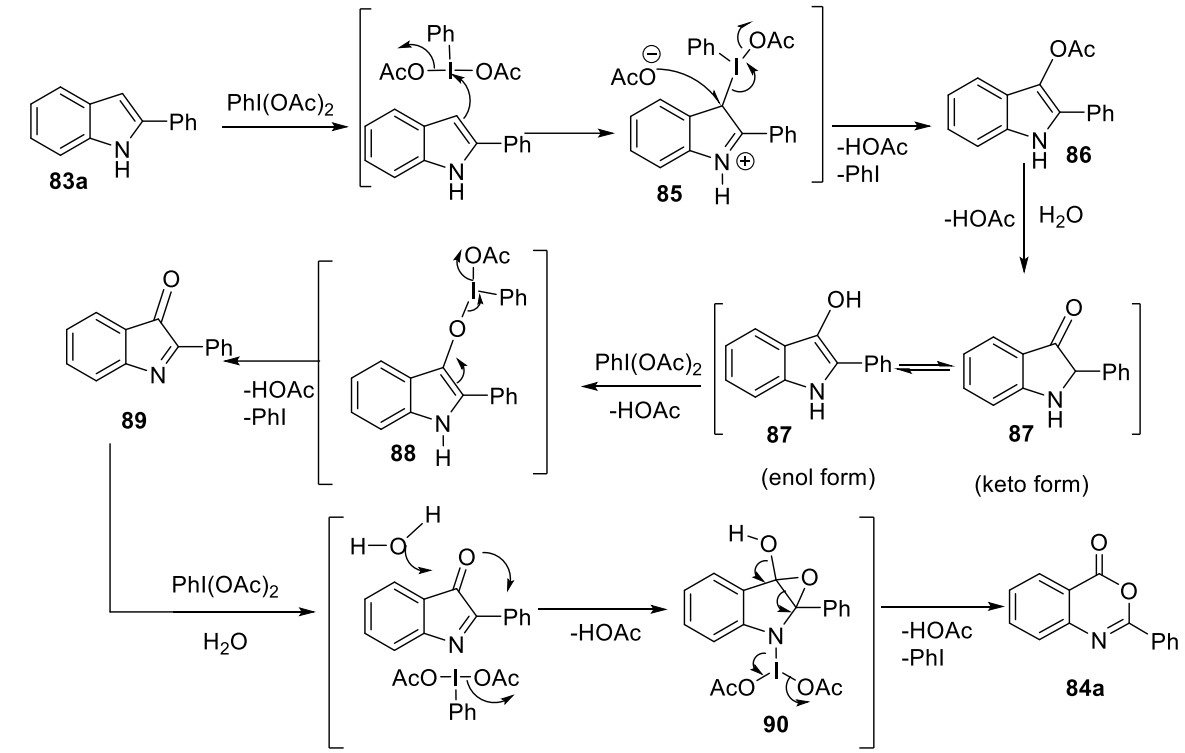
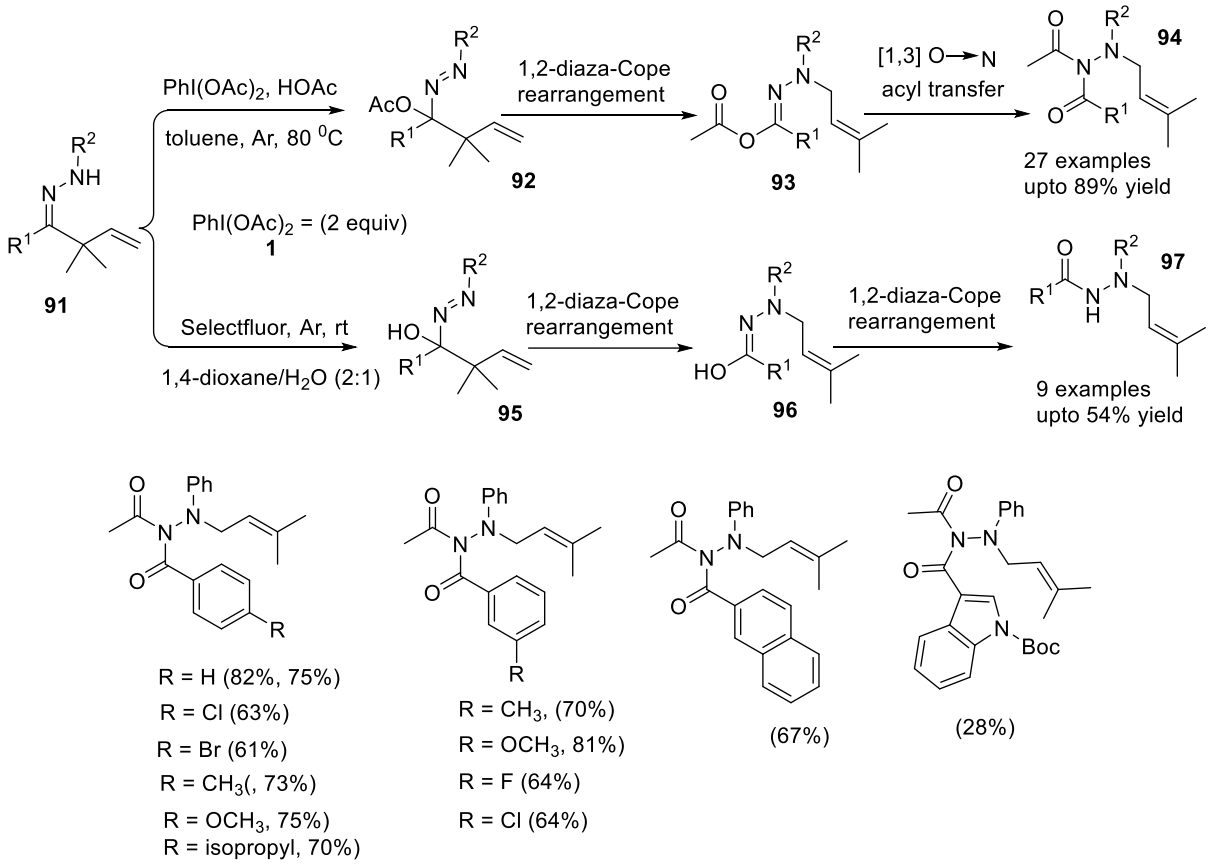


Figure 13. Proposed mechanism for PIDA-mediated oxidative reaction.



Scheme 15. PIDA-mediated 1,2-diaza-cope rearrangement reaction.

The optimized conditions for this methodology are: PIDA (2 equiv.) and HOAc (1 equiv.) in toluene at 80 °C under argon atmosphere. The reaction showed broad functional group compatibility, as hydrazone substrates bearing either electron-withdrawing (Cl, Br, F) or electron-donating (methyl, methoxyl, isopropyl) aryl substituents interacted well to produce the desired rearrangement products in moderate to good yields (58–82%).

However, in this transformation, aryl groups with an electron-rich group performed better than those with an electron-deficient group. Later, the authors carried on exploring the potential structural range of the *N*-phenyl moiety. Under the reaction conditions, a wide range of functional groups with different electronic characteristics were well tolerated, and the corresponding rearrangement products were produced in moderate to good yields (52–89%). However, *N*-aliphatic substrates could not function under the ideal circumstances; thus, a stable N radical I-I was essential to figuring out the regioselectivity (Figure 14).

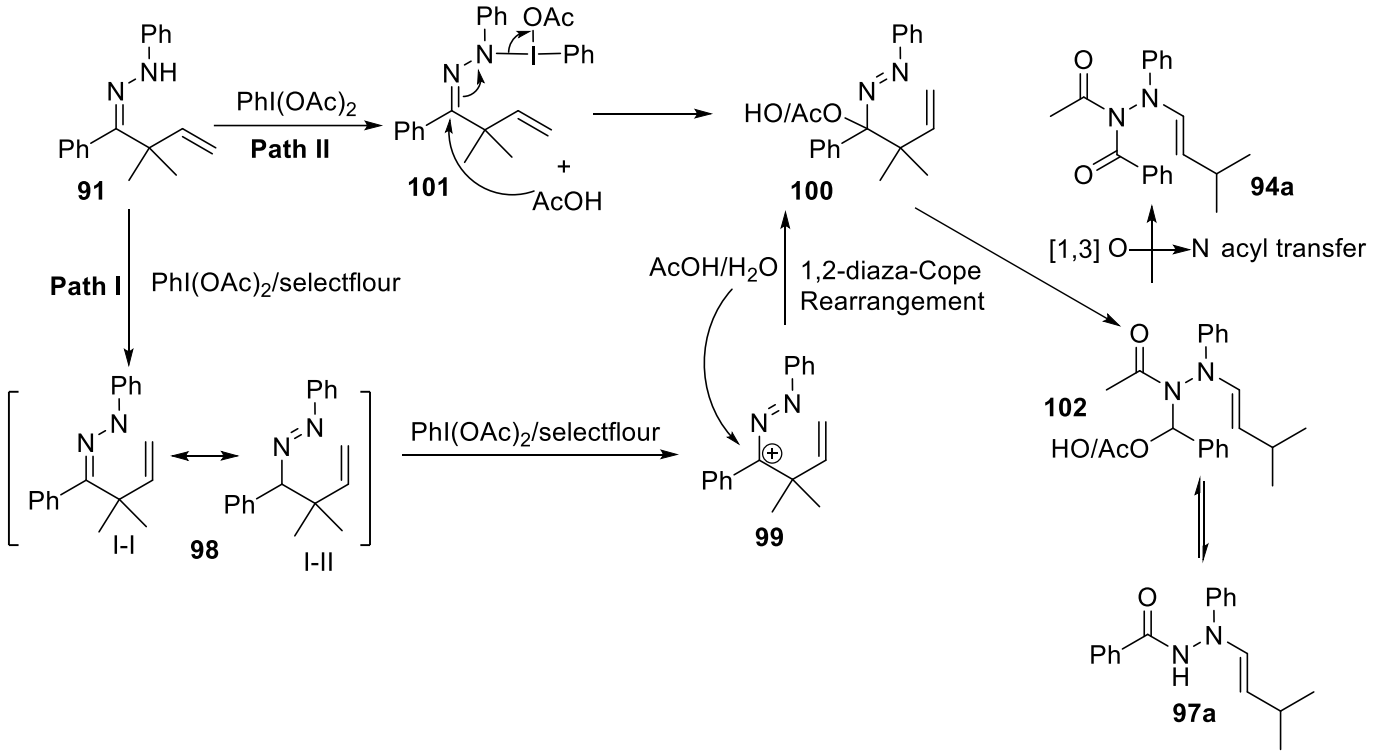


Figure 14. Proposed mechanism for PIDA-mediated 1,2-diaza-Cope rearrangement.

