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高价碘试剂介导下的氧化重排反应

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摘要 在过去的 40 年间, 高价碘化学得到了迅猛发展, 受到了广大有机合成工作者的广泛关注. 高价碘试剂具有低毒、易制备、环境友好等优点, 可以参与多种类型的氧化偶联、官能团化及重排等多种类型的反应; 其中, 就高价碘试剂参与的氧化重排反应而言, 类型众多, 常见的反应包C—X重排(X=C, N, O), X—C重排(X=N, O, S, Si, I), I—X重排(X=O, N)以及sigmatropic重排. 对高价碘试剂参与的氧化重排反应进行了全面总结, 以方便读者了解该领域的相关研究进展.

关键词 高价碘试剂; 氧化反应; 重排反应

Oxidative Rearrangement Reactions Mediated by Hypervalent-Iodine Reagents

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Abstract During the past 40 years, hypervalent-iodine chemistry has developed rapidly and extensive attention has been received from many organic researchers. For their advantages of low toxicity, easy preparation and environmental benignity, hypervalent iodine reagents have been widely applied in various types of organic transformation including oxidative coupling, functionalization, and rearrangement reactions. Among them, there exist a series of oxidative rearrangement reactions, which can be classified into many types including C to X migration (X=C, N or O), X to C migration (X=N, O, S, Si or I), I to X migration (X=O or N) and sigmatropic rearrangement. This review comprehensively summarizes the oxidative rearrangement reactions enabled by hypervalent iodine reagents, providing convenience for organic readers to learn the progress of this research field.

Keywords hypervalent-iodine reagents; oxidative reaction; rearrangement reaction

1 Introduction

During the past four decades, hypervalent-iodine chemistry has gained prosperous development and many useful organic transformations have been realized by hypervalent iodine reagents.[1] The great interest from synthetic community in these non-metallic reagents lies in not only their chemical stability and environmental friendliness, but also their versatile reactivities. Usually, Hypervalent iodine reagents can be used as multipurpose oxidizing agents and effective functional-group transfer reagents.[2] Meanwhile, the hypervalent iodine reagents, especially these prepared *in situ* or advanced λ^3-iodane compounds, also play an important role in the construction of highly functionalized molecules via an exclusive rearrangement process, resulting from their particular ability to react first as an electrophile and then to be transformed into an excellent leaving group.[3] Accordingly, numerous hypervalent iodine reagents-mediated rearrangement reactions have been reported in the literature. Although several review papers have finely summarized these migratory transformations,[4] it should be still necessary to update the readers with recent advances of the chemistry due to its fast development. Furthermore, it might also be desirable to summarize these reactions in a comprehensive and systematic way. Due to the massive examples of migratory transformations enabled by hypervalent iodine reagents, these rearrangement reactions are classified into C to X migration (X=C, N or O), X to C migration (X=N, O, S,

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Si or I) and I to X migration (X=O or N), sigmatropic rearrangement as well as other miscellaneous rearrangement transformations in this reviewer paper.

2 Oxidative rearrangement reactions

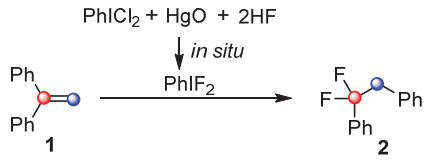
2.1 C to X migration (X=C, N or O)

2.1.1 C to C migration

The hypervalent iodine reagents can be utilized to realize a plethora of rearrangement reactions involving C to C migration. Specifically, the types of these C to C migration include 1,2-C to C migration, 1,2-C to C migration/cyclization or cyclization/migration tandem, fluorinated or fluoroalkylated 1,2-C to C migration tandem, C to C ring expansion, C to C ring contraction and Wagner-Meerwein rearrangement or Prins-pinacol tandem reaction.

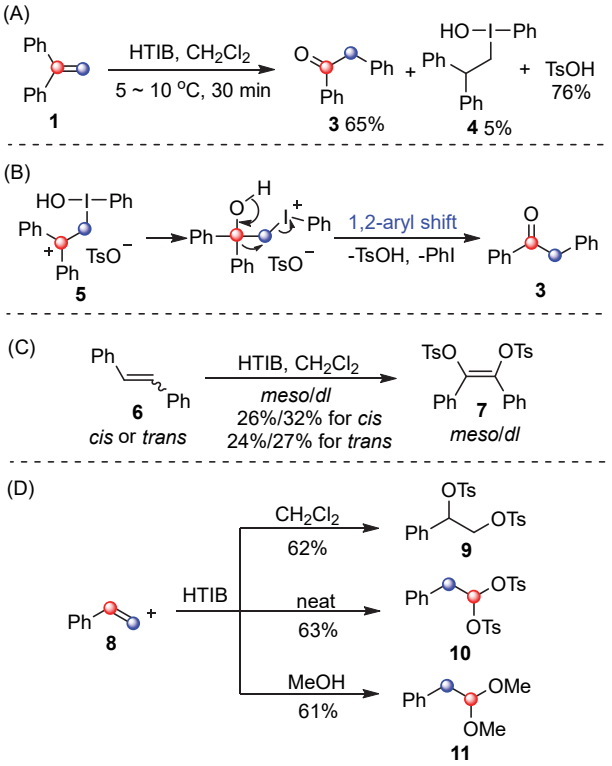
2.1.1.1 1,2-C to C migration

Before 1980s, the application of hypervalent iodine reagents for oxidative rearrangements of arylalkenes has received limited attention. As early as 1931, Bockemüller *et al.*[5a] treated 1,1-diphenylethylene **1** with $PhIF_2$ and obtained a difluoro compound which he assumed to be 1,1-diphenyl-1,2-difluoroethane but was later proved to be 1,2-diphenyl-1,1-difluoroethane **2** by Bornstein[5b] and Cabpenter[5c] via a $PhIF_2$-mediated 1,2-aryl migration process. $PhIF_2$ was generated *in situ* from a one-step reaction of mercuric oxide and aqueous hydrofluoric acid with $PhICl_2$ in dichloromethane (Scheme 1). Our literature survey showed that this could represent the first 1,2-aryl migration reaction mediated by a hypervalent iodine reagent.



Scheme 1 Difluorinated 1,2-phenyl migration mediated by $PhIF_2$ generated *in situ*

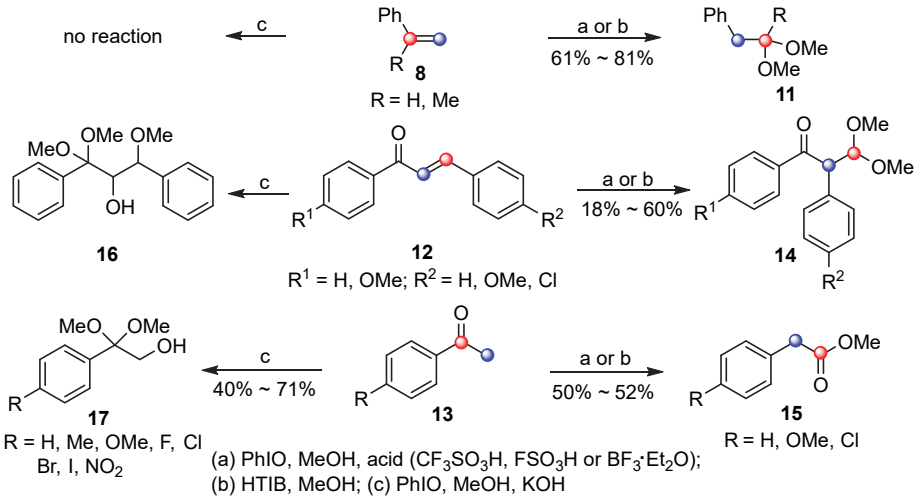
In 1981, Koser *et al.*[6a] reported that the reaction of 1,1-diphenylethylene **1** with [hydroxy(tosyloxy)iodo]-benzene (HTIB) in dichloromethane could generate 1,2-aryl migratory deoxybenzoin **3** as the major product (65% yield) and an unprecedented vinyliodonium salt, *i.e.*, phenyl (*β*,*β*-diphenylvinyl)iodonium tosylate **4** (5% yield) at the same time (Scheme 2A). A plausible mechanism was proposed for this rearrangement reaction. First, the reaction of 1,1-diphenylethylene **1** with HTIB generated cation intermediate **5**, which was transformed into iododium spontaneously. Then the 1,2-phenyl migration occurred in iododium intermediate to give deoxybenzoin **3** with loss of PhI and TsOH (Scheme 2B). It is worth noting that subjecting 1,2-diphenylethylene **6** or styrene **8** at the same reaction conditions only produced bis(tosyloxy)alkane **7** or bis(tosyloxy)alkene **9**, without any formation of the 1,2-aryl migratory products (Scheme 2C-D). Furthermore, an interesting medium effect was observed by Moriarty *et al.*[7] through the further study with styrene **8** as substrate. Contrary to the unrearranged product **9**, the reaction of neat styrene **8** or in MeOH with HTIB[6] delivered 1,2-aryl migration products 1,1-ditosyloxy-2-phenylethane **10** and phenylacetaldehyde dimethyl acetal **11**, respectively (Scheme 2D).



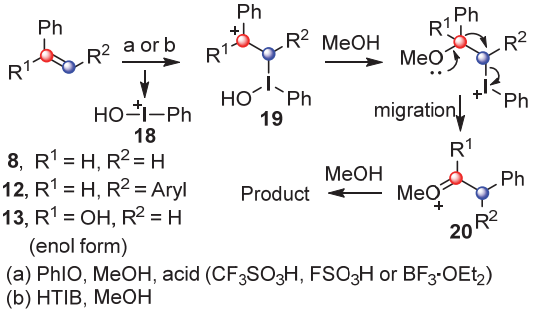
Scheme 2 Different outcomes of reactions between HTIB with styrene derivatives

In addition to styrene **8**, Moriarty *et al.*[7] found that the reactions of chalcones **12** and ketones **13** with HTIB in MeOH or PhIO in MeOH under acidic conditions (*i.e.*, FSO_3H, CF_3SO_3H or BF_3•Et_2O) also afforded the corresponding 1,2-aryl migration products, *i.e.*, 3,3-dimethoxy-1,2-diarylpropan-1-ones **14** and methyl 2-arylacetates **15** (Scheme 3, a or b). However, it is worth noting that when chalcones **12** and ketones **13** were treated with PhIO in MeOH in the presence of KOH, there was no migratory products observed in each case, with the reaction afforded 1,1,3-trimethoxy-1,3-diarylpropan-2-ols **16** and 2,2-dimethoxy-2-arylethan-1-ols **17**, respectively (Scheme 3, c).

Moriarty *et al.* proposed the term of 'solvohyperiodination' to account for the rearranged results observed in the above reactions. The electrophilic cation **18**, formed either by protonation of PhIO or simple dissociation of HTIB,[8] was first captured by carbon-carbon double bond to give carbenium intermediate **19**. Then nucleophilic attack of **19** by MeOH with the subsequent dissociation of I—O bond gave iodonium intermediate. Next, 1,2-phenyl migration with loss of PhI converted iodonium intermediate to oxonium **20**, which was added by MeOH to afford the rearranged dimethoxy ketone products (Scheme 4).



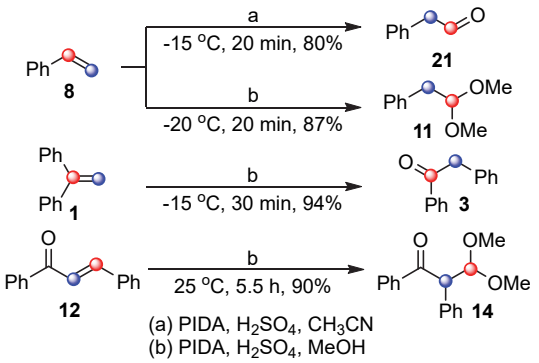
Scheme 3 1,2-Aryl migration of chalcones and ketones mediated by HTIB or PhIO



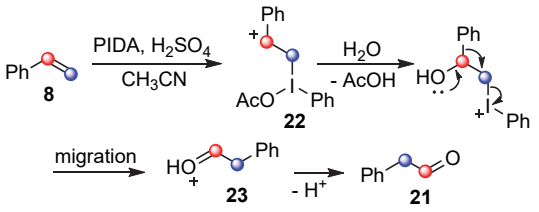
Scheme 4 Mechanism of 1,2-phenyl migration of styrenes, chalcones and ketones

In addition to PhIO and HTIB, PIDA has also been applied by Kapoor and Yusubov to realize the 1,2-aryl migration of phenylethylene derivatives. For examples, the reaction of styrene **8** with PIDA and H_2SO_4 in MeCN furnished phenylacetaldehyde **21**, while in MeOH the reaction afforded (2,2-dimethoxyethyl)benzene **11**. Similarly, when ethene-1,1-diyldibenzene **1** and chalcone **12** were treated with PIDA and H_2SO_4 in MeOH, the reaction afforded 1,2-diphenylethan-1-ones **3** and 3,3-dimethoxy-1,2-diphenylpropan-1-ones **14**, respectively (Scheme 5). Noteworthy is that for the reaction of **1** with PIDA and H_2SO_4 in MeOH, additional hydrolysis step is required for formation of ketones **3**. While for the reaction of **12** under the same conditions, the reaction afforded dimethoxy ketone **14** as the stable products. It is also worth noting that the 1,2-aryl migration approach was not applicable to (*E*)-stilbene **6**.[9a-9b] The mechanistic pathways of these transformations in the presence of MeOH are quite similar to 'solvohyperiodination' pathway mentioned in Scheme 4.

Similarly, the reaction of styrene **8** with PIDA and H_2SO_4 in MeCN generated cation intermediate **22**, which was nucleophilically attacked by the residual water in the solvent followed by the I-OAc dissociation to give iodonium intermediate **23**. Deprotonation of the latter gave aldehydes **21** (Scheme 6).[9]

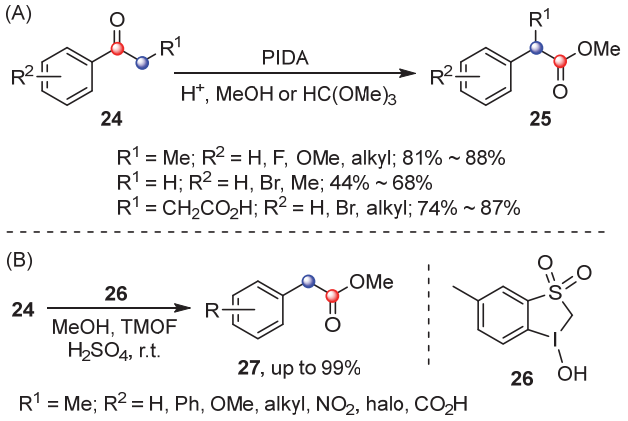


Scheme 5 1,2-Aryl migratiom of styrenes or chalcones triggered by PIDA



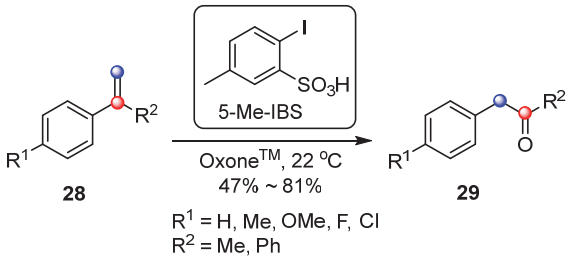
Scheme 6 Mechanism of 1,2-migratiom of styrene mediated by PIDA

Actually, no matter what the acidic condition is, H_2SO_4 CH_3SO_3H or CF_3SO_3H, in the system of PIDA in MeOH or CH_3CN/H_2O would enable PIDA to be converted *in situ* to more active analogues of HTIB. Since 1984, Tamura *et al.*[10a-10b] and Togo *et al.*[10c-10e] independently reported the synthesis of 2-arylpropanoates **25** through the PIDA/MeOH-mediated 1,2-aryl migration of aryl ketones **24** under acidic conditions (Scheme 7A). In 2007, Justik and coworkers[10f] employed a novel λ^3-iodane HMBI **26**, realizing an efficient preparation of esters **27** from aryl ketones **24** via a similar 1,2-aryl migration pathway (Scheme 7B). Both of the mechanisms of these two reactions are quite similar to that mentioned in Scheme 5.



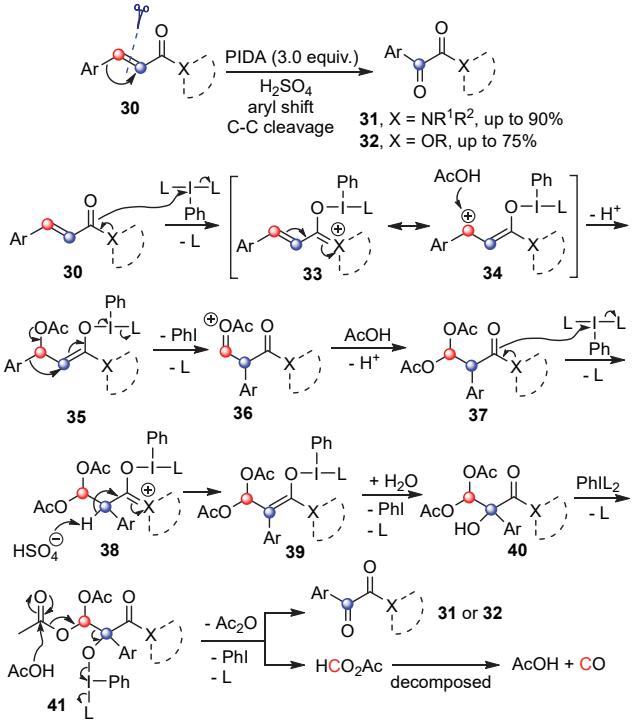
Scheme 7 Oxidative 1,2-migration of ketones mediated by PIDA or HMBI

Meanwhile, hypervalent iodine species generated *in situ* were also found to be applicable for such oxidative rearrangement reactions. In 2013, Purohit and co-workers[11] described the synthesis of the *β*-benzoketones **29** via a catalytic hypervalent iodine-mediated oxidative 1,2-shift of 1,1-disubstituted olefins **28**. The pre-catalyst (5-Me-IBS) was oxidized by oxone to produce *in situ* either a catalytic I(III) or I(V) oxidative species. Mechanistically, it was postulated that after finishing the oxidative rearrangement, the I(III) or I(V) oxidative species was converted back to 5-Me-IBS and entered the next catalytic circle (Scheme 8).



Scheme 8 *In situ* generated hypervalent iodine species-mediated oxidative rearrangement of 1,1-disubstituted olefins

In addition to delivering products 3,3-dimethoxy-1,2-diarylpropan-1-ones **14** with the 1,2-aryl migration of chalcones **12**, in 2014, Zhao and Du *et al.*[12a] found that the reaction of chalcone analogues **30** with 3 equiv. of PIDA in the presence of H_2SO_4 afforded *α*-ketoamides **31** or esters **32**, respectively, depending on the substrates applied (Scheme 9). It is well-known that hypervalent iodine reagent could be activated by Lewis acid or Bronsted acid.[10] Thus, it was proposed that PIDA was first activated by protonation with H_2SO_4, which increased the electrophilicity of the iodine center. Then the nucleophilic attack on the iodine center by **30** gave iminium salt **33**, whose resonance **34** was subsequently trapped by acetate acid to give intermediate **35**. Aryl migration occurred with the assistance of the oxygen lone pair conjugation, followed by the nucleophilic attack of the resulting oxonium **36** by another acetate to give intermediate **37**. Oxidation of the latter by activated PIDA in a similar fashion afforded iminium salt **38**, which underwent deprotonation to generate intermediate **39**. Nucleophilic attack of **39** by water delivered alcohol **40** with the release of iodobenzene and acetic acid. Further oxidization of the latter by a third equivalent of PIDA gave intermediate **41**. Finally, acetic acid attacked the electrophilic carbonyl carbon in the ester moiety of **41** led to the cleavage of C—C bond and C—I bond, thus releasing the desired products **31** or **32**, along with acetic anhydride, iodobenzene and acetic anhydride. Decomposition of formic anhydride generated acetic acid and CO gas.

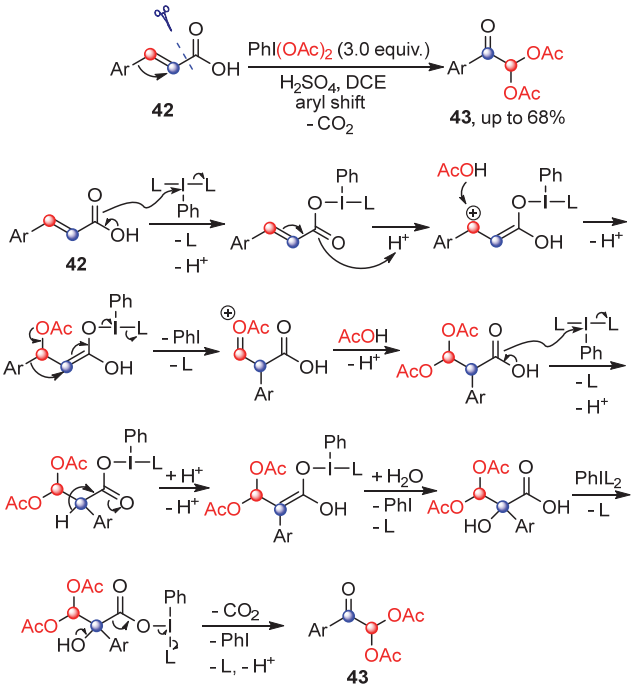


Scheme 9 PIDA-mediated oxidative 1,2-aryl shift of chalcones under acidic conditions

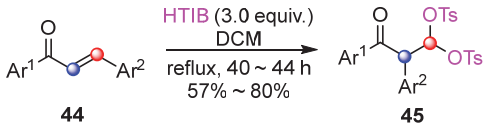
Differently, when cinnamic acids **42** were exposed in the same reaction conditions, *α*-keto diacetates **43** were achieved. Its mechanism is similar to that shown in Scheme 9. In addition to the 1,2-aryl shift step, the reaction still involves a decarboxylation process (Scheme 10).[12b]

In 2020, Kamal and co-workers[12d] conducted the HTIB-mediated oxidative 1,2-aryl-shift of chalcones **44** in reflux DCM, affording a series of *gem*-ditosyloxy ketones **45**. In this reaction, 3 equiv. of hypervalent iodine reagents are also required. Mechanically, the Ar^2 substituted at the alkenyl moiety underwent 1,2-aryl migration followed by the subsequent di-tosylation (Scheme 11).

In 2018, Yu's group[12c] reported a PIDA-mediated oxidative 1,2-alkylthio-migration of enaminones **46** to alkylthio substituted *α*,*β*-unsaturated amides **47** via intermediates **48** and **49**. A plausible mechanism proposed that the reaction was initiated from the oxidation of enaminones **46** by PIDA to form intermediate **48** as well as acetic acid via deprotonation of the amino group. The following redox



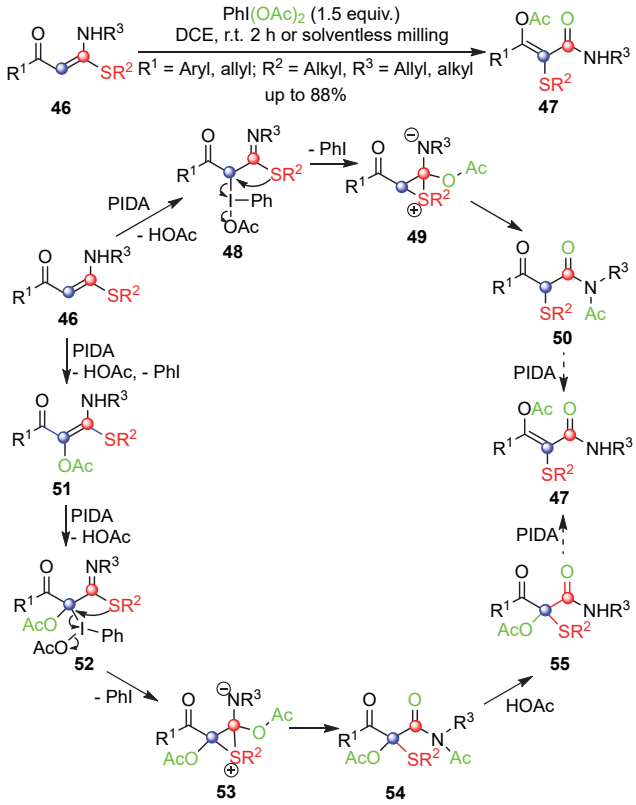
Scheme 10 Oxidative 1,2-aryl shift of cinnamic acids mediated by PIDA under acid condition



Scheme 11 Oxidative 1,2-aryl-migration of chalcones to *gem*-ditosyloxy ketones with HTIB

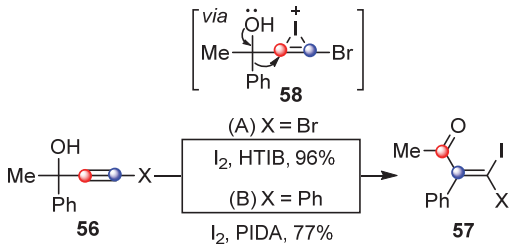
process of **48** afforded the three-membered alkylthionium species **49** and PhI through intramolecular partial alkylthio group migration and nucleophilic attack of OAc anion at the imino carbon center. Then, ring-opening of **49** triggered by 1,3-acetyl migration gave the intermediate **50**. Enolization of the latter followed by *N*-deacetylation/*O*-acetylation accomplished the terminal *α*,*β*-unsaturated amides **47**. Alternatively, reaction of enaminones **46** with PIDA generated the olefinic C—H acetoxylation intermediate **51**. Oxidation of the latter by PIDA followed by deprotonative addition formed intermediate **52**. A process similar to the formation of species **50** occurred to access species **54**, whose reaction with acetic acid generated *in situ* gave intermediate **55**. The conversion of **55** to **47** was the same to the transformation of **50**. In this reaction, PIDA acted not only as an oxidant, but also the oxygen source for the introduction of the carbonyl oxygen (Scheme 12).

In addition to alkenes mentioned above, other substrate type may also undergo 1,2-C to C migration. These substrates include bromo-substituted phenylpropynol,[13] allenes (*i.e.*, 1-alkoxyallenes or phenyl-substituted allene),[14] nonterminal alkynes,[15] trialkylamines or enamines[16] and flavonone.[17-18] In 1992, McNelis and co-workers[19a-19b] reported a rearranged conversion of 3-bromo-l-phenyl-



Scheme 12 Oxidative 1,2-alkylthio-migration of *α*,*β*-unsaturated amide to enaminones by employing PIDA

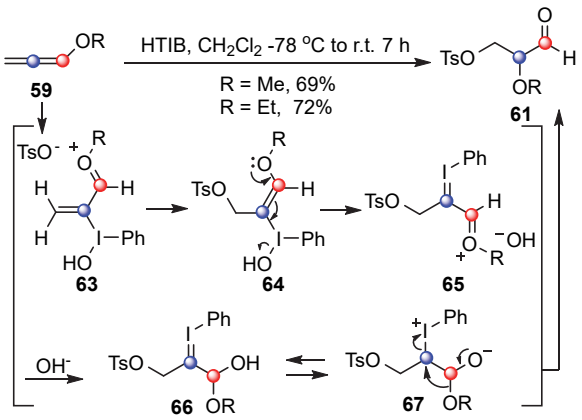
propynol **56** by utilizing stoichiometric amounts of I_2 and Koser's reagent. The reaction first generated a cyclic hypervalent iodine intermediate **58**, which underwent a 1,2-aryl migration to (*Z*)-3-bromo-3-iodo-2-phenylpropenal **57** on the basis of their previous research (Scheme 13A).[19c] In 2004, Huang's group[13] further accomplished the similar preparation of compound **57** (X = Ph) by changing HTIB into PIDA (Scheme 13B).



Scheme 13 1,2-Aryl migration of 3-bromo-l-phenylpropynol mediated by stoichiometric amounts of I_2 and HTIB or PIDA

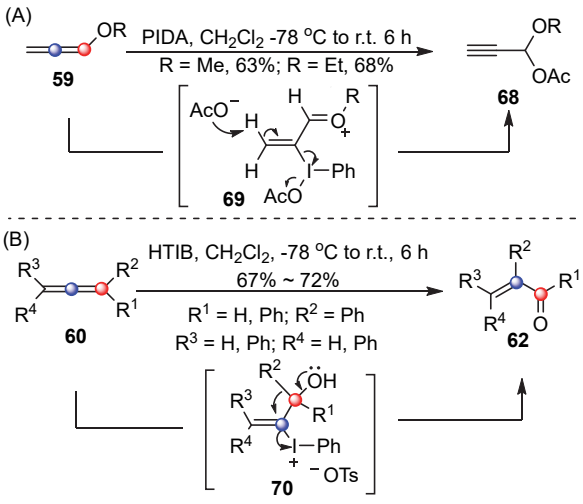
In 1992, Moriarty and co-workers[14] reported a conversion of 1-alkoxyallenes **59** to 2-alkoxy-3-toxyloxypanals **61** (Scheme 14), and oxidative migration of phenyl-substituted allene **60** to phenyl-substituted propenal **62** mediated by HTIB also proceeded smoothly at −78 ℃ in dichloromethane (Scheme 15). For the first conversion, it was initiated with the electrophilic addition of HTIB to allene **59**, followed by a conjugate addition of tosylate to

the resulting **63**. The obtained intermediate **64** was converted to iodine-carbine analogue **65** by losing one molecule of hydroxyl anion. Then the formed hydroxyl anion acted as a nucleophile to convert **65** to **66**. Proton transfer of **66** and the following pinacol-type rearrangement of **67** provided the final 1,2-migration product **61** (Scheme 14). It is worth noting that when the same 1-alkoxyallenes **59** was treated with PIDA in dichloromethane (DCM), no migration product but 2-acetoxy alkoxylpropynes **68** was formed.