It is crucial to consider the following pathway of a potential mechanism in the reaction for producing the desired product: it was possible that $PhI(OAc)_2$ first reacted with *N*-phenyl β,γ unsaturated hydrazone **91** to produce an N-I(III) intermediate **101**. Intermolecular nucleophilic attack of the carbon-nitrogen double bond on intermediate **101** by AcOH resulted in intermediate **100**, which was then produced by a 1,2-diaza-Cope rearrangement process to yield intermediate **102**. The final product **94a** was then obtained by transferring **102** through a [1,3] O→N acyl transfer (Path II).

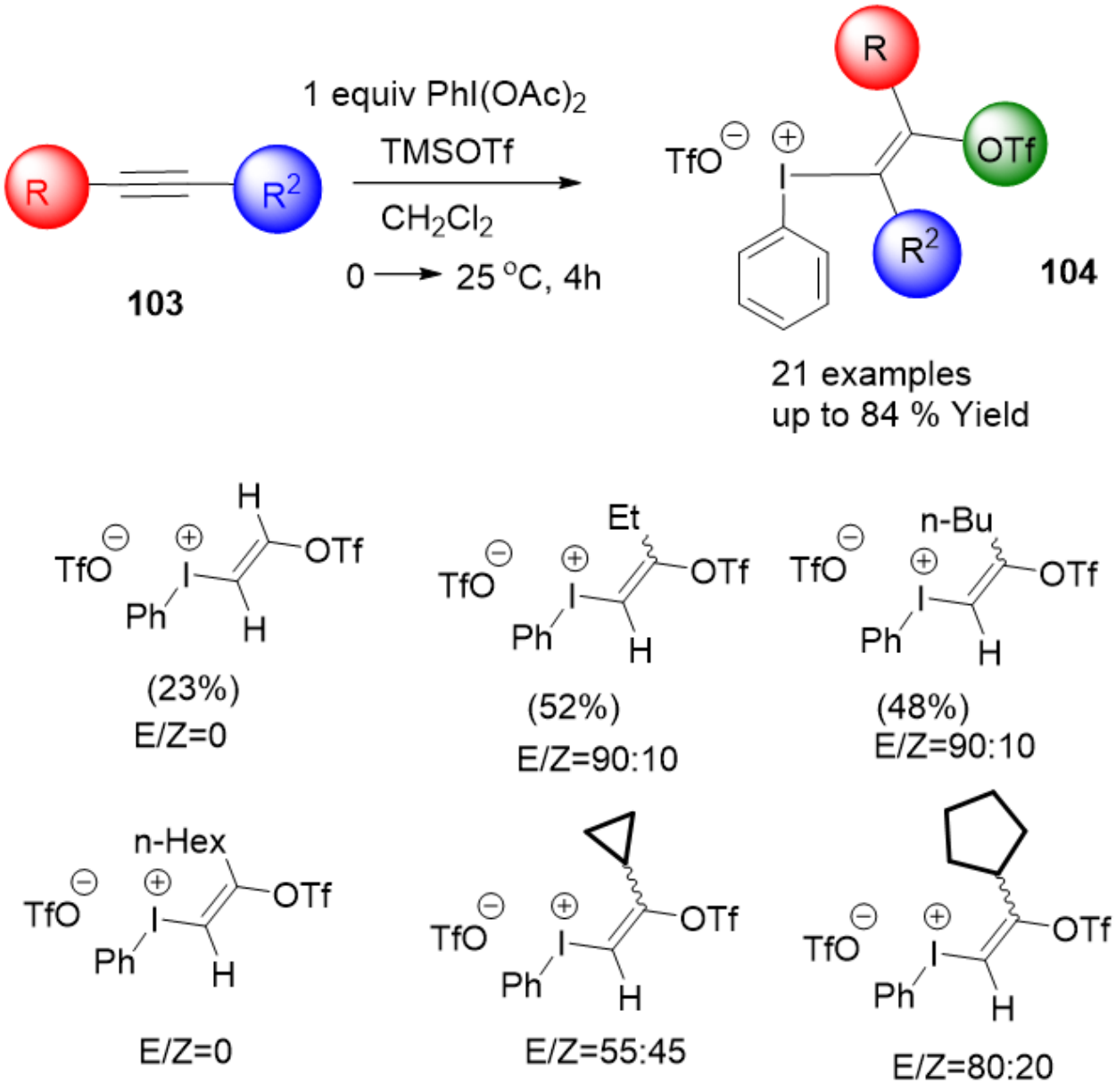
2.4. Miscellaneous Reactions

2.4.1. Synthesis of Aryl(trifloxyalkenyl)iodonium Triflate Salts

Numerous useful chemical compounds have been synthesized where the alkenyl activity appears as a significant molecular motif. Therefore, there is enormous synthetic potential in the development of direct alkenylation processes and multifunctional alkenyl building blocks. To meet this synthetic need, (trifloxyalkenyl)iodonium triflate salts were created and put to use in ligand exchange processes that produced different diaryliodonium

species, cross-coupling events catalyzed by palladium, as well as metal-free substituted oxazole ring formation reactions.

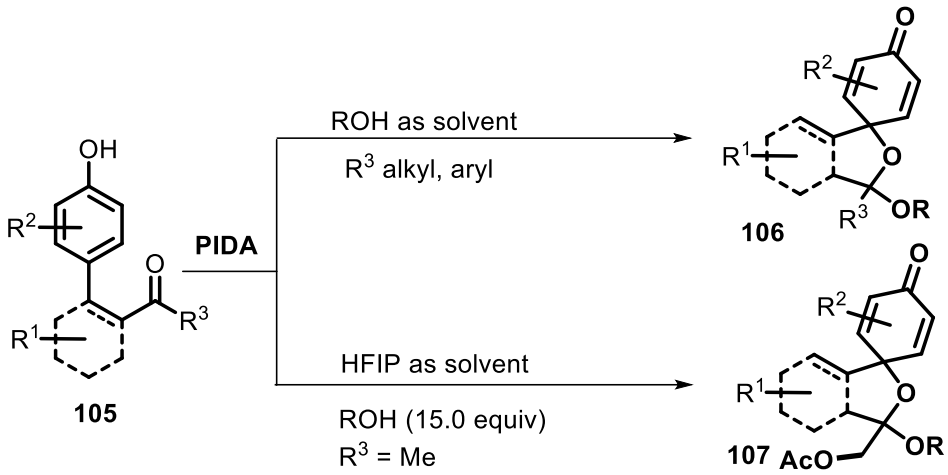
Using widely available (diacetoxyiodo)benzene, trimethylsilyl trifluoromethanesulfonate, and acetylenes (**93**), a straightforward procedure was established by Toth and Novak research groups, to quickly produce aryl(trifloxyalkenyl)iodonium triflate salts (**104**, Scheme 16) [30]. They created nucleophilic and electrophilic multifunctional hypervalent vinyliodonium salts which could be employed as novel C2 synthons in organic transformations. The optimized conditions for this methodology are: PIDA (1 equiv.) and TMSOTf (2 equiv.) in dichloromethane at 0 °C to RT. The authors investigated the synthesis of phenyl-(alkenyltrifloxy)iodonium triflate salts using alkyl acetylene reactants because, fortunately, the reaction was not restricted to the aromatic acetylenes. They investigated how various terminal alkylacetylenes functionalized with OAc, OH, Br, Cl, and CN groups at the alkyl terminal could be applied synthetically. With the aid of nucleophilic or electrophilic reagents, these functionalities allow for further side chain modifications. However, the ester functionality was not tolerated at the reaction conditions. They even discovered that an alkyl or aryl group was preferred in the *E* position of the (vinyltrifloxy)-iodonium molecule.



Scheme 16. PIDA-mediated synthesis of aryl(trifloxyalkenyl)iodonium triflate salts.

2.4.2. Dearomative Spirocyclization

Peng, Wang and co-workers reported PIDA-promoted/HFIP-controlled dearomative spirocyclization of phenolic ketones (**105**) through a spirocyclohexadienone-oxocarbenium cation species [31]. It was found that 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) inhibits and PIDA promotes dearomative spirocyclization of phenolic ketones (Scheme 17). Under favorable conditions, this protocol generated two libraries of structurally intriguing scaffolds, including spirocyclohexadienonic ketals (**106**) and their acetoxylated counterparts (**107**), with moderate to good yields.

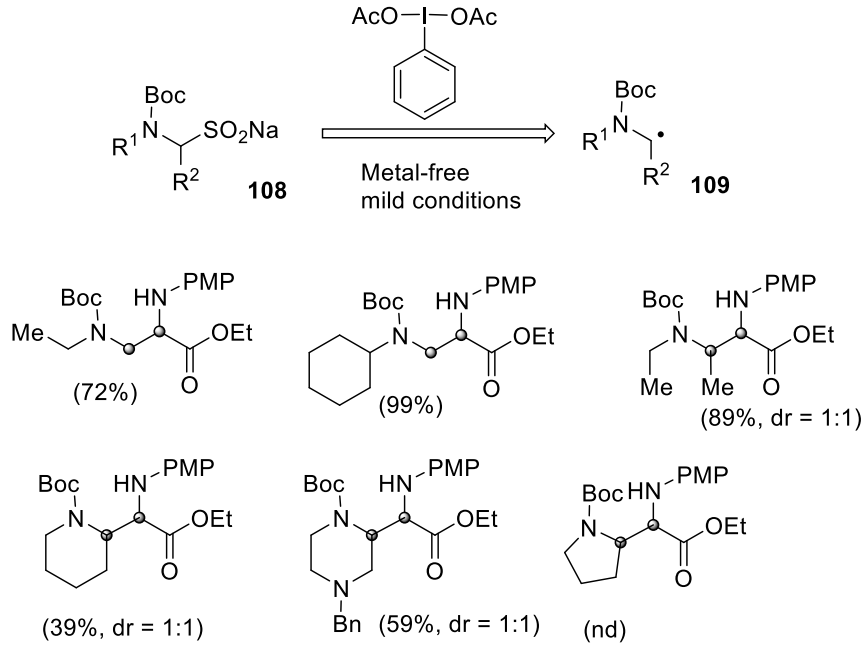


Scheme 17. PIDA-mediated synthesis of spirocyclohexadienonic ketals and their acetoxylated counterparts.

2.4.3. Generation of α-Aminoalkyl Radicals

Since radical reactions allow for transformations of organic compounds that are not seen in ionic reactions, significant research efforts have been put into developing new protocols for creating organic radicals in synthetic organic chemistry. Particularly, the creation of functional group-containing organic radicals is a very promising method for adding functional groups to other molecules. Among these radicals, α-aminoalkyl radicals (**109**) have garnered a lot of interest due to the significance of scaffolds containing nitrogen for synthetic purposes.

It was reported by Maruoka et al. that sodium α-aminoalkanesulfinates (**108**) can be made synthetically and used as α-aminoalkyl radical precursors (Scheme 18) [32]. The reaction between the anions of *N*-Boc-protected alkylamines and 1,4-diazabicyclo[2.2.2]octanebis(sulfur dioxide) produced a range of α-aminoalkanesulfinates (**99**) easily. The corresponding α-aminoalkyl radicals were easily produced by treating sodium α-aminoalkanesulfinates with (diacetoxyiodo)benzene under benign conditions. These radicals were then used in radical 1,2-addition to imines, radical 1,4-addition to electron-deficient olefins, and radical addition/cyclization to 2-isocyanobiphenyls. The optimized conditions for this methodology are: PIDA (1 equiv.) in DMSO or DMF at RT. The range of the addition reaction between aminoalkyl radicals and imines is shown in Scheme 18. The application of primary sulfinates in the addition reaction between α-aminoalkyl radicals and imines resulted in good yields for the corresponding α,β-diamino ester derivatives. A diastereomeric product combination of secondary sulfinate was produced. Cyclic sulfinates made from piperidine and piperazine provided the appropriate products; however, those made from pyrrolidine did not. Alkyl, alkenyl, and aryl-containing α-keto imines were also well-tolerated and produced moderately to favorably yields of α,β-diamino ketone derivatives.



Scheme 18. PIDA-mediated generation of α-aminoalkyl radicals.

The authors proposed that the present reaction should proceed via a radical chain process; in order to produce RSO_2. (**109**), DIB should specifically act as an activator for the oxidation of **108a** (Figure 15). The removal of sulphur dioxide from **109** should then result in the production of an aminoalkyl radical (**110**). Then, adding **110** to an imine should provide a **111**-type aminyl radical that might oxidize sulphate to create a simultaneous formation of **113** via **112**.

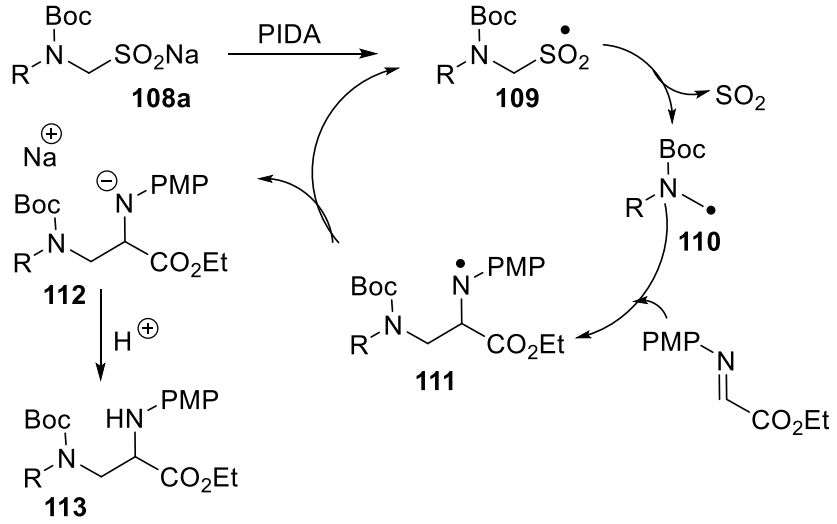


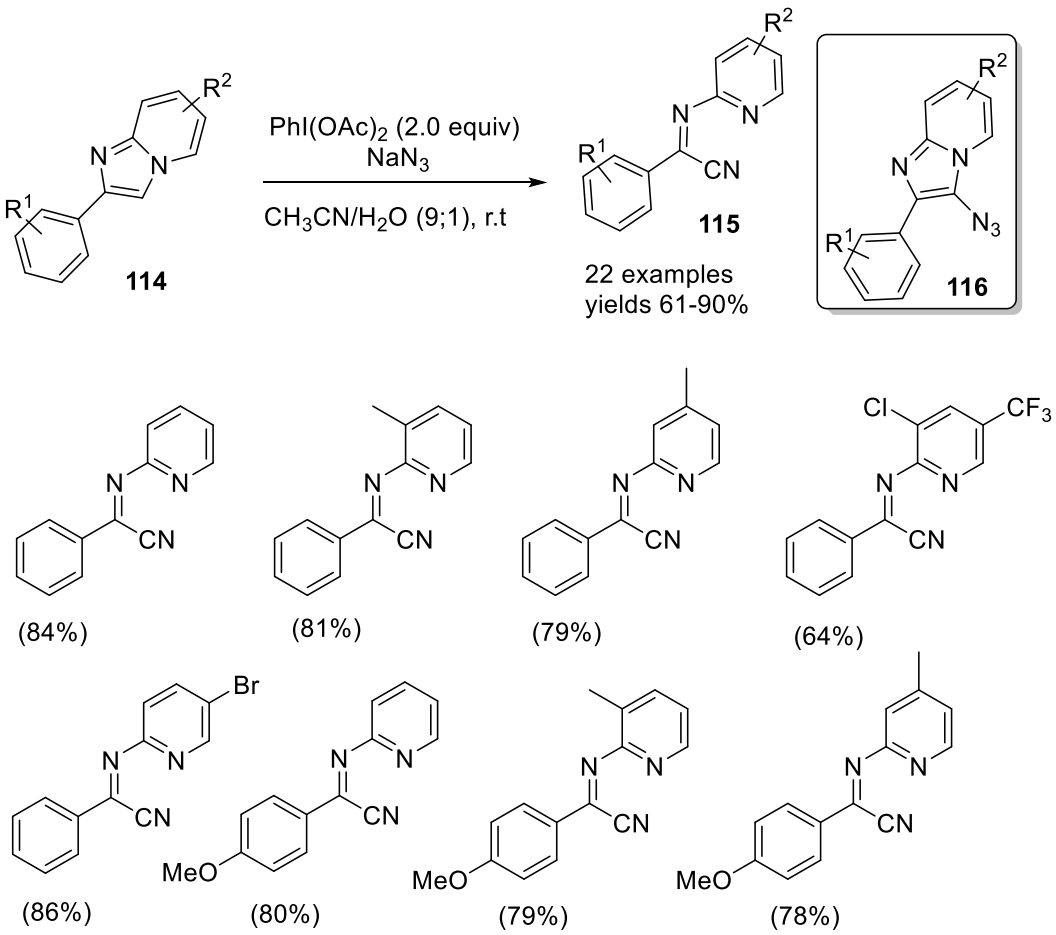
Figure 15. PIDA-mediated synthesis of α-aminoalkyl radicals.

2.4.4. Ring Opening Reaction

Due to their bifunctionality, α-iminonitriles are adaptable intermediates in the synthesis of organic compounds. They can be thought of as a veiled form of α-amino acids because of their near structural similarity to Strecker α-aminonitriles. A latent possibility to produce optically active α-amino acid derivatives would be served by the presence of a sp^2-prochiral centre (a C=N bond) in α-iminonitriles. Amidines, *N*-alkylketene-imines, amides, and cyanoenamides are just a few of the additional valuable building blocks that may be made using α-imimonitriles as a precursor. Imidazo[1,2-*a*]pyridines, on the

other hand, are a significant class of fused heterocyclic motifs that exhibit a wide range of biological activities, including antitumor, antiprotozoal, antiviral, antimicrobial, antiherpes, anticancer, anticonvulsant, and others. Due to their unique pharmacological profile, imidazo[1,2-*a*]pyridines are being synthesized and structurally decorated to create novel scaffolds with altered biological functions.

Imidazo[1,2-*a*]pyridine and NaN_3 interacted under friendly conditions via ring opening reaction (RoR) strategy to produce extremely high quantities of α-iminonitriles in the presence of PIDA. Through this method, Karade et al. synthesized α-iminonitriles (**115**) in cyanide- and metal-free reaction conditions (Scheme 19) [33]. The optimized conditions for this methodology are: PIDA (2 equiv.), NaN_3 (3 equiv.) in CH_3CN: H_2O (9:1) at RT. This approach worked well with a wide range of imidazo[1,2,*a*]pyridines that had aryl or pyridine type rings with electron-donating and -withdrawing groups. It was discovered that the electronic impact of the substituents was not a factor in the yields of the reactions. The impact of steric hindrance was also not seen because imidazo[1,2,*a*]pyridines bearing methyl groups in various positions were able to generate the corresponding α-iminonitriles with DIB/NaN_3 in efficient reactions with good yields. α-Iminonitriles were produced in good yields when imidazo[1,2,*a*]pyridines with -OMe, -Cl, -Br, and -CF_3 substituents were used. This approach can also be used to successfully synthesize α-iminonitriles with pyrimidine and naphthalene moiety.



Scheme 19. PIDA-mediated synthesis of α-iminonitriles.

Figure 16 illustrates a possible process for the synthesis of α-iminonitriles from imidazo[1,2-*a*]pyridines. PhI(OAc)N_3 is created when PhI(OAc)$_2$ and NaN_3 swap ligands. The intermediate **117** is created when the imidazo[1,2-*a*]pyridines attack the electrophilic PhI(OAc)N_3 through the C3 position.