Scheme 14 1,2-Migration of 1-alkoxyallenes triggered by HTIB and the possible pathway

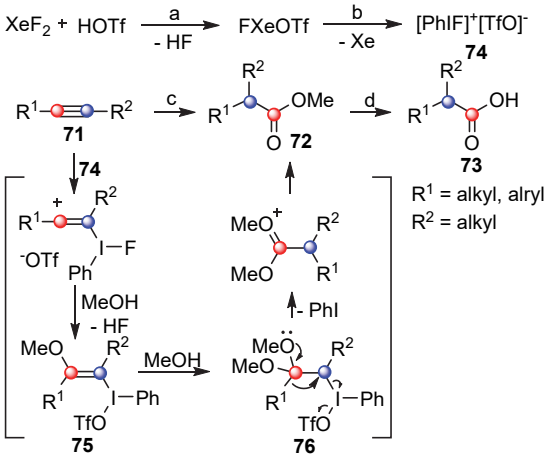
While control reaction by changing HTIB with PIDA did not afford migration compounds but 2-acetoxy-alkoxylpropynes **68**, which could be regarded as a result of the initial electrophilic addition of PIDA to **59**, followed with a reductive elimination of PhI and a subsequent addition of acetic acid to oxonium salt **69** (Scheme 15A). The difference between them was that acetate anion reacted as a base (Scheme 15A), while tosylate enabled a conjugation addition (Scheme 14). As for aryl-substituted allene **60**, the reaction did not occur when treated with PIDA, even under



Scheme 15 1,2-Migration of allenes mediated by HTIB and its control reaction by employing PIDA

refluxing conditions. However, its reaction with HTIB in dichloromethane also afforded rearranged phenyl-substituted propenals **62**, the process of which also involved a pinacol-type rearrangement process of intermediate **70** (Scheme 15B).

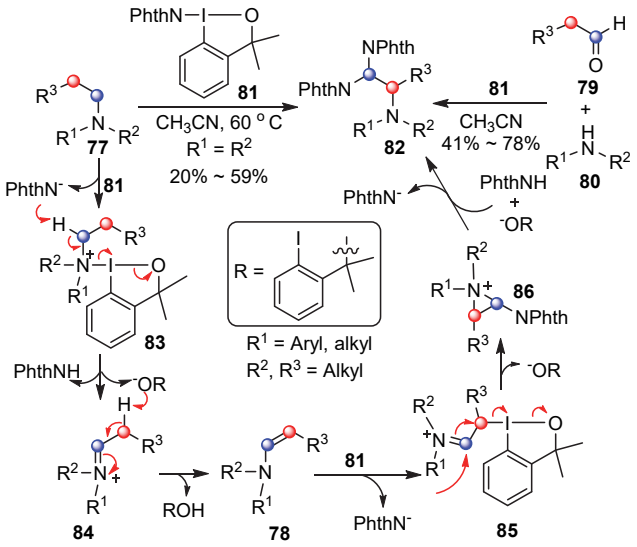
In 1999, Zefirov and Brel *et al.*[15a] described an oxidative rearrangement of non-terminal alkynes **71** to esters **72** and arylalkanoic acids **73** enabled by phenyl(fluoro)-iodonium triflate **74**, which was prepared *in situ* from a 1∶1 molar ratio of ArI and FXeOTf in dichloromethane under mild conditions (Scheme 16). A likely mechanism for these oxidative rearrangements need the initial formation of 2-methoxy-1-alkenyl(phenyl)iodonium triflates **75**, obtained from the electrophilic addition of $PhIF^{+}OTf^{-}$ with terminal alkynes **74** in MeOH.[20] Michael addition followed by a 1,2-shift of the R^1 group in **76** with dissociative reductive elimination of PhI would ultimately afford **72**. This protocol provided an alternative approach to synthesize arylalkanoic, a class of compounds possessing anti-inflammatory bioactivity.[21]



Scheme 16 1,2-Migration of non-terminal alkynes mediated by *in situ* formed phenyl(fluoro)iodonium triflate

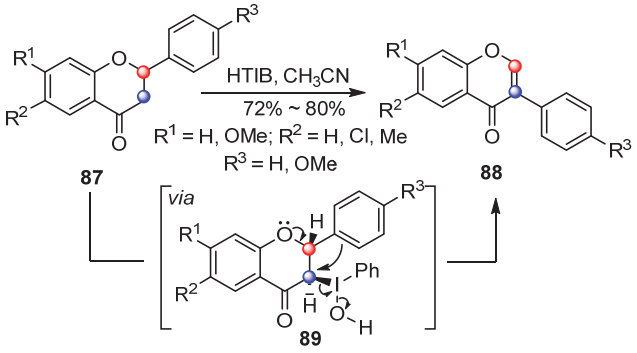
In 2015, Minakata and co-workers[16] reported the oxidative rearrangement of trialkylamines **77** to the 1,2-shift product **82** containing two phthalimide moieties, utilizing 2 equiv. of phthalimide-containing I(III) compound **81**. Additionally, the reaction of trialkylamines **77**, generated *in situ* from the reaction of secondary amines **79** and dehydes **80** could also afford the same product under same reaction conditions. A rational mechanism for this transformation indicated that a key enamine intermediate **78** must be produced *in situ*. First, attack of substrate **77** to the electrophilic iodine center of **81** formed the ammonium intermediate **83**, which provided enamine intermediate **78** through deprotonation of species **84**. Subsequently, further reaction of enamine **78** with another molecule of **81** formed the C—I bond. The resulting intermediate **85** was then attacked by phthalimidate followed by intramolecular cyclization, affording aziridinium intermediate **86**, which was nucleo-

philically attacked by a phthalimidate to afford the rearrangement product **82** (Scheme 17).



Scheme 17 1,2-Migration and possible pathway of trialkylamines mediated by phthalimide-containing I(III) reagent

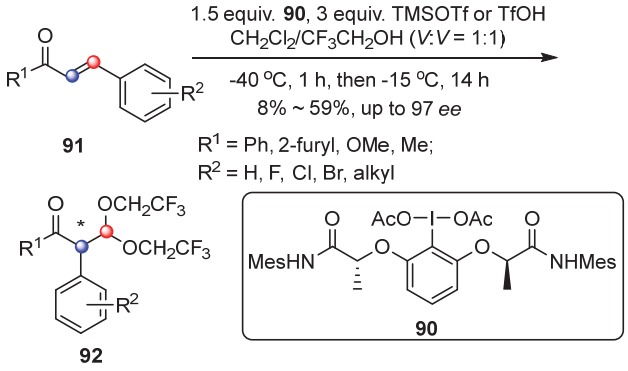
Additionally, 1,2-shift of flavonone employing hypervalent iodine reagents is also an important transformation. By utilizing the oxidative rearrangement of flavanone **87** by HTIB, Moriarty *et al.*[17] demonstrated an alternative synthesis of isoflavones **88** with good yield (72%~80%) (Scheme 18). Mechanistically, the key intermediate **89** was obtained by electrophilically attack of HTIB by the enol form of **87**. Then **89** underwent migration of the aryl group with reductive cleavage of C—I bond to give the migratory product.[18]



Scheme 18 1,2-Migration of flavonones to isoflavones with HTIB.

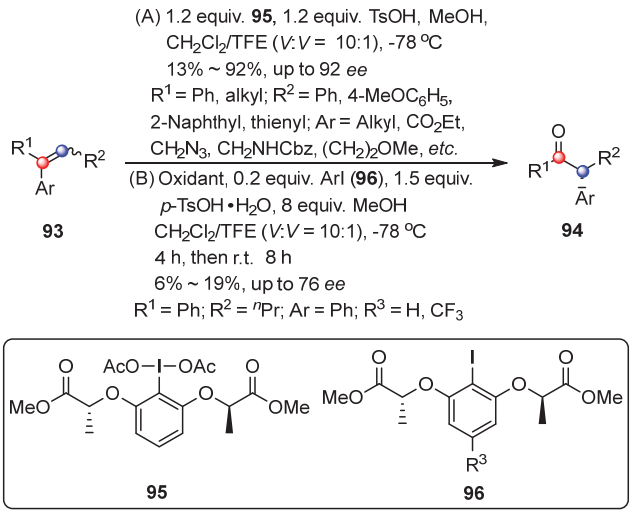
2.1.1.2 1,2 C to C stereoselective migration

Chiral hypervalent iodine reagents could enable the stereoselective oxidative 1,2-aryl migration reaction, realizing a unique class of asymmetric transformations. Substrates including the substituted or unsubstituted *α*,*β*-unsaturated ketone,[22] styrene,[23-25] acetophenone[26] and allylic alcohols[27-28] have been well investigated. In 2013, Wirth and co-workers[22] achieved the first asymmetric synthesis by using chiral hypervalent iodine reagent **90**, converting a series of chalcone derivatives **91** to chiral *α*-aryl ketones **92** with good enantioselectivity (up to 97 *ee*) via an asymmetric 1,2-aryl migration (Scheme 19).



Scheme 19 1,2-Aryl migration of chalcones to *α*-aryl ketones mediated by chiral hypervalent iodine reagent.

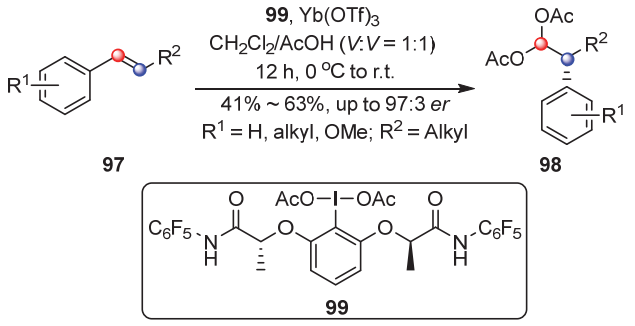
In 2016, the Wirth group[23] demonstrated the conversion of 1,1-disubstituted alkenes **93** to enantioenriched *α*-arylated ketones **94** with chiral hypervalent iodine **95** via oxidative rearrangement under metal-free conditions (Scheme 20A). In 2017, they[24] also realized this conversion with the *in situ* prepared chiral I(III)-species from the oxidation of **96** (R^3=H or CF_3) by oxidants (*i.e. m*CPBA, Selectfluor) (Scheme 20B).



Scheme 20 1,2-Shift of 1,1-disubstituted alkenes to *α*-arylated ketones mediated by catalytic chiral aryliodine

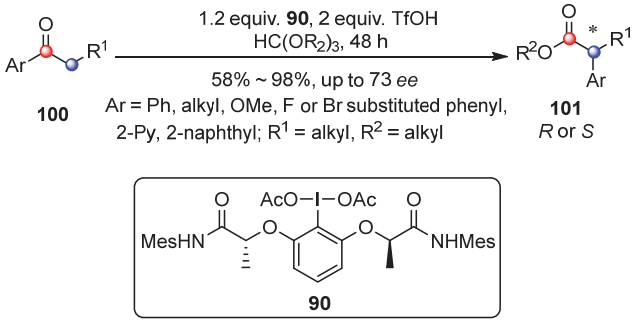
Similarly, in 2020, Tiwari and co-workers[25] reported an asymmetric oxidative rearrangement of disubstituted unactivated olefins **97** to *tert*-*α*-arylated aldehydes **98** mediated by chiral hypervalent iodine(III) reagent **99**. This reaction was regarded as a direct protocol for the preparation of challenging compounds **98** containing a benzylic stereocenters (Scheme 21).

As for substituted acetophenone, Wirth and co-workers[26] described the first stereoselective synthesis of *α*-arylated esters **101** (up to 73 *ee*) from the reaction of arylketones



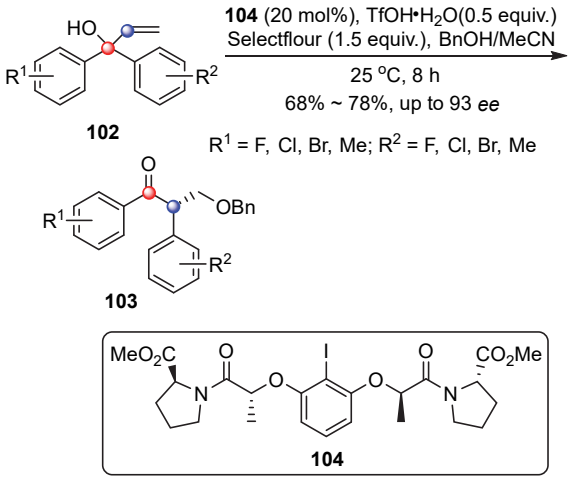
Scheme 21 1,2-Shift of disubstituted olefins to *tert*-α-arylated aldehydes mediated by chiral iodine(III) reagent

100 with the chiral iodine(III) reagent **90** mentioned above, thus expending the chemical application of chiral iodine(III) reagents (Scheme 22).



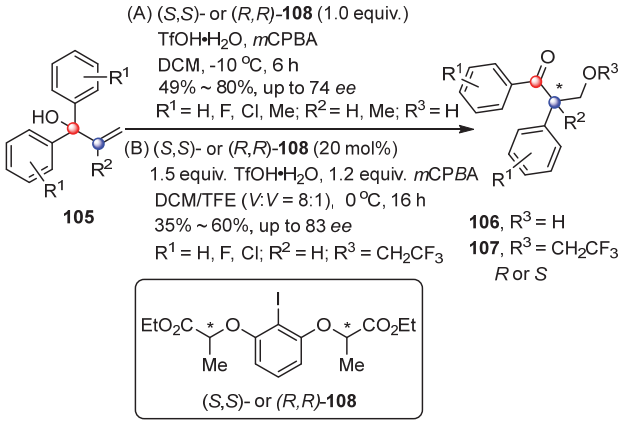
Scheme 22 1,2-Shift of arylketones with α-arylated esters mediated by the chiral iodine(III) reagent

In 2019, Gong and co-workers[27] demonstrated an enantioselective alkoxylation/oxidative rearrangement of allylic alcohols **102** utilizing catalytic chiral iodine(III) species, *in situ* generated from the oxidation of chiral iodine(I) compound **104** by selectfluor (Scheme 23). This reaction afforded the enantioenriched rearranged α-arylated β-alkoxylated ketones **103** with good enantioselectivity (up to 93 *ee*).



Scheme 23 1,2-Shift of allylic alcohols to α-arylated β-alkoxylated ketones mediated by *in situ* generated I(III)-species

Similarly, utilizing *m*CPBA as the oxidant and chiral iodine(I) compound **108** as the organo catalyst, Hu's group[28] also achieved an asymmetric conversion of allylic alcohols **105** to two types of different arranged α-arylated β-alkoxylated ketones **106** and **107** in different solvent (up to 74% *ee* and 83% *ee*, respectively) (Scheme 24). Meanwhile, they also got 1,2-shift products **106** of allylic alcohols **105** by directly using non-chiral iodine(III) reagent HTIB despite the *ee* value was not very high.



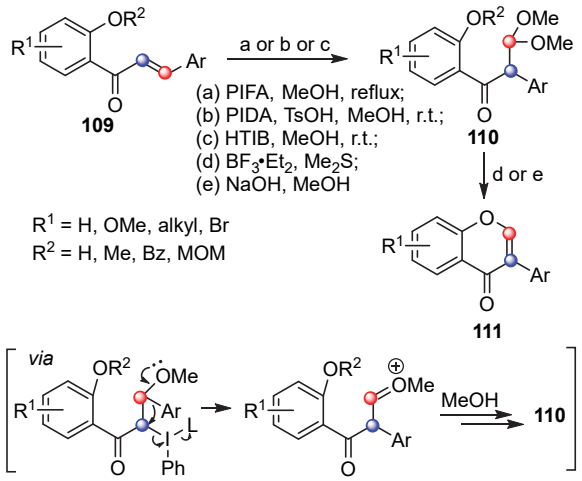
Scheme 24 Asymmetric 1,2-shift of allylic alcohols to α-arylated β-alkoxylated ketones and mediated by *in situ* generated I(III)-species

2.1.1.3 1,2 C to C migration/cyclization or cyclization/migration tandem

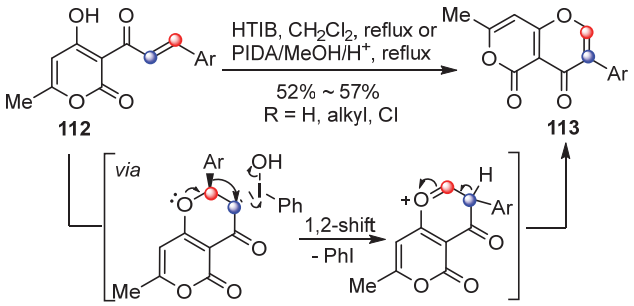
Hypervalent iodine reagents-mediated 1,2-C to C migration/cyclization or cyclization/migration tandem protocol is a useful chemical transformation for synthesizing heterocyclic compounds. In addition to the carbazole analogues described above, isoflavone derivatives could also be obtained by the hypervalent iodine reagent-mediated 1,2-C to C migration/cyclization approach. Miki *et al.*[29a] applied the conventional hypervalent iodine reagents (PIDA, PIFA, HTIB) or the *in situ* generated iodine(III) species, realizing the convertion of chalcones **109** to acetals **110**. Usually, the OR^2 group (R^2=H, Me, Bz or MOM) in **109** is necessary to enable the intramolecular cyclization of **110** into isoflavones **111** promoted by BF_3•Et_2O, SMe_2 or NaOH in MeOH (Scheme 25).[29] Mechanistically, the C=C bond in **109** was oxidized and aryl rearrangement occurred, a process similar to the one shown in Scheme 9, followed by intramolecular cyclization.

In 2006, Prakash and co-workers[30] presented a HTIB or PIDA-mediated one-pot synthesis of heterocycles **113**, a special class of oxygen-containing heterocyclic compounds, via the oxidative cyclization/1,2-aryl migration of α,β-unsaturated ketones **112** (Scheme 26).

The 1,2-migration/lactonization could also be achieved by hypervalent iodine reagents, providing a series of lactone compounds. In 2003, Wirth and co-workers[31] described the reaction of 4-aryl-4-pentenoic acids **114** and PIDA, which could enable the lactonization/1,2-migration to access aryl-migrated lactones **115**. This transformation

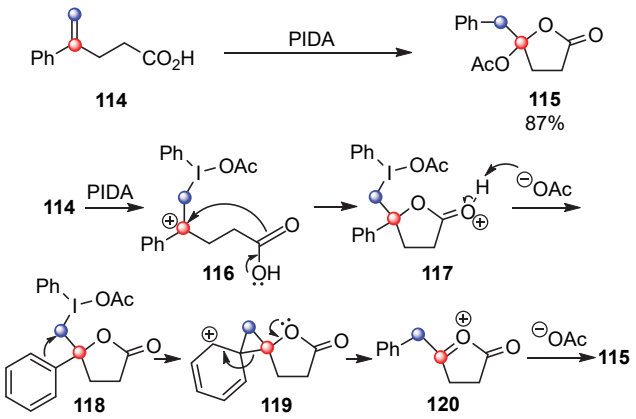


Scheme 25 1,2-Aryl migration of chalcones to isoflavones involving hypervalent iodine reagents



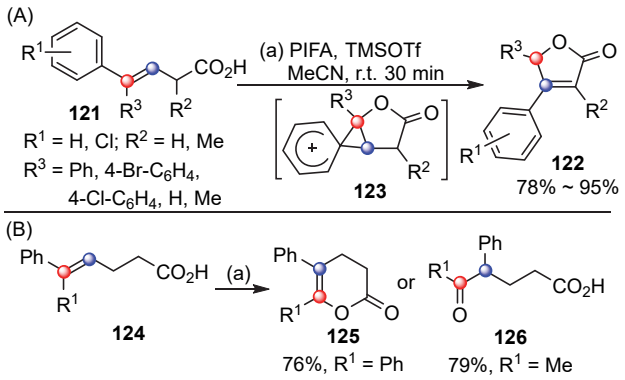
Scheme 26 1,2-Shift of chalcones to isoflavone derivatives mediated by HTIB or PIDA under refluxing

initiated from the activation of C=C bond by PIDA, giving the stable carbocation **116**. Then, intramolecular nucleophilic attack to **116** by the carboxylic acid moiety afforded oxonium ion **117**, followed with a deprotonation to give lactone **118**. The participation of the phenyl moiety of **118** resulted in the formation of a phenonium ion intermediate **119**, followed by the 1,2-aryl migration. Finally, the capture of the resulting oxonium ion **120** by acetate leads to the formation of lactones **115** (Scheme 27).



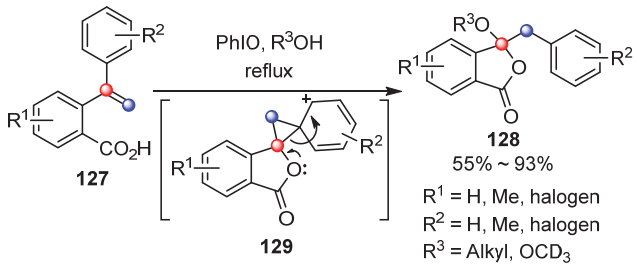
Scheme 27 Cyclization/migration of 4-aryl-4-pentenoic acids to aryl-migrated lactones mediated by PIDA

In 2012, Wirth's group[32] accomplished the synthesis of 4-arylfuran-2(5*H*)-ones **122** from 4-arylbut-3-enoic acids **121** via PIFA-mediated lactonization/1,2-aryl migration, achieved through the key intermediate **123** (Scheme 28A). Furthermore, diphenylpent-4-enoic acids **124** (R^1=Ph) is also suitable for this transformation, providing the lactonization/1,2-aryl migration product **125** with a yield of 76% (Scheme 28B). However, no cyclization but only rearrangement occurred to give acid **126** when substrate 5-phenylhex-4-enoic acid **124** (R^1=Me) was applied in the same conditions (Scheme 28B).



Scheme 28 Cyclization/migration of enoic acids mediated by PIFA

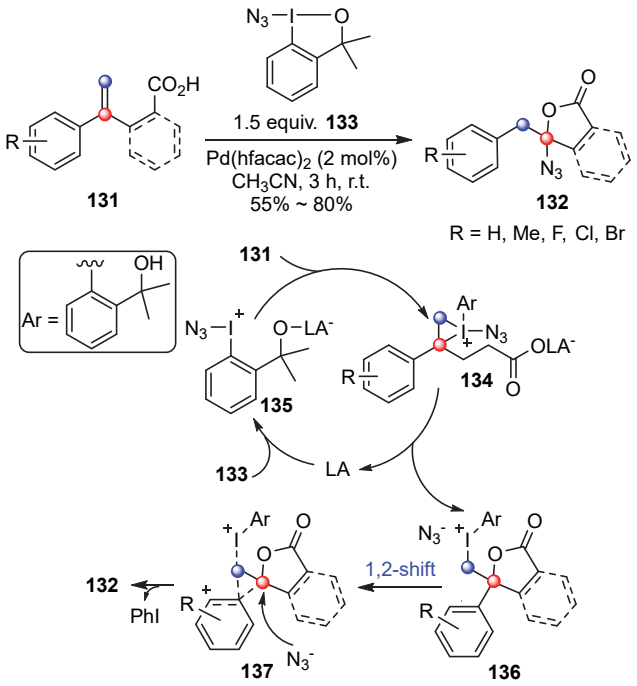
In 2021, Du and colleagues[33] reported that treating 2-(1-arylvinyl)benzoic acids **127** with PhIO in alkyl alcohols furnished alkoxylated isobenzofuranones **128**. Its mechanism is similar to the one described in Scheme 27, and the carbonium ion **129** is the key intermediate for this lactonization/1,2-aryl migration/alkoxylation cascade reaction (Scheme 29).



Scheme 29 Cyclization/migration of 2-(1-arylvinyl)benzoic acids triggered by I(III) species originated *in situ* from the reaction of PhIO and alkyl alcohols

In 2017, Waser and co-workers[34] demonstrated the other lactonization involving 1,2-aryl migration and the introduction of azido group. They realized the conversion of 4-aryl-4-pentenoic acids **131** to azido lactones **132** utilizing azido-based hypervalent iodine reagent **133** as oxidant and $Pd(hfacac)_2$ (2 mol%) as the Lewis acid. It is postulated that the electrophilic complex **135** will react with alkene **131** to give iodocyclopropylium cation **134**. Then ring opening through the attack of the carboxylic acid delivers the highly electrophilic intermediate **136**. In the case

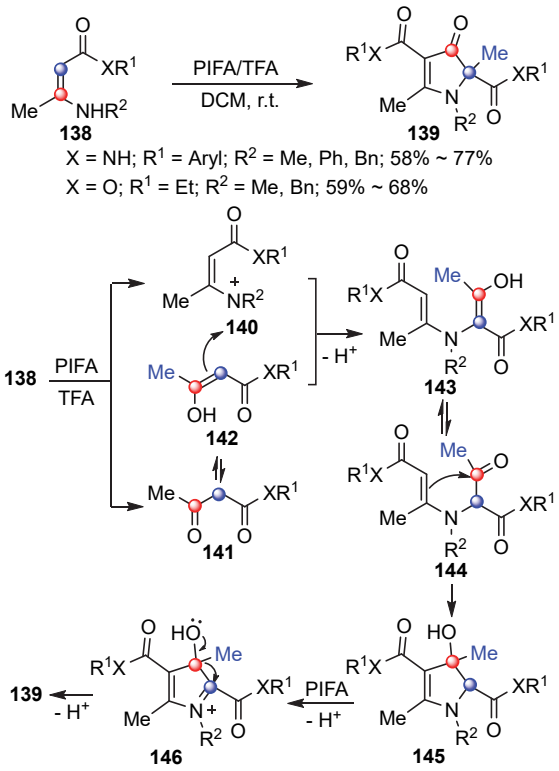
of aryl substituents, 1,2-migration via a phenonium ion or a non-classical carbocation **137** is favored and thus gives product **132**. (Scheme 30).



Scheme 30 Cyclization/migration of 4-aryl-4-pentenoic acids to azido lactones mediated by azido-containing I(III) compound

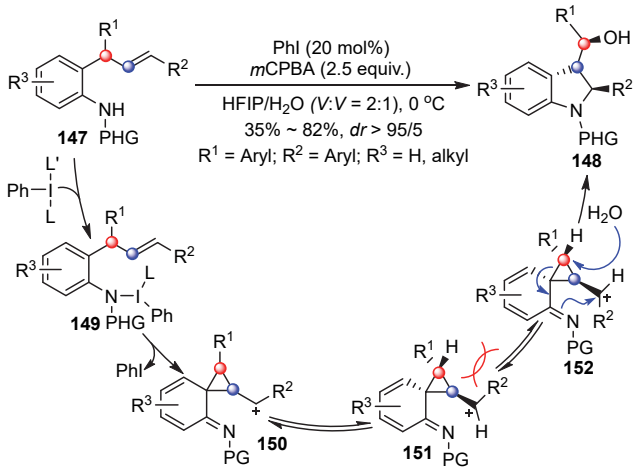
Aside from the oxygen-containing heterocycles described above, heterocyclic compounds containing nitrogen atom could also be access via hypervalent iodine-mediated cyclization/migration protocol. In 2007, Dong's group[35] completed the synthesis of substituted pyrrolin-4-ones **139** from the reaction of enaminones **138** and PIFA in the presence of trifluoroacetic acid (TFA) in DCM (Scheme 31). It was postulated that the reaction initiated with the interaction of **138** with PIFA under acidic condition to give nitrenium ion **140**, which underwent simultaneous hydrolysis to give compound **141**. The enol tautomer of the later trapped intermediate **140** to afford intermediate **143**, which underwent an intramolecular cyclization to give intermediate **145**. Then a subsequent PIFA-mediated oxidation converted **145** to iminium **146**, which underwent a benzilic acid type rearrangement to afford the final product **139**.

In 2007, Fan's group[36] demonstrated a useful method for the synthesis of indolin-3-ylmethanols derivatives **148** (*dr*>95∶5) from the reaction of 2-allylanilines **147** and I(III) species, generated *in situ* from *m*CPBA and catalytic PhI. Mechanistically, ligand exchange of the *in situ* generated iodine(III) compound with the nitrogen atom of substrates through a tricoordinated iodine intermediate produced intermediate **149**. Dearomatization of the benzene ring was trapped by the *o*-alkenyl group to afford a spirocyclic intermediate **150** after reductive elimination of iodobenzene. It is worth noting that the conformer **152** is more favorable than **151** due to the lack of the steric repul-



Scheme 31 Cyclization/migration of enaminones to substituted pyrrolin-4-ones in the presence of PIFA

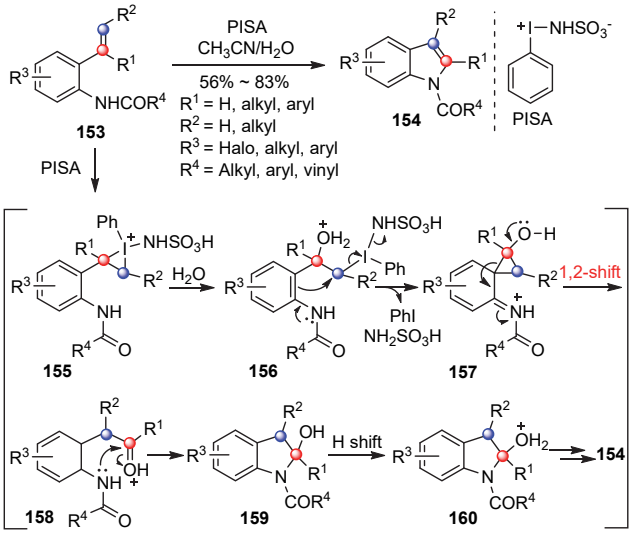
sion between the R^2 group and the three-membered ring. Aromatization of **152** might be the driving force to promote the opening of the three-membered ring with water attack and the closure of five-membered ring in a concerted fashion, affording indolin-3-ylmethylium with high diastereoselectivity (Scheme 32).



Scheme 32 Cyclization/migration of 2-allylanilines to indolin-3-ylmethanols mediated by I(III) species prepared *in situ* from the interaction of PhI and *m*CPBA

Zhang and co-workers[37] realized the transformation of 2-alkenylanilines **153** into indoles analogues **154**, utilizing a water-soluble hypervalent I(III) reagent PISA-mediated 1,2-migration/intramolecular cyclization cascade protocol.

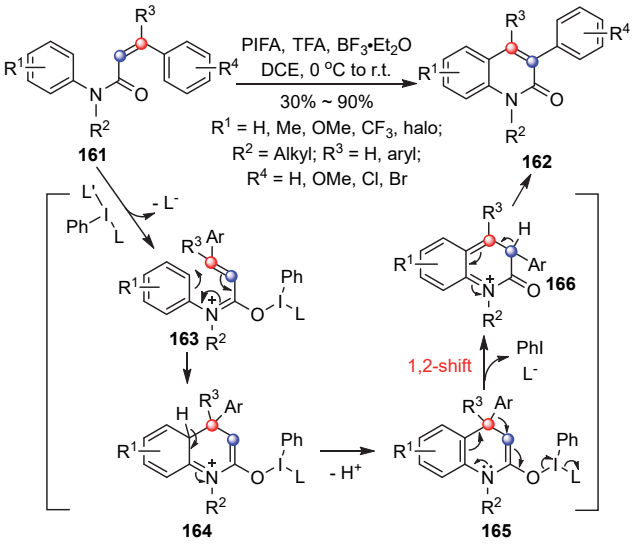
The method also provided an effective protocol for the synthesis of the bioactive molecules including the derivatives of indometacin and zidometacin. Mechanistically, nucleophilic attack on PISA by the double bond in substrate formed iodonium ion **155**, which was then opened by H_2O selectively at the benzylic carbon to afford intermediate **156**. Nucleophilic attack of the phenyl ring of **156** on the carbon center of the newly formed hypervalent iodine(III) species afforded spiro intermediate **157**, accompanied by dearomatization of **156** and the release of iodobenzene and NH_2SO_3H. Then, in the key step, ring opening of spiro intermediate **157** proceeded exclusively and smoothly under the driving force of rearomatization to give **158**. Finally, the intramolecular condensation occurred in **158** to give the final indole products **154**, accompanied by the release of H_2O (Scheme 33).