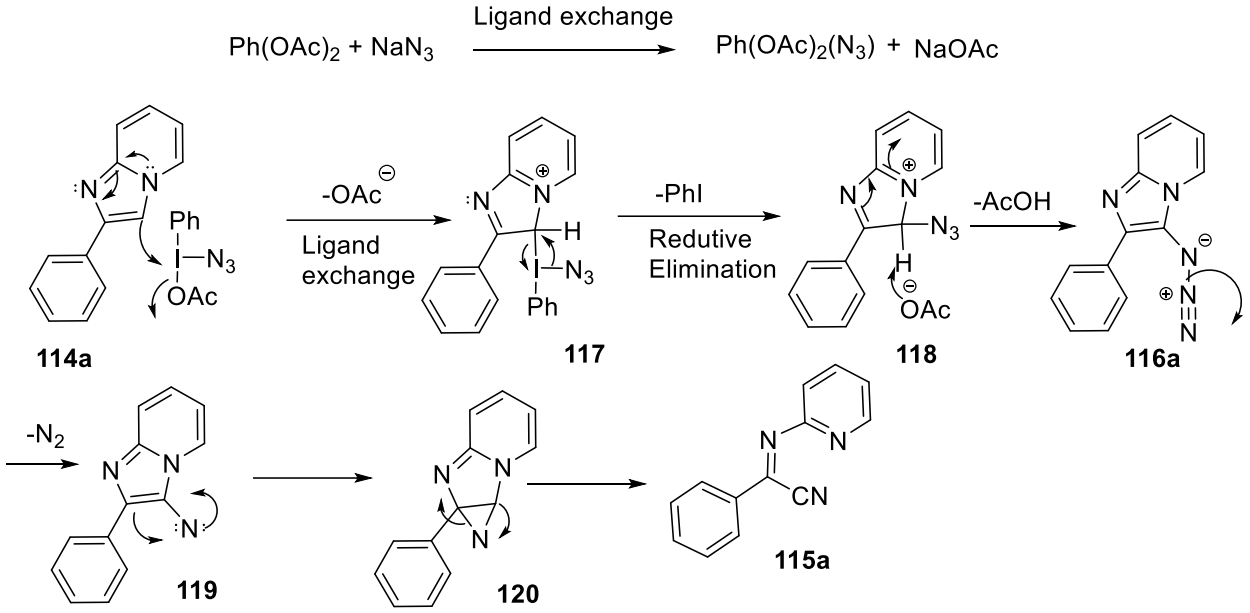
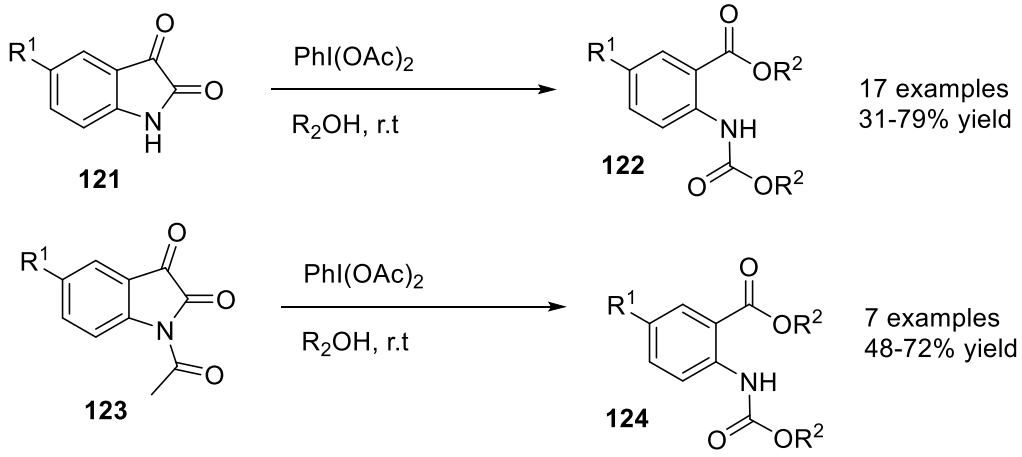


Figure 16. Proposed pathway for the formation of α-iminonitriles.

Thus, two reactive ligands have been gathered around the coordination sphere of the hypervalent iodine(III). Due to intermediate **117**'s propensity for reductive elimination of iodobenzene, an azide group is introduced to imidazo[1,2-*a*]pyridines at position C3, forming a complex called σ-complex **118**, which then undergoes aromatization to produce 3-azido imidazo[1,2-*a*]pyridines **116a**. It is well known that the heat breakdown of aryl azides produces nitrene as an intermediate. Thus, **116a** is capable of thermally decomposing to produce nitrene **119**, which is then trapped intramolecularly to produce strained azirine **120**. In order to create α-iminonitrile **115a**, **120** finally suffers ring opening of the azirine unit while simultaneously cleaving the five member ring.

2.4.5. Oxidative Cleavage of C2–C3 Bond

Isatin is a classic indole derivative that contains both keto and lactam carbonyl groups. Isatin can be attacked by nucleophiles at the C2 and/or C3 locations, and the chemoselectivity of these reactions depends on a number of variables, including the type of nucleophile. Karade and group reported that when isatin and *N*-acetyl isatin (**112**/**114**) interact with PIDA, oxidative C2–C3 bond cleavage occurs, resulting in carbamates of alkyl anthranilates (**113**) and alkyl 2-acetamidobenzoate (**115**), respectively (Scheme 20) [34].



Scheme 20. PIDA-mediated oxidative C2–C3 bond cleavage.

Even after refluxing for 24 hours in methanol, molecular iodine was found to be insufficient to cause oxidative C2–C3 cleavage of isatin. The C2–C3 oxidative cleavage of isatin was tried by the authors using in situ produced hypervalent iodine(III) reagents from catalytic iodoarene reactions with terminal oxidants such as *m*CPBA or oxone. However, they were never able to find the corresponding carbamate, which was consistent with the literature's claim that the Baeyer–Villiger oxidation product is created when isatin is oxidized with *m*-CPBA. The optimized conditions for this methodology are: PIDA (1.7 equiv.) in alcohol at RT. For the oxidative C2–C3 cleavage of isatin, a variety of primary alcohols including methanol, ethanol, propanol, CF_3CH_2OH, and ethoxyethanol have been utilized successfully. The use of methanol as a solvent was shown to maximize the output of carbamates. The kind of the substituents affected the yields of isatin's oxidative C2–C3 cleavage. Isatins with electron-withdrawing groups (F, Cl, Br, and NO_2) produced corresponding compounds in higher yields than isatins with electron-releasing groups (Me and OMe). It was significant to note that just one carbamate derivative produced by the modified isatins resulted in the oxidative cleavage of the C2–C3 bond.

Figure 17 depicts the possible mechanism for the C2–C3 oxidative cleavage of isatin utilizing PIDA and alcohol. Isatin (**121a**) can create hemiketal **125** and then produce **126**, because of a ligand-exchange reaction with PIDA. The affinity of **126** for iodobenzene reductive elimination facilitates the concurrent oxidative breakage of the C2–C3 bond, which results in the creation of the isocyanate derivative **129**, which is then trapped by alcohol to produce the carbamate derivative **122a**.

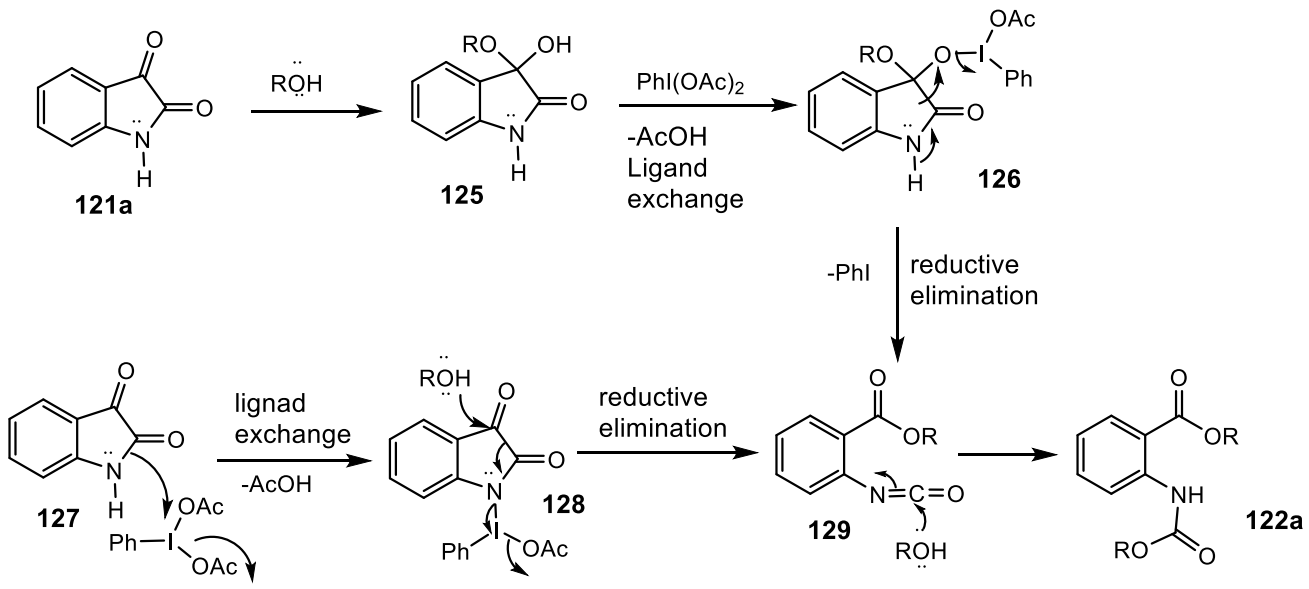
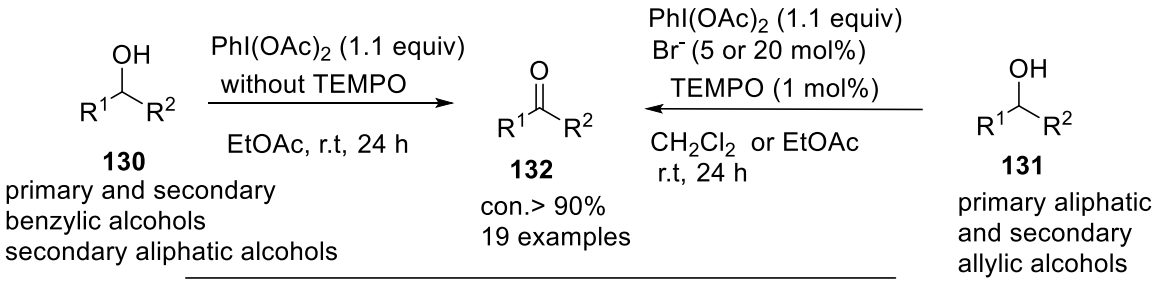


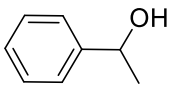
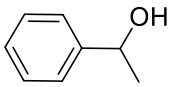
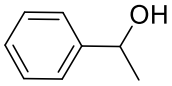
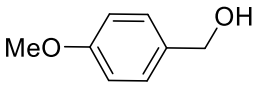
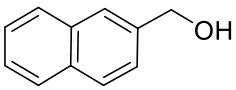
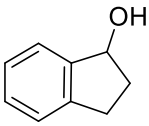
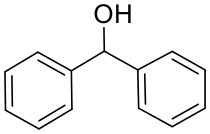
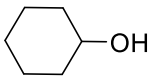
Figure 17. Plausible mechanism for the oxidative cleavage of C2–C3 bond.

2.4.6. Oxidation

Alcohol oxidation is a process that has garnered interest for a very long time. The recent need for environmentally friendly oxidation methods has prompted the creation of cleaner and more secure oxidation processes. By utilizing supported metal catalysts, the usage of soluble metal-based oxidants or catalysts can be eliminated. On the other hand, it is highly desirable to use metal-free catalysts for the selective oxidation of organic substrates.

Using PIDA and a catalytic quantity of bromide ions from tetrabutylammonium bromide or KBr in ethyl acetate, primary and secondary benzylic alcohols (**130**) and secondary aliphatic alcohols (**131**) were oxidized to the corresponding aldehydes and ketones (**132**), as reported by Gruttadauria and co-workers (Scheme 21) [35]. In the oxidation of primary aliphatic alcohols and secondary allylic alcohols carried out in the presence of 1 mol% TEMPO, the catalytic significance of the bromide ions was also underlined.



Entry	Catalyst	Alcohol	conv,(%)
1.	NaBr		>95
2	KBr		>95
3	NaBr		90
4	KBr		60
5	KBr		60
6	KBr		>95
7	KBr		>95
8	KBr		>95

Scheme 21. PIDA-mediated oxidation of alcohols.

The creation of bis(acyloxy)bromate(I) anions, which in turn release acetyl hypobromite (AcOBr) and potassium acetate (Figure 18, pathways a and b), explains how bromide ions promote reactions in the presence of PIDA. The carbonyl molecule is produced via oxidation mediated by AcOBr (route c), while the initial bromide salt is produced by proton exchange between acetate and HBr (path d). The extra pathways e-i can be used to explain how primary aliphatic alcohols are oxidized with PIDA, TEMPO, and bromide.

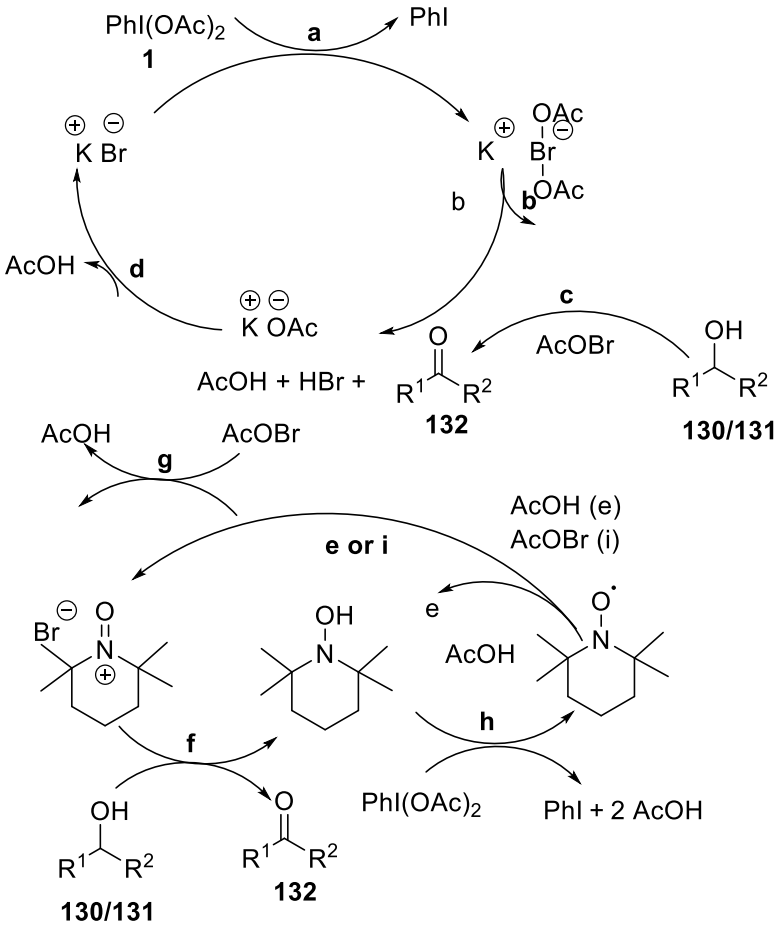
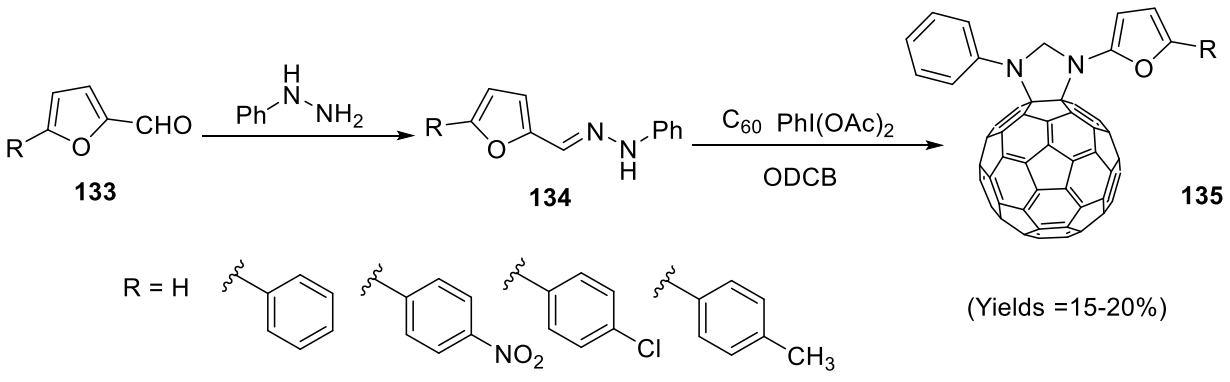


Figure 18. Proposed mechanism for the PIDA-mediated oxidation of alcohols.

2.4.7. Synthesis of Furylpyrazolino[60]fullerene Derivatives

Due to their distinctive structure, fullerenes have drawn attention from all around the world from the first discovery of the well-known class of spherical molecules and have pioneered the way in numerous scientific fields. Due to their intriguing physical and chemical characteristics, such as their ability to form endohedral and exohedral derivatives, electrical properties, electron-accepting nature (which facilitates their use in the preparation of photovoltaic cells), mechanical strength, and minimal biotoxicity, researchers are interested in studying these unusual molecules. By using PIDA as an oxidant in *o*-dichlorobenzene (ODCB), a [3+2] cycloaddition procedure was efficiently developed by Shalaby et al. to create a new series of furylpyrazolino[60]fullerene derivatives (**135**, Scheme 22) under microwave conditions [36].



Scheme 22. PIDA-mediated synthesis of furylpyrazolino[60]fullerene derivatives.

In addition, researchers also looked into the photophysical and electrochemical properties of the new compounds. Three of these pyrazolino[60]fullerene compounds displayed higher ground-state electron affinities than the parent C60. First, the reaction between $PhI(OAc)_2$ and substituted furylhydrazone (**134**) produced the nitrile imine intermediate. The resultant intermediate (**136**) is then subjected to a 1,3-dipolar cycloaddition reaction with C60 to produce derivatives of furylpyrazolino[60]fullerene (**135**), as depicted in Figure 19.

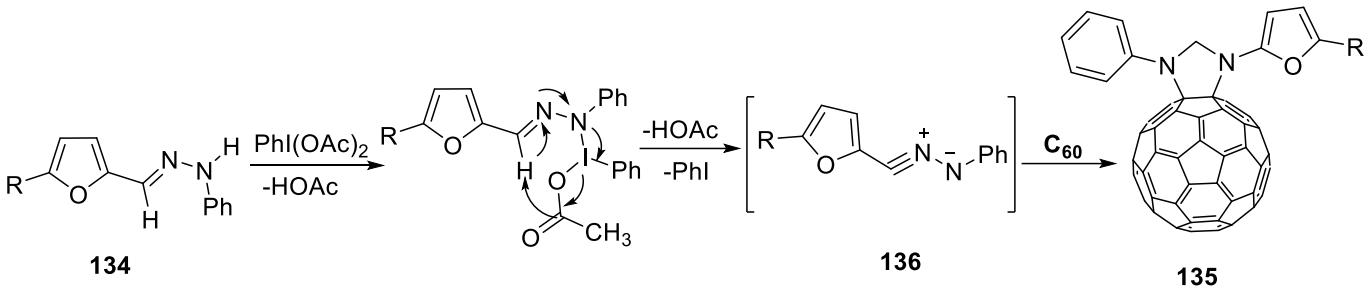
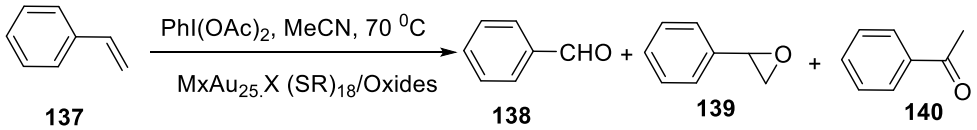


Figure 19. Possible mechanism for the formation of furylpyrazolino[60]fullerene derivatives.

2.4.8. Catalytic Oxidation of Styrene

As oxide-supported catalysts for the catalytic oxidation of styrene, atomically precise bimetallic $M_xAu_{25-x}(SR)_{18}$ (M=Cu and Ag, R = CH_2CH_2Ph) nanoclusters were explored by Jin and Li (Scheme 23) [37]. They were compared to the homogold $Au_{25}(SR)_{18}$ nanocluster in terms of their catalytic characteristics. Using PIDA (0.1 equiv.) as the oxidant, the oxide-supported $M_xAu_{25-x}(SR)_{18}$ catalysts resulted in a 42–82% conversion of styrene at 70 °C. The activity (i.e., conversion of styrene, **137**) and selectivity to styrene epoxide (**139**) or benzaldehyde (**138**) were discovered to be modulated by the Ag and Cu dopants (major products).