Scheme 33 Cyclization/migration of 2-alkenylanilines to indoles analogues mediated by I(III) compound PISA

In 2013, Zhao, Du and coworkers[38] discovered that *N*-methyl-*N*-phenylcinnamamides **161** could be converted to 3-arylquinolin-2-one compounds **162** by reacting with PIFA in the presence of TFA and BF_3•Et_2O in 1,2-dichloroethane (DCE). Interestingly, the process involves both an oxidative C(sp^2)—C(sp^2) bond formation and an exclusive 1,2-aryl migration. The following possible mechanistic pathway was initially proposed. First, the nucleophilic attack on the iodine center by the carbonyl oxygen of the amide moiety in **161** afforded 3-azatriene **163**, which underwent an electrocyclic ring closure and the subsequent proton elimination to give intermediate **164**. Assisted by the nitrogen lone-pair conjugation, a concerted process including the 1,2-aryl shift and the breakage of the O—I bond occurred to convert **164** to iminium salt **165**, along with the release of phenyl iodide and the trifluoroacetate. Finally, intermediate **165** gave 3-phenylquinolin-2-ones **162** with the removal of one proton (Scheme 34).

Another special hypervalent iodine mediated migration/cyclization protocol, reported by Mal and Maiti[39a] in 2017, was the intermolecular dehydrogenative annulation



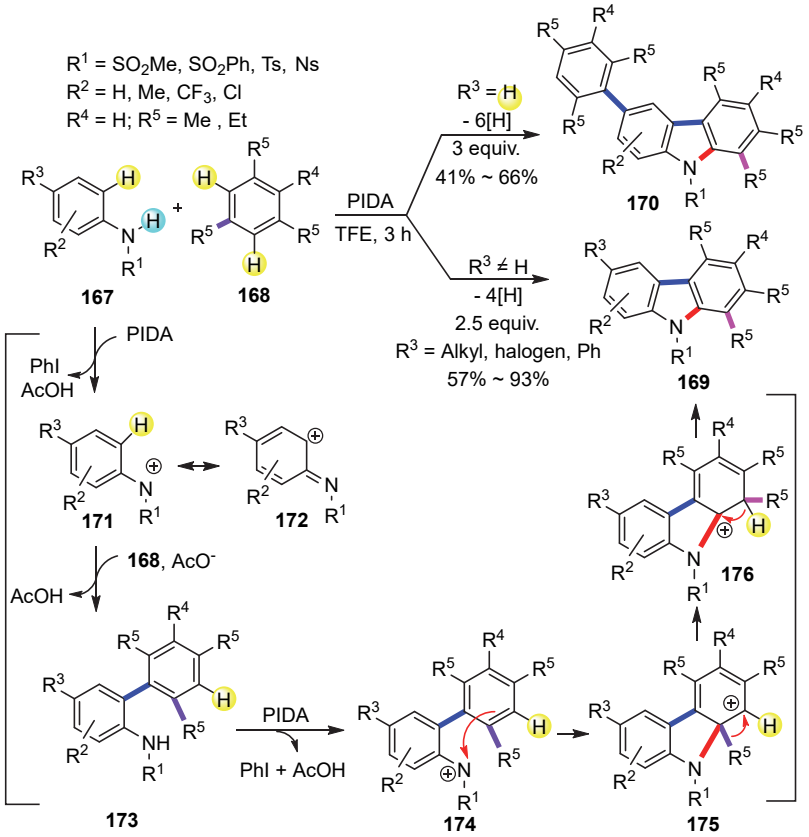
Scheme 34 Cyclization/migration of *N*-methyl-*N*-phenylcinnamamides to 3-phenylquinolin-2-ones mediated by PIFA

of 1,3,5-trialkylbenzenes **167** and anilides **168**, the reaction of which led to the synthesis of carbazole, **169** or **170**. It was achieved by utilizing PIDA via a sequential formation of C—C/C—N bond and a selective alkyl group migration. The plausible pathway indicates that the reaction was initiated from the activation of 1,3,5-trialkylbenzenes **167** by PIDA to give nitrenium ion **171** and its stable charge-delocalized form, *i.e.*, carbenium ion **172**, which was trapped by compound **168** to give the nucleophilic addition product **173**. The second oxidation of **173** by PIDA afforded nitrenium ion **174**, which underwent the electrophilic aromatic substitution to generate carbenium intermediate **175**. The adjacent quaternary alkyl group (R^5) migration in **175** and the further deprotonation of **176** would provide the final products **169** or **170** (Scheme 35).

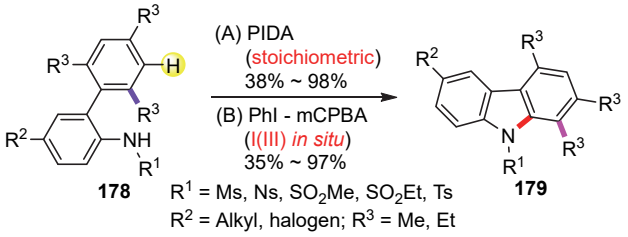
On the basis of above reaction, they[39b] further realized the intramolecular cyclization/rearrangement of biarylsulfonanilides **178**, affording 1,2,4-trialkyl-substituted carbazole **179** via C-N coupling reaction mediate by either the beforehand prepared PIDA or *in situ* formed (III)-iodine species generated from the oxidation of ArI by *m*CPBA (Scheme 36).

2.1.1.4 1,2 C to C migration/fluorination or migration/fluoroalkylation tandem

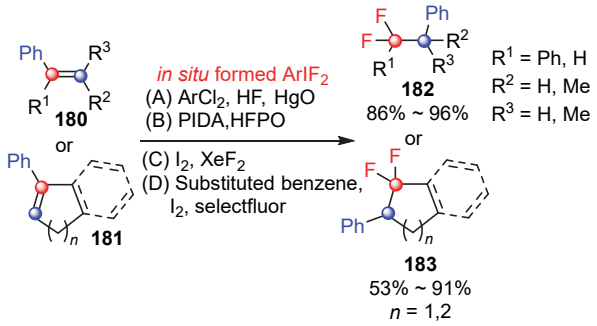
The 1,2 C to C migration/fluorination or migration/fluoroalkylation tandem of electron-rich systems with diverse hypervalent iodine reagents containing fluorine and fluoroalkyl is an important class of migration transformation. One outstanding reagent is Togni's reagent, the various reactions of which have been well summarized and discussed by Zhang.[1e] In this review, we mainly describe the fluorination/migration and fluoroalkylation/migration employing prepared aforehand or *in situ* hypervalent iodine reagents. As mentioned above, the fluorination/migration involving hypervalent iodine compounds could be traced back to the preparation of difluorinated 1,2-migration



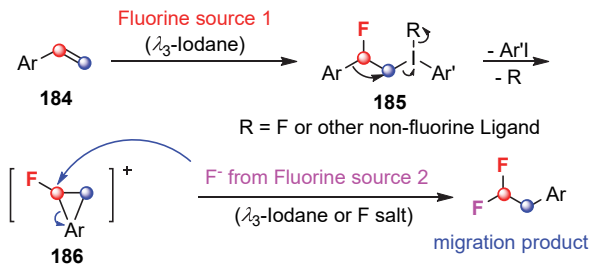
Scheme 35 Cyclization/rearrangement of 1,3,5-trialkylbenzenes to access carbazoles with PIDA



Scheme 36 Cyclization/rearrangement of biarylsulfonanilides to carbazole derivatives with PIDA or *in situ* formed I(III) species



Scheme 37 Difluorinated 1,2-migration of substituted or unsubstituted styrenes with *in situ* generated $ArIF_2$



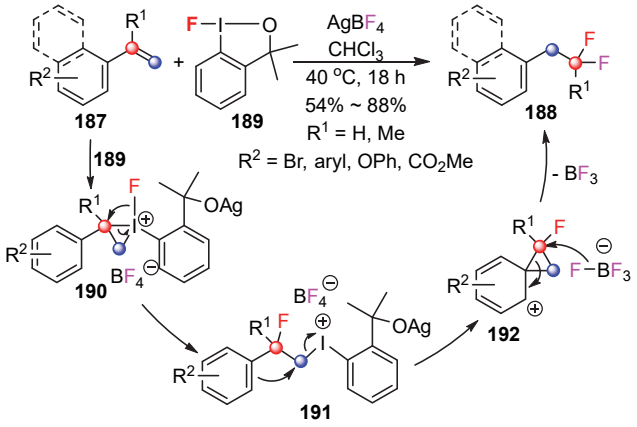
Scheme 38 General mechanism of difluorination/migration of substituted or unsubstituted styrenes

product **2** with 1,1-diphenylethylene **1** conducted by Bockemüller[5a] in 1931 (Scheme 1). Reactions of this type of transformation were indeed less explored in the past century, mainly due to the difficult preparation of the iodine(III) species containing fluorine. Thus all of these reactions were realized with the interaction of substituted or unsubstituted styrene (**180** and **181**) with the formed *in situ* or readily prepared $ArIF_2$ (Scheme 37).[5,40] However, there is a huge progress and development of this type of rearrangement reactions in recent years because of the wide application of λ^3-iodane reagents, the employment of many other substrates as well as the availability of other fluorine sources (*i.e.* Pyr•$(HF)_x$ or Amine•$(HF)_x$).

With regard to the reactions of *gem*-difluorination/migration of substituted or unsubstituted styrenes **184**,[40-59] the mechanism can be generalized as follows, shown in Scheme 38.[40e,41] Generally, it initiated with the addition of the first hypervalent iodine compound (λ^3-iodane prepared beforehand or *in situ* generated) to the double bond of **184**, forming intermediate **185** with the first C—F bond. Then followed an aryl migration and the elimination of ArI, in-

termediate **185** was converted to intermediate **186**. Next, the second fluorine anion released from the first hypervalent iodine compound or additional fluorine salt, such as $AgBF_4$, would nucleophilically attack the electron-deficient carbon center in **186** to open the three-member ring, affording the terminal difluorinated migration product.

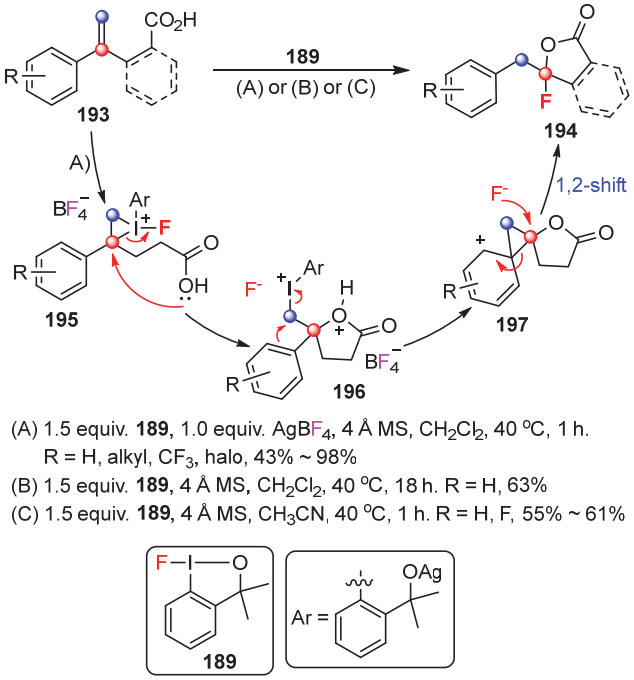
In 2014, Szabó's group[42] reported that the reaction of *geminal* difluorination of styrenes **187** and λ^3-iodane **189** in the presence of $AgBF_4$ could afford the difluorinated 1,2-migration products **188** under mild conditions. The mechanism indicated that one of the C—F bonds is constructed via electrophilic addition to the double bond of starting material **187** by λ^3-iodane **189**, accompanied with the formation of intermediates **190** and **191**. While the other is formed through the attack of fluoride from $AgBF_4$ to the carbonium ion intermediate **192**, generated through the attack to iodine(III) center by the neighbouring aryl group of **191** (Scheme 39). They[43] also realized a similar rearrangement transformation of styrenes **187** utilizing λ^3-iodane **178** and other fluorine sources including $Pd(MeCN)_4(BF_4)_2$ or $Cu(MeCN)_4PF_6$ in 2017.



Scheme 39 Difluorination/migration of styrenes mediated by λ^3-iodane **189** and $AgBF_4$

By treating unsaturated carboxylic acids **193** with λ^3-iodane **189** and $AgBF_4$, Stuart's group[44] obtained the fluorinated migration lactones **194** (Scheme 40). Control experiments (Schemes 40B and 40C) indicated that the F atom was introduced from λ^3-iodane **189**. Mechanically, a cyclic iodonium intermediate **195** was generated via electrophilic addition to the alkene **193** by λ^3-iodane **189**. The π donation of the aromatic ring on **196** resulted in the phenonium ion intermediate **197** with the iodoaryl group acting as an excellent leaving group. Finally, **197** underwent a ring-opening by fluoride, thus resulting in **194** with fluorination at the quaternary center.