Entry	Catalyst	Conversion	Selectivity (%)		
			138	**139**	**140**
1	Only TiO_2	15.8	76.1	23.9	Trace
2	$Au_{25}(SR)_{18}/TiO_2$	58.9	54.0	44.3	1.7
3	$Ag_2Au_{25}x(SR)_{18}/TiO_2$	60.1	86.9	12.4	0.7
4	$Cu_2Au_{25}x(SR)_{18}/TiO_2$	41.9	88.3	11.7	Trace
5	Only CeO_2	14.1	53.2	46.8	Trace
6	$Au_{25}(SR)_{18}/CeO_2$	64.2	46.7	51.9	14
7	$Ag_2Au_{25}x(SR)_{18}/CeO_2$	82.1	46.4	53.6	Trace
8	$Cu_2Au_{25}x(SR)_{18}/CeO_2$	66.3	52.9	47.1	Trace
9	Only SiO_2	13.3	53.3	46.5	Trace
10	$Au_{25}(SR)_{18}/SiO_2$	54.5	50.3	48.7	1.0

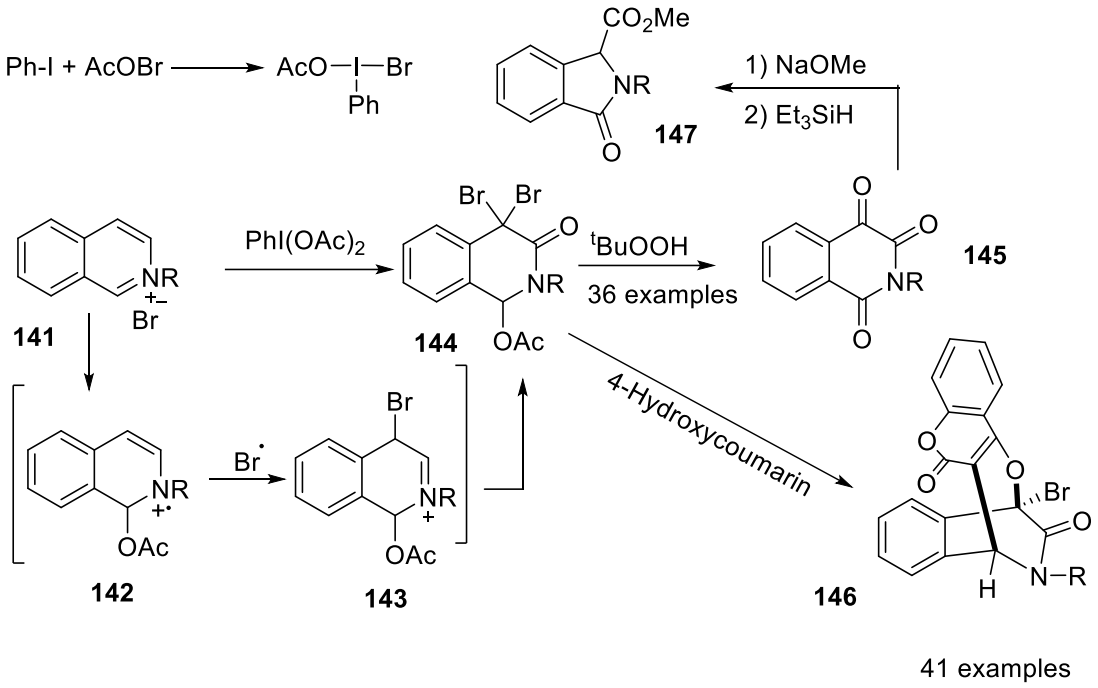
Scheme 23. PIDA-mediated oxide-supported catalytic oxidation of styrene.

2.4.9. Synthesis of 1,4-Bridged Dihydroisoquinolin-3-Ones

The isoquinoline structural core can be found in a wide variety of naturally occurring products as well as bioactive compounds. There are a lot of bridging isoquinoline derivatives that exist naturally, and many of them have interesting bioactivities. The building of

bridging cyclic skeletons having dense functionalities has been the focus of a significant amount of study over the past few decades. This has been done in an effort to discover methods for the synthesis of these molecules. Because isoquinolinium ions include two electrophilic sites, the tandem dearomatizative annulation of isoquinolinium salts with tethered bis-nucleophiles is a straightforward protocol.

Cai et al. presented a metal-free switchable synthesis of isoquinoline-1,3,4-triones (**137**) and 1,4-bridged dihydroisoquinoline-3-ones (**138**) from isoquinolinium salts. The first 1,4-bridged dihydroisoquinolin-3-ones (**138**) were made in excellent yields by sequentially oxidizing and annulating isoquinolinium salts with 4-hydroxycoumarins (Scheme 24) [38]. The combination of the bromide anion and PIDA was found to be a good carrier of very labile carboxyl radicals and moderately stable bromine radicals, as shown by these site-selective transformations that rely on an iodine(III)-mediated dual radical addition/radical coupling strategy.



Scheme 24. PIDA-mediated synthesis of 1,4-bridged dihydroisoquinolin-3-ones by site-selective transformations.

The optimized conditions for this methodology are: PIDA (3 equiv.) and KBr (1 equiv.) in MeCN at 50 °C. At first, a variety of alkyl groups were attached to the N atom of the isoquinolinium salts. With a wide variety of bridging dihydroisoquinoline-3-ones, it was possible to successfully synthesize isoquinolinium salts that contained *para*-, *meta*-, or *ortho*-substituted phenylmethyls. Substituent electronic effects did not seem to have much of an influence on the yields for the vast majority of benzyl-substituted substrates, with the exception of those that were replaced with strong electron-withdrawing substituents.

Other *N*-primary alkyl-substituted isoquinolinium salts performed admirably as well. These isoquinolinium salts included fused and hetero arylmethyl-, long-chain alkyl-, allyl-, cycloalkylmethyl-, 2-methoxyethyl-, and 2-alkoxycarbonylethyl-substituted substrates. These substrates produced the corresponding products in satisfactory yields. Compared to their *N*-secondary alkyl equivalents, which are more sterically hindered and less stable, *N*-primary alkyl substrates performed significantly better. The benzene ring of the isoquinolinium salts was then modified by the addition of a variety of substituents. Because of steric hindrances, isoquinolinium salts with the substitution at the 6-position were found to be of higher quality than those with the substitution at the 5-position. Initiation of the

PIDA-mediated oxidation of **133a** occurred not via a nucleophilic addition pathway, but rather via a radical addition pathway (Figure 20).

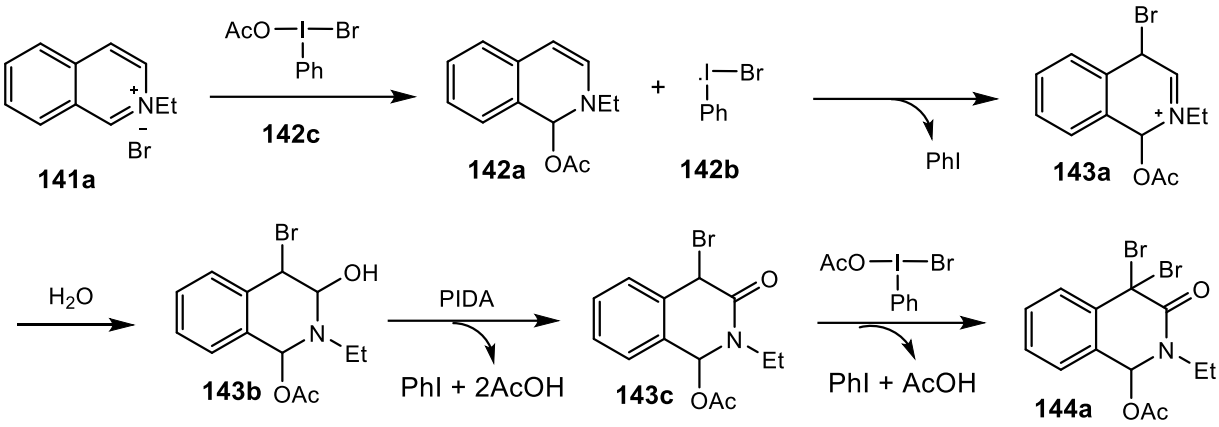


Figure 20. Possible mechanism for the PIDA-mediated oxidation.

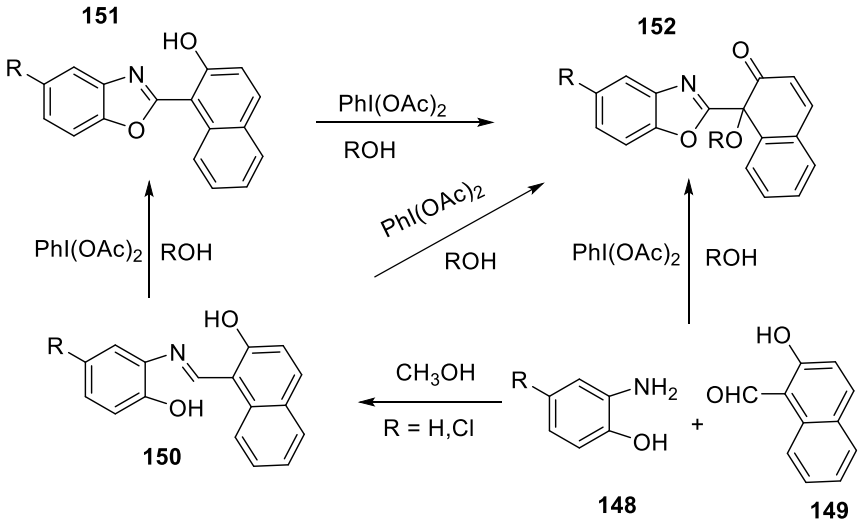
Through the process of ligand exchange, PIDA was able to produce **142c** after reacting with the bromide anion **141a**. **142c** was the catalyst that started the oxidative process, which then produced radical cation **142a** and radical **142b**. As a result of the transfer of the bromine atom from **142b** to C-4 of **142a**, iminium **143a** and PhI were produced. Lactam **143c** was produced as a result of a nucleophilic attack on lactam **143a** by water, which was then followed by PIDA oxidation. The polysubstituted dihydroisoquinoline-3-one (**144a**) was produced when the benzyl hydrogen of compound **143c** was brominated by compound **142c**.