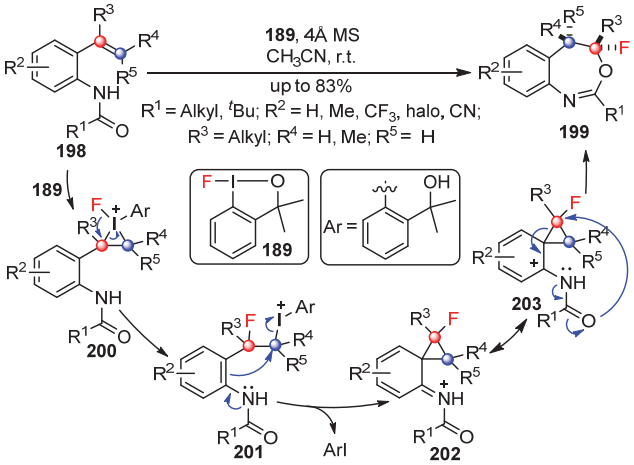
Gulder and co-workers[45] in 2016 reported the reaction of 2-alkenylanilines **198** with the λ^3-iodane **189**, which followed the similar fluorination/migration/cyclization cascade reaction to afford 4-fluoro-1,3-benzoxazepines **199**. In the first step, the fluoro reagent **189** was nucleophilically attacked by the olefinic double bond, forming the



(A) 1.5 equiv. **189**, 1.0 equiv. $AgBF_4$, 4 Å MS, CH_2Cl_2, 40 °C, 1 h. R = H, alkyl, CF_3, halo, 43% ~ 98%
(B) 1.5 equiv. **189**, 4 Å MS, CH_2Cl_2, 40 °C, 18 h. R = H, 63%
(C) 1.5 equiv. **189**, 4 Å MS, CH_3CN, 40 °C, 1 h. R = H, F, 55% ~ 61%

Scheme 40 Fluorinated migration of unsaturated carboxylic acids to lactones mediated by λ^3-iodane **189**

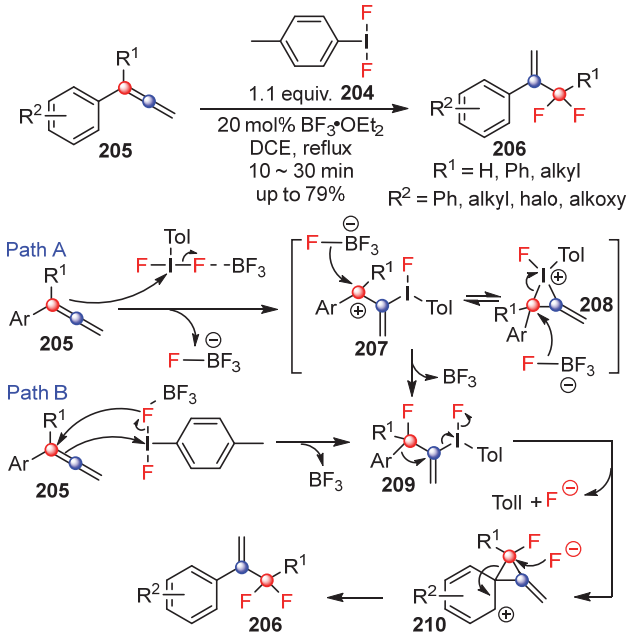
iodo(III)ranium ion **200**. The three-membered heterocycle was then selectively opened at the benzylic position by an intramolecular 1,2-fluoro shift. The 1,2-iodofluorine species **201** obtained from **200** was stabilized by displacement of the iodobenzene by nucleophilic attack of the aryl ring, furnishing the cyclopropyl compound **202**. The latter is in an equilibrium with phenonium ion **203**. Ring opening of the spirocyclopropyl ring in **203** took place intramolecularly via a 6-endo cyclization with simultaneous ring expansion to give the seven-membered oxazepine **199** (Scheme 41).



Scheme 41 Fluorinated migration of 2-alkenylanilines to 4-fluoro-1,3-benzoxazepines triggered by λ^3-iodane **189**

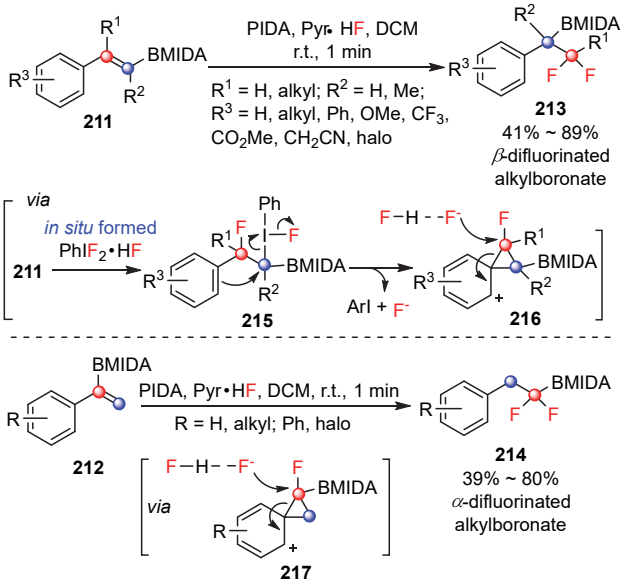
Murphy's group[46] in 2017 reported that the application of λ^3-iodane **204** ($TolIF_2$) as both oxidant and fluorine

source could enable the conversion of phenylallenes **205** to α-difluoromethyl styrenes **206** in the presence of Lewis acid (20 mol% BF_3•OEt_2). The proposed mechanism indicated that there are two possible pathways forming the key intermediate **209**. Path A initiated from an attack iodane by **205** and gave benzylic cation **207**, in which additional stabilization might be achieved through formation of iodocy-clopropylium cation **208**. Fluorination of this intermediate produced the first C—F bond to give **209**. The path B was derived from the studies of Szabl *et al.*[42-43]: in the presence of BF_3, phenylallenes **205** reacted with $TolIF_2$ directly to provide intermediate **209**. Once intermediate **209** was formed, the arene woulddisplace iodotoluene and fluoride, possibly with assistance from BF_3•OEt_2. The resulting phenonium ion **210** was nucleophilically attacked by fluoride to open the three-member ring, affording the terminal difluorinated migration product **206** (Scheme 42).



Scheme 42 Fluorination/migration cascade of phenylallenes to α-difluoromethyl styrenes mediated by $TolIF_2$

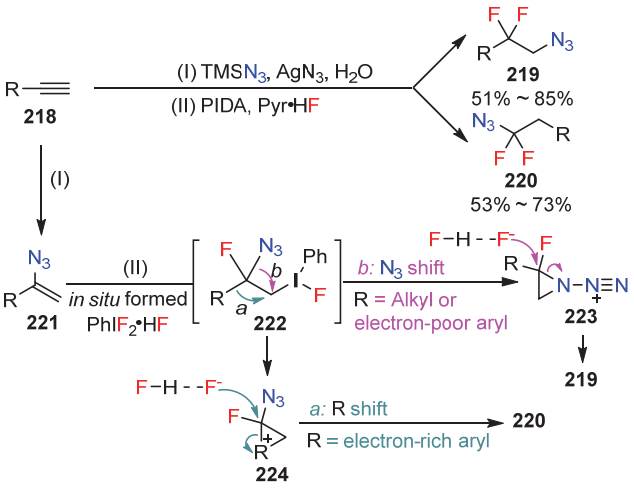
It is well known that HF complex (Pyr•$(HF)_x$ or amine•$(HF)_x$) is a good complement of fluorine source. Treating HF complex with the regular non-fluorine-containing hypervalent iodine reagents or aryliodine in the presence of an appropriate terminal oxidant could result *in situ* formation of $ArIF_2$, which could then trigger the fluorination/migration cascade reaction.[47] Differently, there is an additional activation of $ArIF_2$ in the presence of HF complex. In 2018, Wang and co-workers[48] obtained a series of *α*- and *β*-difluorinated alkylborons **213** and **214** via the difluorination/aryl migration of deuterated alkenyl MIDA boronates **211** and 1,1-disubstituted alkenyl MIDA boronates **212** mediated by $ArIF_2$, which was formed *in situ* from the interaction of Py•HF complex with λ^3-iodane (PIDA). The effective transformation provided a vital method for the challenging synthesis of the difluorinated alkylborons under mild reaction conditions, possessing advantages including broad substrate scope, good functional group tolerance and moderate to good yields (Scheme 43). Possible mechanisms to explain the paths are provided here. Initially, the interaction between the double bond within styrenyl MIDA boronates **211** and (difluoroiodo)benzene, generated *in situ* from the reaction of PIDA and Py•HF, triggered a regioselective vicinal fluoroiodination to give intermediate **215**. Thereafter, the intramolecular nucleophilic attack of phenyl ring on the C—I bond led to the formation of a phenonium ion species **216**. The second regioselective fluoride attack resulted in the ring-opening, which was accompanied by the homotopic 1,2-aryl migration, providing *β*-difluorinated alkylborons **213**. Likewise, 1,1-disubstituted alkenyl MIDA boronates **212** underwent through a similar path via the key intermediate **217** to give the terminal difluorinated product **214**.



Scheme 43 Effective transformation of alkenyl MIDA boronates to prepare *α*-and *β*-difluorinated alkylborons mediated by *in situ* formed $ArIF_2$

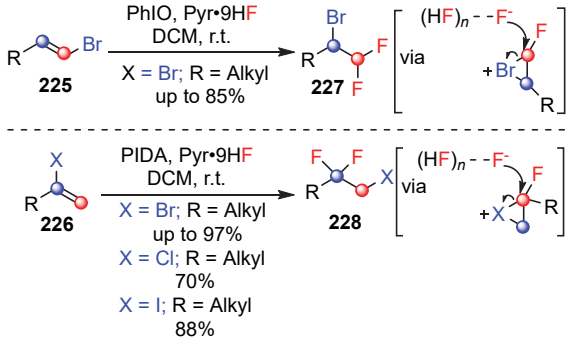
In 2019, Bi's group[49-50] reported a one-pot procedure for synthesis of *β*-difluorinated alkyl azides **219** via 1,2-azide migratory hydroazidation/difluorination tandem of alkynes **218**. Meanwhile, 1,2-aryl migratory/difluorination compounds **220** could be obtained when R group of alkynes **218** is an alkyl or an electron-rich aryl group, and both these procedures underwent the same intermediate **222** generated from the interaction of vinyl azides **221** and $PhIF_2$•HF (Scheme 44). Mechanistically, regioselective vicinal fluoroiodination of the vinyl azide using $PhIF_2$•HF, generated *in situ* from the reaction of PIDA and Py•HF, delivered intermediate **222**. Thereafter, intramolecular nucleophilic attack of the C—I bond by the aromatic ring or azide moiety resulted in the formation of a bridged ethylenearenium ion **224** or aziridine-N diazonium ion **223** depending on the nature of the substituent. Finally, the

second regioselective fluoride attack led to ring-opening, which was concomitant with a 1,2-migration of either the azide or aryl group, providing α- or β-difluorinated alkyl azides (**220** or **219**).



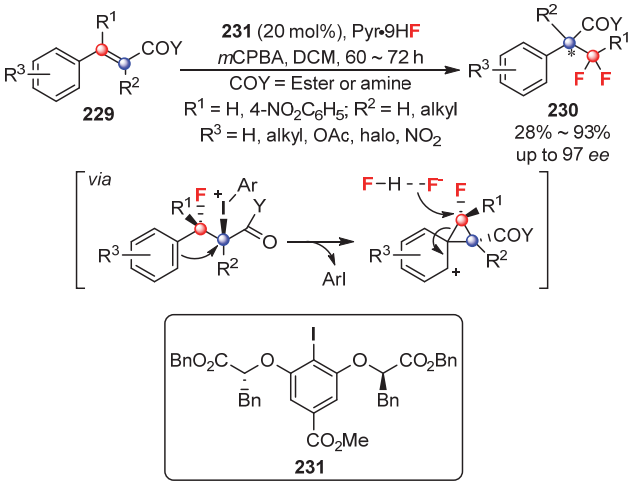
Scheme 44 One-pot two-step procedure of alkynes to α- or β-difluorinated alkyl azides mediated by *in situ* formed $PhIF_2$

Additionally, in 2021, Liu and co-workers[51] realized the synthesis of difluoroalkyl halides **227** and **228** by treating α- or β-bromostyrenes **225** and **226** with $PhIF_2$, which was *in situ* formed from the fluorination of PIDA or PhIO with Pyr•$(HF)_x$ (Scheme 45). To our knowledge, this could represent the first difluorination/1,2-chloro-migration and difluorination/1,2-iodo-migration employing hypervalent iodine compound, compared with the first difluorination/1,2-broro-migration reported by Jacobsen in 2020.[52]



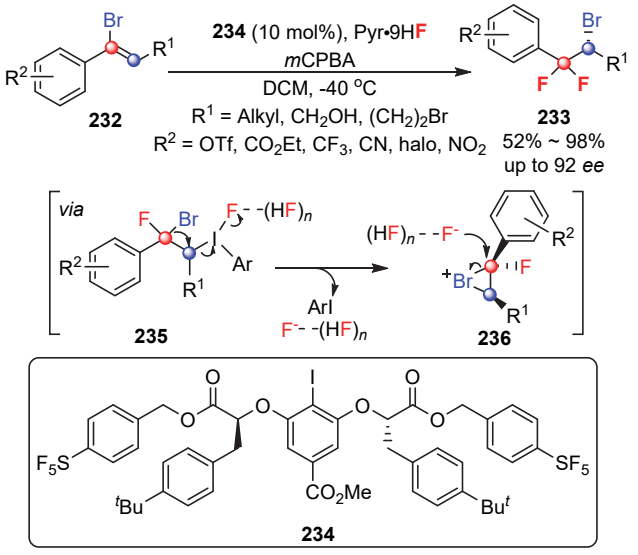
Scheme 45 Difluorination/1,2-halo-migration of α- or β-bromostyrenes by employing *in situ* formed $PhIF_2$

In addition to the reaction of λ^3-iodane (*i.e.* PhIO, PIDA) with HF complex that could yield $ArIF_2$ *in situ*, the system of a catalytic amount of ArI, terminal oxidant and HF complex could also accomplish the formation of $ArIF_2$ *in situ*. In 2016, Jacobsen and coworkers[53] finished the asymmetric conversion of alkenes **229** to difluoro methylated stereocenters **230** (up to 97 *ee*) in the presence of chiral ArI **231**, *m*CPBA and Pyr•9HF (Scheme 46). Its migration procedure is similar to the one described in Scheme 43.



Scheme 46 Asymmetric difluorination/migration of alkenes to difluoro methylated stereocenters mediated by *in situ* chiral formed $ArIF_2$

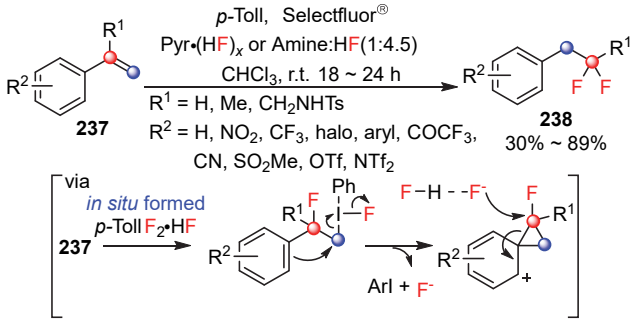
In 2020, Jacobsen *et al.*[52] further applied the similar catalytic protocol to the asymmetric synthesis of β,β-difluoroalkyl bromide compounds **233** via the oxidative rearrangement of α-bromostyrenes **232** triggered by $ArIF_2$, *in situ* generated from chiral ArI **234** and *m*CPBA. This transformation realized the first hypervalent iodine compound mediated bromo-migration and provided excellent building blocks for chemical synthesis. Mechanically, intramolecular stereospecific displacement of intermediate **235** generated bromonium ion **236**. Then regioselective ring opening of **236** by fluoride would then afford the desired product **233** (Scheme 47).



Scheme 47 Asymmetric difluorination/bromo-migration of α-bromostyrenes to β,β-difluoroalkyl bromide compounds mediated by *in situ* chiral formed $ArIF_2$

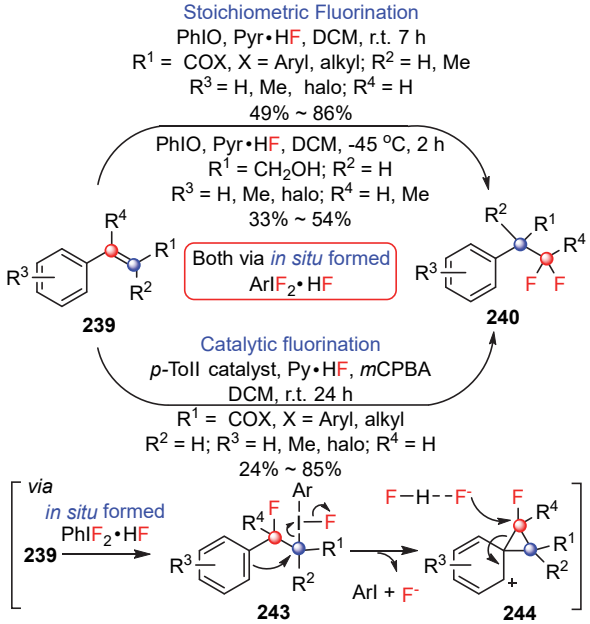
Other HF complex could also be utilized in the hypervalent iodine-mediated difluorination/migration reactions. In 2018, Gilmour's group[54] reported the *gem*-difluorination/migration of alkenes **237** to acess electronically and

substitutionally diverse styrenes **238** mediated by $ArIF_2$, *in situ* formed from the interaction of *p*-TolI, Selectfluor® and amine•$(HF)_x$ or Pyr•$(HF)_x$ complex (Scheme 48).

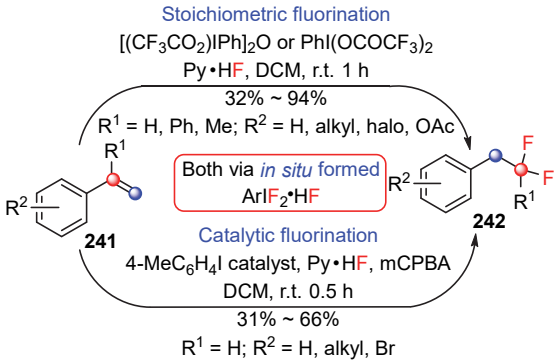


Scheme 48 Difluorination/migration of alkenes mediated by *in situ* formed *p*-$TolIF_2$

Importantly, more and more functionalized arylalkene substrates can undergo both $ArIF_2$-triggered stoichiometric and catalytic fluorination/migration. Examples include transformation from functionalized arylalkenes **239** and **241** to difluorinated aromatic olefins **240** and **242**, reported by Kitamura in 2015 (Scheme 49)[47] and 2018, respectively (Scheme 50).[55] The reaction was mediated by the $PhIF_2$ *in situ* generated from PhIO and HF. Then $PhIF_2$ was activated by HF and reacted with the functionalized arylalkene. Nucleophilic attack of fluoride ion to a bridged iodine intermediate **243** formed a fluorinated iodane intermediate **244**, which underwent simultaneous removal of PhI and migaration of aryl group, followed by attack of fluoride ion. In the catalytic fluorination, regenerated PhI is oxidized by *m*CPBA to PhIO or its equivalent and then completed the catalytic cycle.

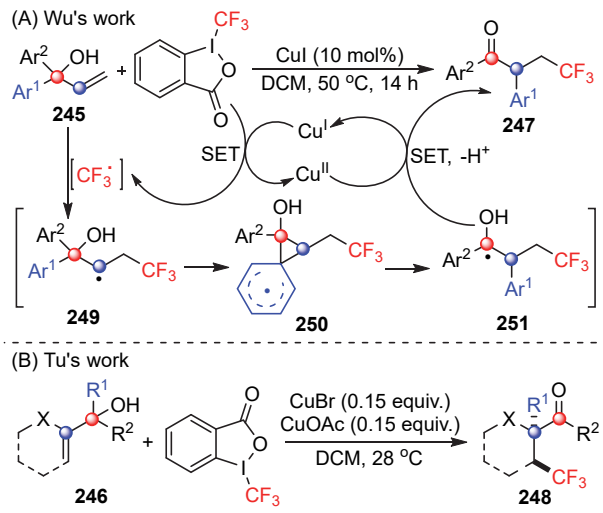


Scheme 49 Stoichiometric and catalytic fluorination/migration of arylalkenes to difluorinated aromatic olefins via *in situ* generated $ArIF_2$



Scheme 50 Stoichiometric and catalytic fluorination/migration of arylalkenes to difluorinated aromatic terminal olefins via *in situ* generated $ArIF_2$

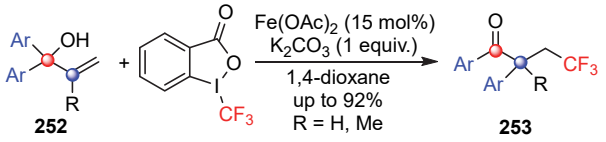
It is noteworthy that fluoroalkylation/migration involving hypervalent iodine reagents includes radical trifluoromethylation/1,2-aryl shift of allylic alcohols[56-58] or radical trifluoromethylation/1,4-aryl shift of homopropargylic alcohols.[59] In contrast to other numerous migratory transformations through cation intermediate pathway, these radical transformations are mediated by Togni's reagent and catalyzed by metal. In 2013, Wu *et al.*[56a] and Tu *et al.*[57] realized the synthesis of *β*-trifluoromethyl ketones (**247** and **248**) from the reaction of allylic alcohols (**245** and **246**) with Togni's reagent in the presence of CuI (Scheme 51A) or the combination of CuBr and CuOAc, respectively (Scheme 51B). Furthermore, substrates with aryl (Ar^1 of **245** or R^1 of **246**) containing electron-poor substituent is more likely to undergo migration compared with substrates containing phenyl or aryl (Ar^2 of **245** or R^2 of **246**) containing electron-rich group. Both of the two reactions underwent the radical mechanism. For Wu's work, mechanistically, a CF_3 radical reacted with alkene **245** to generate radical **249**. Subsequent migration of the electron-deficient aryl group via spiro[2,5]octadienyl radical **250** produced intermediate **251**. Single-electron transfer



Scheme 51 Radical trifluoromethylation/1,2-shift of allylic alcohols by employing Togni's reagent and copper catalyst

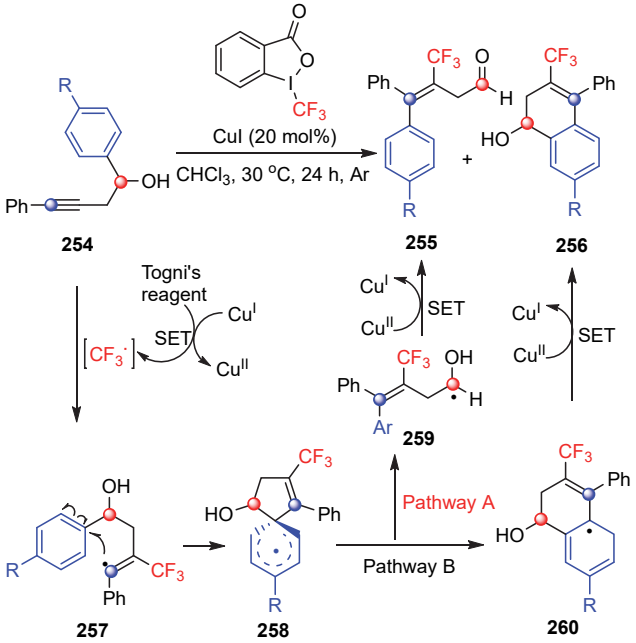
(SET) between Cu and **251** delivered the desired product **247** with concomitant loss of a proton, and regenerated the active copper(I) species. The similar mechanism could be applied to Tu' work.

In the same year, Sodeoka and co-workers[58] employed the similar protocol realizing the preparation of *β*-trifluoromethyl ketones analogues **253** by treating allylic alcohols **252** with Togni's reagent, in the presence of Fe(II) calalyst and base (Scheme 52).



Scheme 52 Radical trifluoromethylation/1,2-shift of allylic alcohols to *β*-trifluoromethyl ketones analogues by employing Togni's reagent and Fe(II) calalyst

Additionally, Liu and Liang *et al.*[59] in 2014 conducted the radical fluoroalkylation/1,4-migration of homopropargylic alcohols **254** mediated by Togni's reagent and CuI catalyst, providing trifluoromethylated 3-butenals **255** or 3-buten- 1-one derivatives **256** (Scheme 53). Generally, the reaction occurred smoothly via the radical pathway A, while cyclization compounds 3-buten-1-one analogues **256** would simultaneously be formed via the pathway B when the R group of **254** is Cl, Br or CF_3 substituent. The proposed mechanism is as follows. The CF_3 radical, generated from Togni's reagent and Cu^I, underwent radical addition to alkyne **254** to afford radical **257**. Then a 5-*ipso* cyclization occurs on the benzene ring, leading to radical **258**, which then underwent intramolecular 1,4-aryl migration to



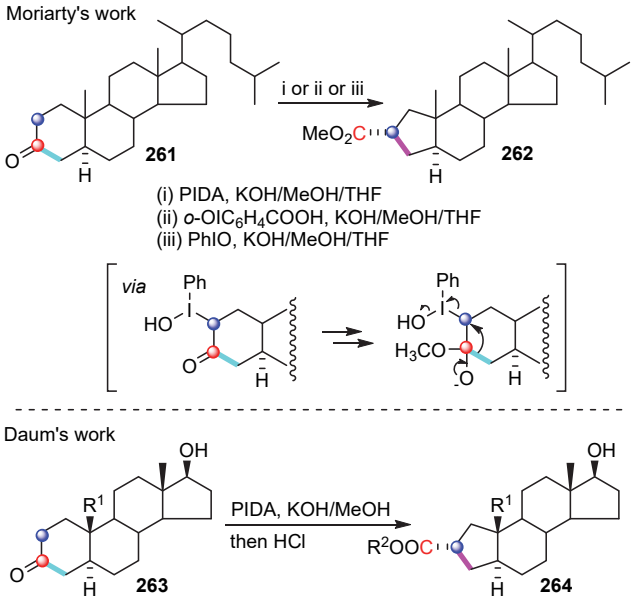
Scheme 53 Radical trifluoromethylation/migration of homopropargylic alcohols to trifluoromethylated 3-butenals by utilizing Togni's reagent and CuI catalyst

form a new C(sp^3)-centered radical intermediate **259**. Finally, oxidation of radical **259** with Cu^{II} gave the desired product **255** and released the Cu^I catalyst (Pathway A). Alternatively, the radical intermediate **258** could also undergo 1,2-migration to afford the radical intermediate **260** (Pathway B), which would give the side products **256** through a SET process.

2.1.1.5 C to C ring contraction

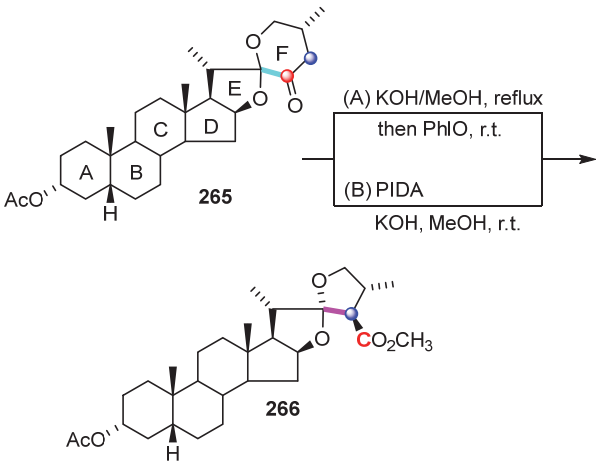
C to C ring contraction reactions provide important approaches to increase molecular complexity in a single step.[4d] Substrates that could undergo hypervalent iodine compounds-triggered oxidative ring contraction reactions mainly include cycloalkanones[10f,60-65] and cycloolefins.[4f,9b,40e,66-74] Furthermore, studies about other types of substrates including 3-hydroxypiperidine,[75] exocyclic *β*-enaminones,[76] cyclobutanols[77] and 2-alkylidenecyclobutanol analogues[78] involving ring contraction reactions have also made great progress in recent years.

It was reported in 1984 by Moriarty[60a] and Daum[60b] independently that the Favorskii rearrangement of steroids **261** or **263** could be realized by PIDA or PhIO in the presence of base, providing access to ring contraction compound **262** and **264**, respectively. For the proposed mechanism, hyperiodination of the enolate system followed by migration of the C(3)—C(4) bond afforded the product. This could be represented the earliest reports about ring contraction reactions mediated by hypervalent iodine compounds (Scheme 54).



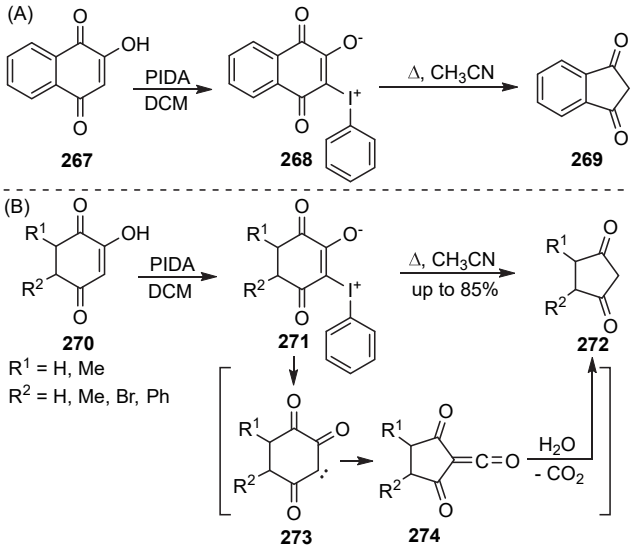
Scheme 54 Ring contraction of steroids via Favorskii rearrangement mediated by hypervalent iodine compounds.

In 2005, Iglesias-Arteaga *et al.*[61] employed the similar method accomplishing the conversion of steroids **265** to the Favorskii rearranged product **266**. It is worth noting that the ring contraction occurred on F ring, rather than on A ring (Scheme 55).



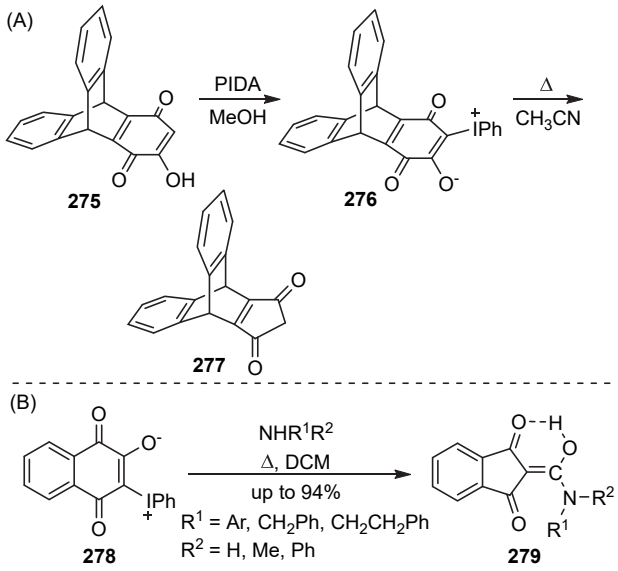
Scheme 55 Ring contraction of steroids mediated by hypervalent iodine compounds

1,4-Naphthoquinones could be regarded as another type of important ketone compound that could also undergo the hypervalent iodine-mediated ring contraction. In 1989, Varvoglis *et al*.[62a] reported that zwitterion **268** was generated from the interaction of 2-hydroxy-1,4-naphthoquinone **267** with PIDA, which delivered product **269** via ring contraction by conducted in acetonitrile or chloroform under heat (Scheme 56A). A Smiles rearrangement/Wolff-type rearrangement pathway was proposed for this kind of transformation when they further conducted the study with zwitterion **271**, which was prepared from hydroxycyclohex-2-ene-1,4-diones **270** with PIDA. Further conversion of **271** to ketene **274** via ketocarbene **273** occurred, and then the hydrolysis and the following decarboxylation of ketene **274** provided the terminal **272** (Scheme 56B).[62b]



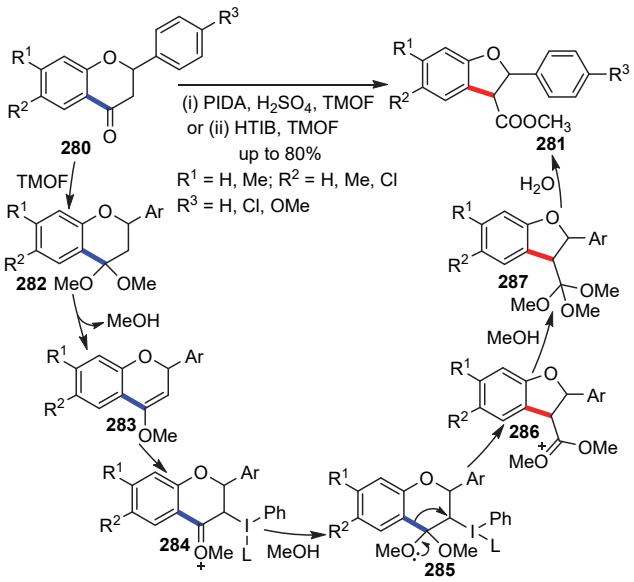
Scheme 56 Ring contraction of 1,4-naphthoquinones and diones via Wolff-type rearrangement triggered by PIDA

In 2002, Spyroudis and co-workers[63a] further expanded this ring contraction protocol. They found that the reaction of triptycene quinones **275** with PIDA in MeOH could be used to prepare cyclopentenedione **277**, through the Wolff-type rearrangement via a phenyliodonium ylide **276** (Scheme 57A). They[63b] even obtained rearrangement/amination product, *i.e.*, amide **279**, through the reaction of compound **278** and amines (Scheme 57B).