2.4.10. Regioselective Synthesis of 1-(Benzoxazol-2-yl)-1-Alkoxynaphthalen-2(1*H*)-Ones

Naphthalen-2(1*H*)-ones are pharmacologically active chemicals; for example, 1-hydroxy-1-methylnaphthalen-2(1*H*)-ones belong to the phytoalexines category. Both 1-alkoxy-naphthalen-2(1*H*)-one and 1-methyl-1-(2-oxazolyl)-naphthalen-2(1*H*)-one are inhibitors of HIV-1 reverse transcriptase and 1-alkoxy-naphthalen-2(1*H*)-one has been shown to have chemotactic action in vitro toward human polymorphonuclear leukocytes. 1-Hydroxyl-2-naphthalenones are also a key structural motif, scattered throughout a variety of lacinilene derivatives. In recent years, benzoxazole derivatives have grabbed a lot of attention as a result of their utilization as intermediates in the production of novel biological materials.

According to Kumar and co-workers, the dearomatized products 1-(benzoxazol-2-yl)-1-alkoxynaphthalen-2(1*H*)-ones (**152**) and 1-(benzoxazol-2-yl)naphthalene-2,3-diones were produced regioselectively by PIDA-induced oxidation of 2-(2-hydroxynaphthyl)benzoxazoles (**151**) in alcohols (Scheme 25) [39]. Additionally, by adjusting the concentration of PIDA in various alcohols, these products were also produced in one-pot, either from (*E*)-1-(((2-hydroxyphenyl) imino)methyl)naphthalen-2-ol (**150**) or 2-aminophenol (**148**) and 2-hydroxynaphthaldehyde (**149**).

Two different routes seem to be involved in the most likely mechanism for the synthesis of compounds **152** and **158** (Figure 21). Compound **152** is formed via the intermediary of **153** in the pathway a of the reaction. Path b involves the conversion of the intermediate **154** to **155**, which exists in the form of keto-enol tautomers. **155** then reacts in situ with $PhI(OAc)_2$ to produce **157**, which ultimately affords **158**. There is also the potential that **155** might be formed through an intramolecular rearrangement of **150**, which would most likely result in **159** being derived from **151** and $PhI(OR)_2$ (which would be created in situ from $PhI(OAc)_2$ and ROH).



Scheme 25. PIDA-mediated oxidation of 2-(2-hydroxynaphthyl)benzoxazoles in alcohols.

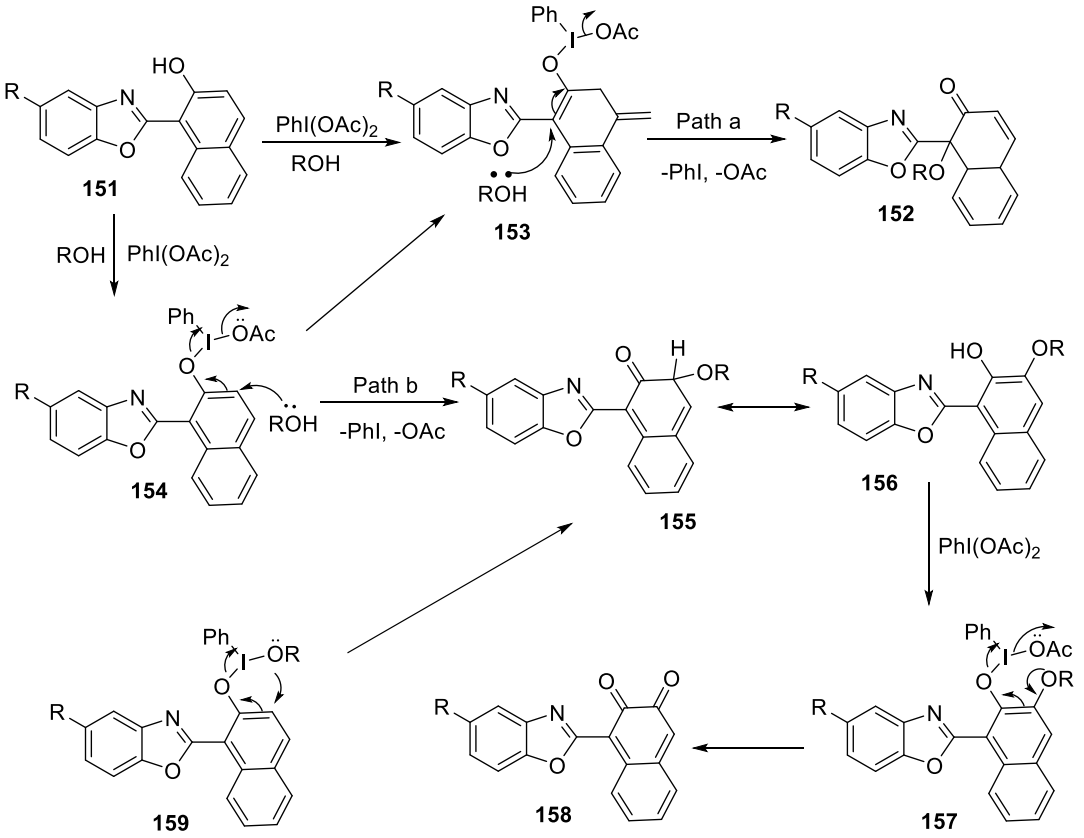


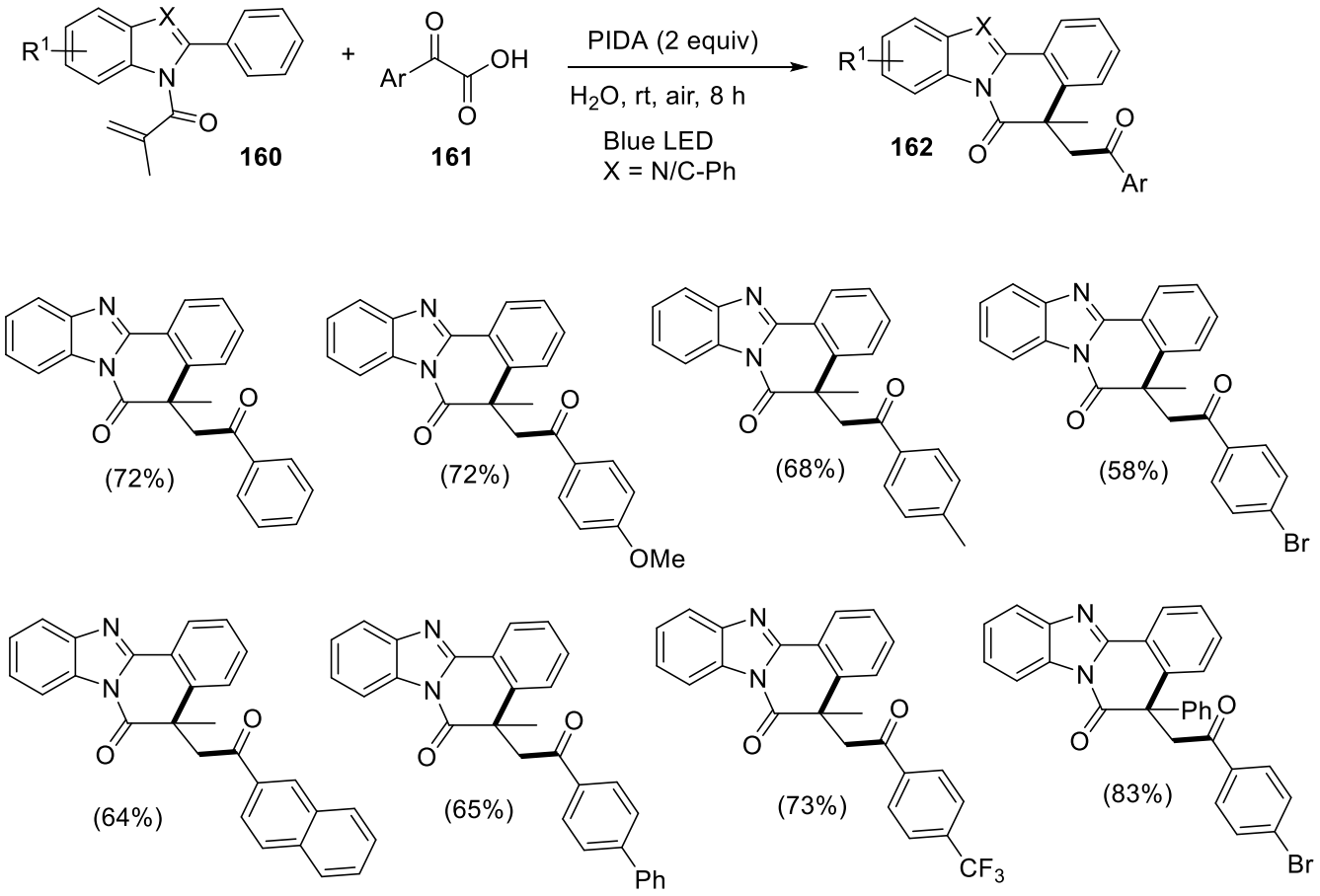
Figure 21. Plausible mechanism for the formation of dearomatized products.

2.4.11. Synthesis of Acylated Benzimidazo/Indolo[2,1-*a*]isoquinolines

In recent years, photocatalysis has established itself as a sustainable and environmentally friendly synthetic platform that is able to convert light energy into chemical energy in an effective manner. This allows for the formation of new chemical bonds. In particular, the benzimidazole-isoquinoline fused framework and the indole[2,1-*a*]isoquinoline containing tetracyclic core structure are not only widely present in some biologically active molecules, but they are also important components of synthetic intermediates and functional materials. This is because they contain tetracyclic cores. Several typical polyheterocycles that

contain skeletons are known to have potentially useful applications in the treatment of hemoglobinopathies and cancer, as a peripheral benzodiazepine receptor ligand, in the modulation of the potassium ion flux, and in organic electronics.

Sun and others described the synthesis of acylated benzimidazo/indolo[2,1-*a*]isoquinolines, a metal-free visible-light-induced decarboxylative radical addition/cyclization process at room temperature. The process was developed in water using a one-step, moderate reaction involving functionalized 2-arylbenzoimidazoles or 2,3-diarylindoles (**160**) and oxocarboxylic acids (**161**) in the presence of PIDA (Scheme 26). Using this protocol, it was possible to get benzimidazo/indolo[2,1-a]isoquinoline-6(5*H*)-ones (**162**) containing 1,4-dicarbonyl in acceptable yields without using conventional heating or metal reagents [40].



Scheme 26. PIDA-mediated metal-free visible-light-induced decarboxylative radical addition/cyclization.

The optimized conditions for this methodology are: PIDA (2 equiv.) in H_2O at RT in the presence of blue LED.

As a result, a feasible mechanism for the reaction was proposed, which can be seen displayed in Figure 22. To begin with, a ligand exchange interaction between PIDA and 152a resulted in the production of hypervalent iodine(III) reagent 163. This reagent **163** then underwent an I-O bond cleavage when it was exposed to visible light, which resulted in the delivery of radicals **164** and **165**.

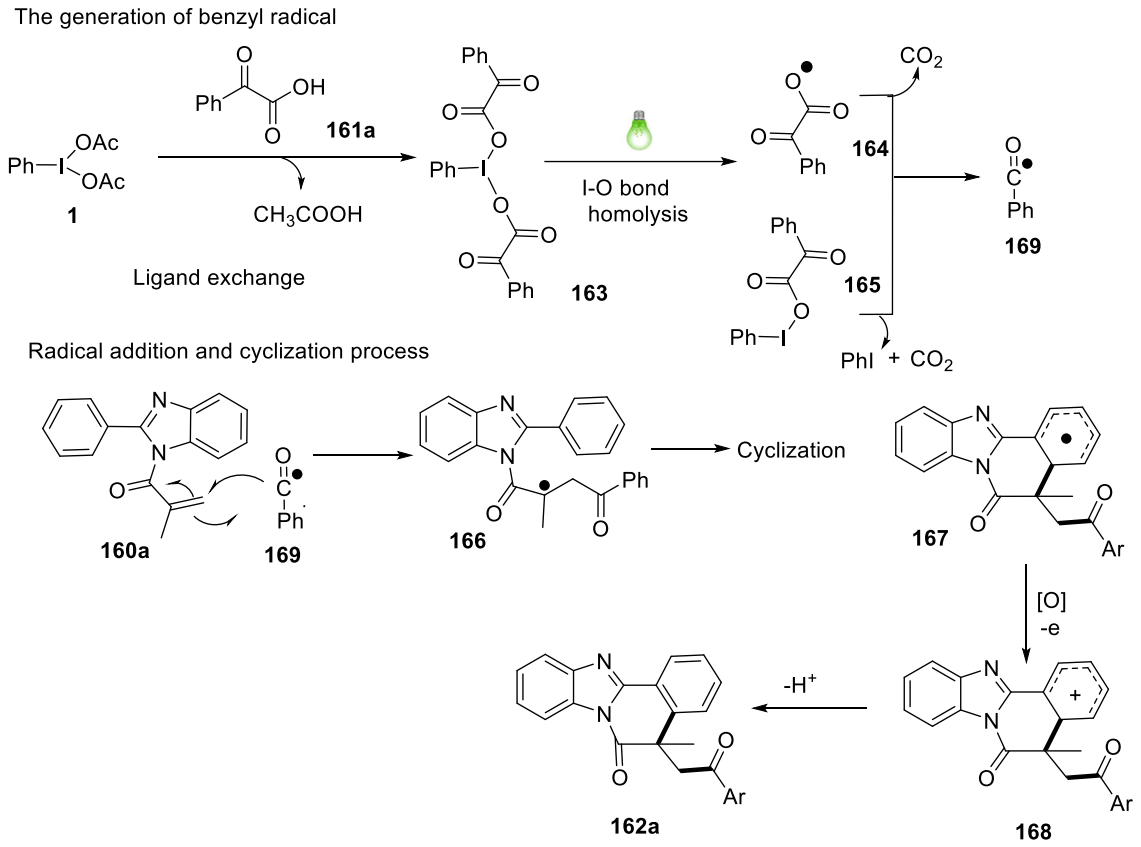
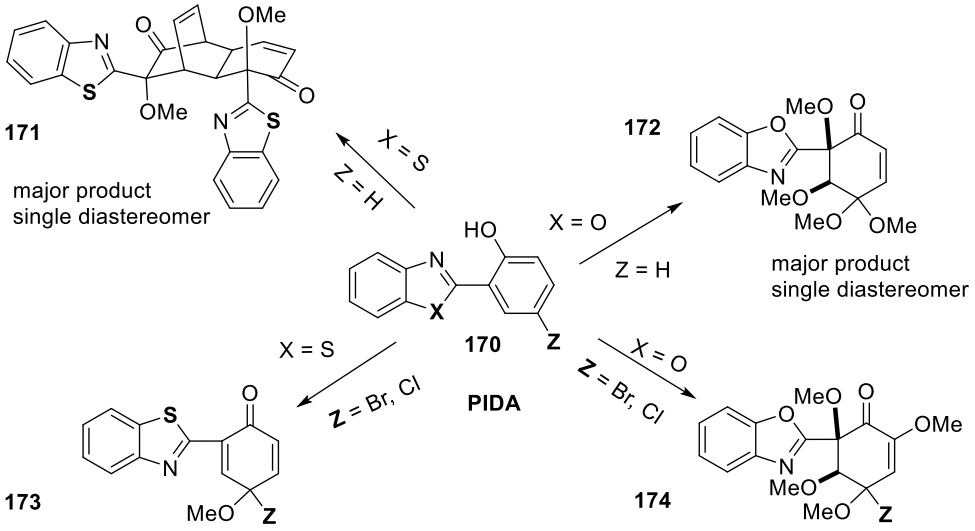


Figure 22. Plausible reaction mechanisms.

Subsequently, the benzoyl radical might be produced through the fragmentation of both **164** and **165**. After this, the benzoyl radical was introduced into the C=C bond of **160a**, which resulted in the production of the radical species **166**. This radical species subsequently underwent an intramolecular cyclization, which led to the formation of the radical **167**. After that, a procedure involving oxidation with a single electron was used to transform radical **167** into carbocation **168** using either PIDA or oxygen. Last but not least, the formation of product **162a** is possible through the fast deprotonation of the carbon cation **168**.

2.4.12. Oxidative Dearomatization

Diels–Alder cycloaddition of 2,4-cyclohexadienones or *ortho*-quinols with activated alkenes is the typical method for synthesizing the bicyclo[2.2.2]octenone skeleton that is present in many natural products. However, 2,4-cyclohexadienones can also undergo spontaneous [4+2] dimerization to homodimeric bicyclo[2.2.2]octenones. Kumar and co-workers described a variety of stereochemically defined oxidative dearomatization products by using PIDA to treat 2-(2-hydroxyaryl)benzoxazoles and 2-(2-hydroxyaryl)benzothiazoles [9]. These products exhibited remarkable regiochemical and stereochemical properties that were determined by the nature of the phenol substituents. Tetramethoxy-substituted cyclohexenones were synthesized using the regio- and stereoselective process of dearomatization of benzoxazole-substituted phenols. However, regio- and stereoselective [4+2] dimerization of benzothiazole-substituted phenols could easily yield bicyclo[2.2.2]octenone (**171**). Additionally, 2-(2-hydroxyaryl)benzoxazoles (**170**) created a variety of tetramethoxy-substituted cyclohexenones (**172**), whilst halogenated 2-(2-hydroxyaryl)benzothiazoles produced 4-methoxycyclohexa-2,5-dien-1-ones (**173**) (Scheme 27).



Scheme 27. PIDA-mediated oxidative dearomatization products.

The optimized conditions for this methodology are: PIDA (2 equiv.) in MeOH at RT. Figure 22 depicts what appears to be a reasonable mechanism for the transformation of compound 1 into product 5. The regiochemistry of the initial oxidative attack determines whether the oxidation of phenols with $PhI(OAc)_2$ in methanol will yield 4, 4-dimethoxy-cyclohexa-2,5-dienones, 4-substituted-4-methoxycyclohexa-2,5-dienones, or 6-substituted-6-dimethoxy-cyclohexa-2,4-dien-1-ones. Therefore, it seems plausible that the cyclohexadienone **176** was one of the initially generated intermediates in the conversion of **175** to **179** (Figure 23). Compound **177** can be produced by performing a regiospecific conjugate addition of methanol to dienone **176** under the direction of the benzoxazole substituent. Oxidation of **177** by $PhI(OAc)_2$ results in the formation of the **178**, which is then intercepted by methanol to produce the product **179** that is seen. It is likely that the decreased ability of higher alcohols to intercept intermediates that are analogous to **176** and **180** is the cause of the observation that reactions carried out in higher alcohol solvents do not afford products that are analogous to **179**, but rather lead only to complex product mixtures. This was observed when reactions were carried out in higher alcohol solvents.

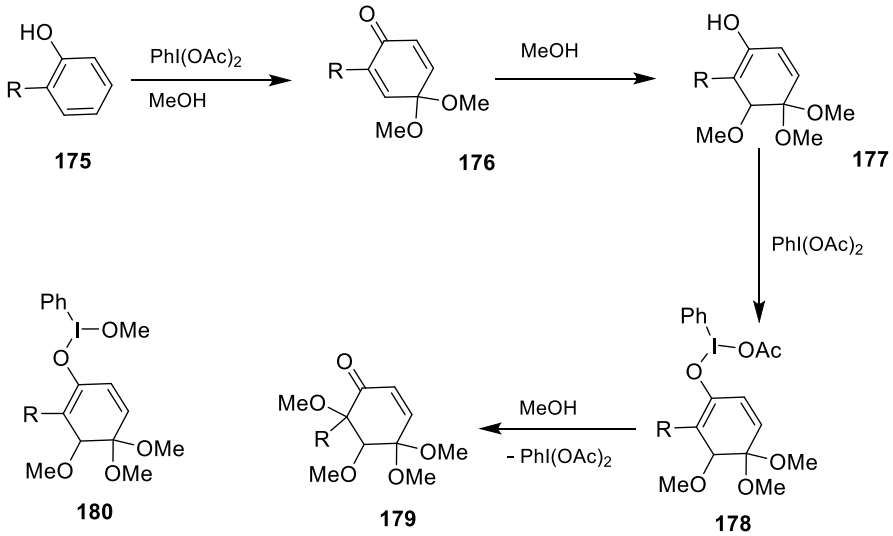


Figure 23. Plausible mechanism for the oxidative dearomatization.

3. Conclusions

In this mini-review, we have concisely and systematically presented the various applications of phenyliodine(III) diacetate (PIDA) in organic synthesis involving C-H functionalization, hetero-hetero bond formations, heterocyclic ring construction, rearrangements or migrations and miscellaneous reactions along with their interesting mechanistic aspects from the summer of 2015 to the present. We do hope that this primitive compilation would be a valuable addition for synthetic organic and allied researchers.

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