Scheme 57 Ring contraction of 1,4-naphthoquinones via Wolff-type rearrangement mediated by PIDA

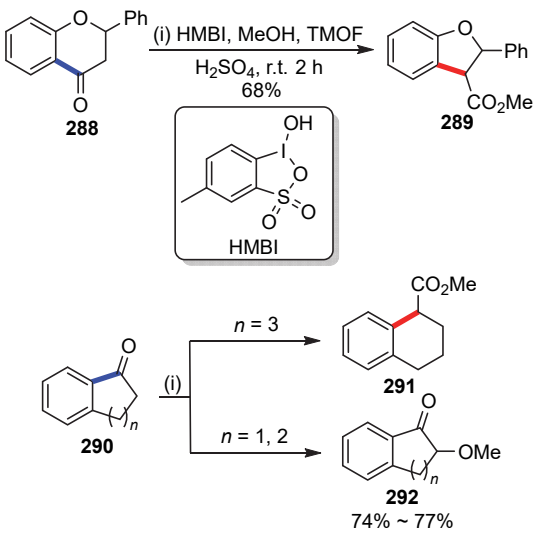
Additionally, Prakash's group[64a] reported the ring contraction of flavanones **280** mediated by PIDA or HTIB and TMOF, which afforded compounds **281** (Scheme 58). It was proposed that the reaction was initiated from the formation of ketal **282**, which was converted to intermediate **283** by elimination of one molecule of MeOH. Next, intermediate **283** reacted with hypervalent iodine reagent to



Scheme 58 Ring contraction of flavanones in the presence of PIDA or HTIB and TMOF

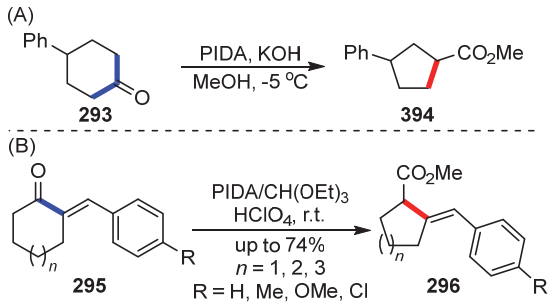
give intermediate **284**, which was nucleophilically attacked by MeOH to afford the key intermediate **285**. Then the ring contraction occurred in **285**, affording the rearranged intermediate **286**, which was nucleophilically attacked by MeOH again to form intermediate **287**. Finally, hydrolysis of intermediate **287** provided the title product **281**.

1*H*-1-Hydroxy-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (HMBI), reported by Justik,[10f] could mediate not only the oxidative 1,2-migration of ketone **24** (Scheme 7B), but also the ring contraction of flavanones **288** and 1-benzosuberone (**290**, n=3) to afford the corresponding ring-contracted product, respectively. Significantly, subjecting cycloalkanones **290** (n=1 or 2) to the standard conditions, no ring contraction occurred but only α-methoxyketones **292** were obtained (Scheme 59).[10f]



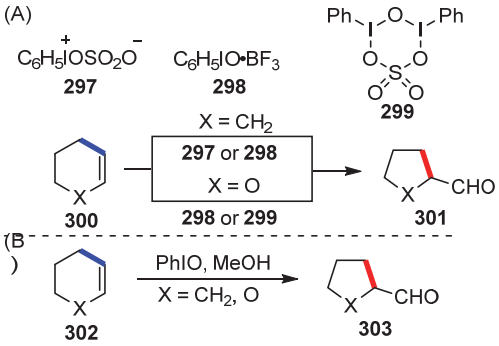
Scheme 59 Ring contraction of flavanones and 1-benzosuberone in the presence of HMBI and TMOF

Other cycloalkanones such as 4-phenylcyclohexanone **293** and 2-arylidenecycloalkanones **295** could also undergo oxidative ring contraction by treating with PIDA to give five-membered esters **294** and **296**, respectively (Scheme 60).[65]



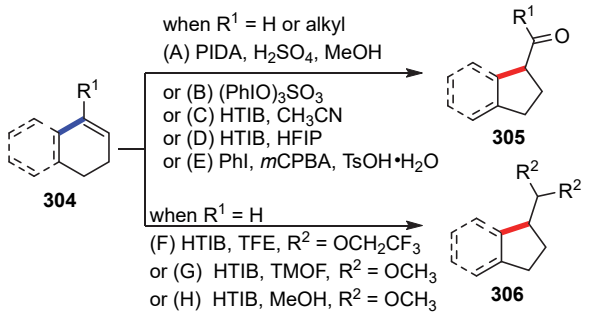
Scheme 60 Ring contraction of cycloalkanones in the presence of PIDA

Ring contractions of cycloolefins was realized under metal-free conditions by Zefirov and Zhdankin, who treated cyclohexenes **300** with the available and nontoxic λ^3-iodane species, **297**, **298** or **299** to give the ring contracted aldehyde **301** (Scheme 61A).[4f,66a] Meanwhile, Moriarty[66b] realized the similar conversion of cyclohexenes **302** to the corresponding aldehyde **303** via PhIO (Scheme 61B).



Scheme 61 Ring contraction of cycloolefines mediated by λ^3-iodane species **297**, **298** or **299**

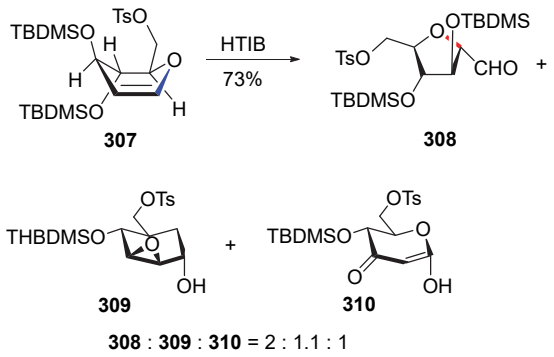
Furthermore, PIDA,[9b,67a] $(PhIO)_3SO_3$,[67b-67c] HTIB[68]or *in situ* formed HTIB[69] could also trigger the ring contraction of cyclohexene **304**. Interestingly, different products would be generated in different solvent when HTIB was used (Scheme 62). When using non-nucleophilic solvents such as HFIP and acetonitrile, the products were mainly aldehydes **305**. While when nucleophilic solvents such as methanol and trifluoroethanol were used, the product changed to acetal **306** of the corresponding aldehyde.



Scheme 62 Hypervalent iodine mediated ring contraction of cycloolefines under different conditions

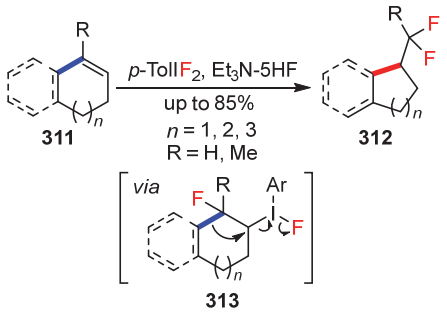
Furthermore, Kirschning *et al.*[70] demonstrated that glycals **307** could be applied as another special substrate of ring contraction reaction mediated by HTIB (Scheme 63). For this transformation, the unique chemical configuration required by the rearrangement reaction played an important role in the rearrangement process. In addition to the formation of ring contraction product tetrahydrofurfural **308**, ether **309** and 1,2-H migration product 2,3-dihydro-4*H*-pyran-4-one **310** were also obtained as co-product in rate of 2∶1.1∶1.

Aside from cyclohexenes that could undergo the hypervalent iodine-mediated ring contraction to give aldehydes or acetals described above, cycloolefins **311** could also undergo ring contraction with concomitant fluorination by



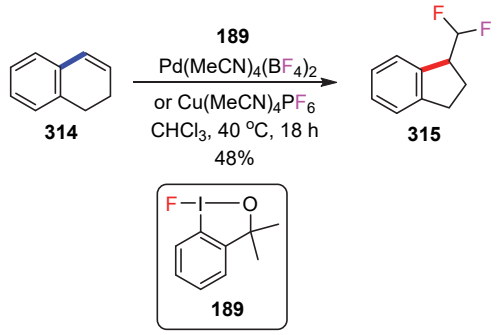
Scheme 63 Ring contraction of glycals triggered by HTIB

treating with fluorine-containing hypervalent iodine reagent. For example, Yoneda *et al.*[40e] and Hara *et al.*[71] reported the iodotoluene difluoride/Et_3N-5HF mediated difluorination/ring contraction of cyclohexenes **311**, which afforded the *gem*-difluorinated products **312** via key intermediate **313** (Scheme 64). Its mechanism in detail might follow the pathway described in Scheme 39.



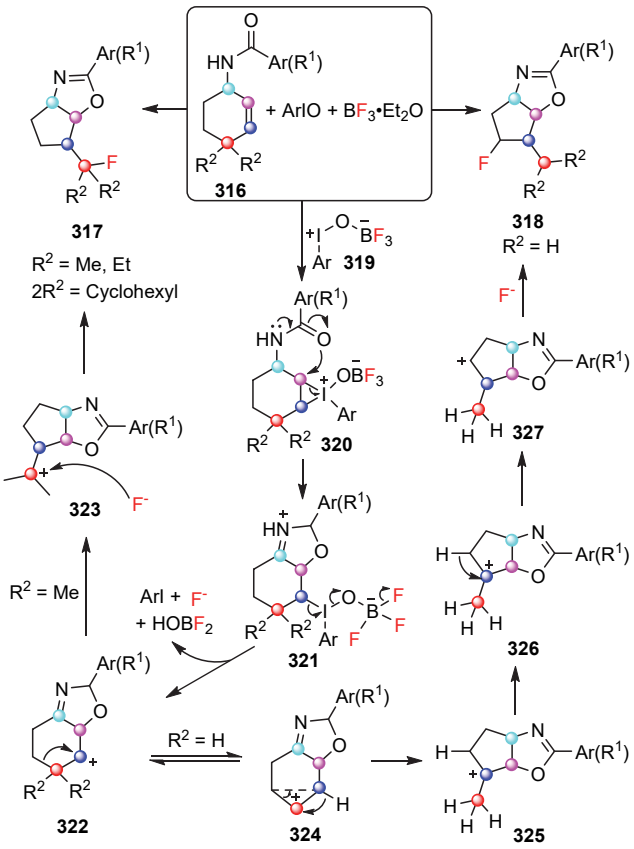
Scheme 64 Difluorination/ring contraction of cyclohexenes by employing *p*-TolIF$_2$ and Et_3N-5HF

Another similar example is the *gem*-difluorination/ring contraction (Scheme 39) reported by Szabó and coworkers,[43] who found that 1-(difluoromethyl)-2,3-dihydro-1*H*-indene **315** would be generated from the reaction of 1,2-dihydronaphthalene **314** with λ^3-iodane **189** in the presence of $Pd(MeCN)_4(BF_4)_2$ or $Cu(MeCN)_4PF_6$ (Scheme 65).[43]



Scheme 65 Difluorination/ring contraction of 1,2-dihydronaphthalene mediated by λ^3-iodane **189** and $Pd(MeCN)_4(BF_4)_2$ or $Cu(MeCN)_4PF_6$

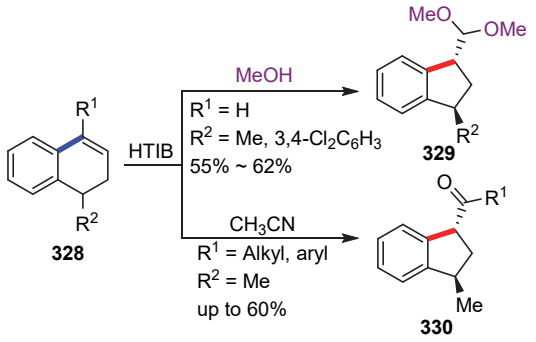
Furthermore, the first I(III)-mediated ring-contraction monofluorination reaction was reported by Zhang's group[72] in 2017. A series of monofluorine-containing ring-fused oxazolines **317** and **318** were obtained from the six-membered starting material **316** via the fluorination/ring contraction triggered by I(III) species **319**, formed *in situ* from the activation of ArIO by BF_3. The key carbocation intermediate **322** is generated from the reductive elimination of intermediate **321**, formed from the activation of oxazolines (**317** or **318**) by λ^3-iodane **319**, and the following intramolecular nucleophilic attack to the resulting iodonium intermediate **320**. Next, when R^2=H, successive alkyl and double hydride shifts occurs to give the carbocation intermediate **327**, which then is captured by fluoride to release product **318**. While a stable tertiary carbocation intermediate **323** forms via the 1,2-migration of carbocation **322** when R^2=Me. A same trap by fluoride to **323** delivers product **317** (Scheme 66).



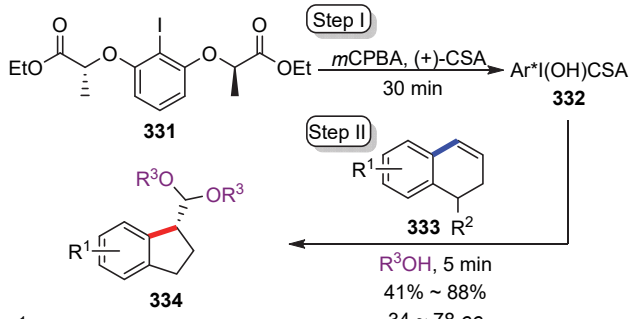
Scheme 66 Monofluorination/ring contraction of cyclohexenes mediated by *in situ* formed I(III) species **319**

In 2007, Silva and co-workers[68a,73] realized the ring contraction of cyclohexenes **328** mediated by I(III) species formed *in situ* with HTIB. Different chiral products, acetals **329** and aldehydes **330**, formed in MeOH and CH_3CN, respectively (Scheme 67). Its mechanism is similar to that shown in scheme 62.

In 2017, they[74] further developed the asymmetric ring contraction of cyclohexenes **333** and obtained the five-membered chiral products **334** (up to 78 *ee*) by utilizing the chiral I(III) compound **332**, formed *in situ* from the oxidation of **331** by *m*CPBA (Scheme 68).



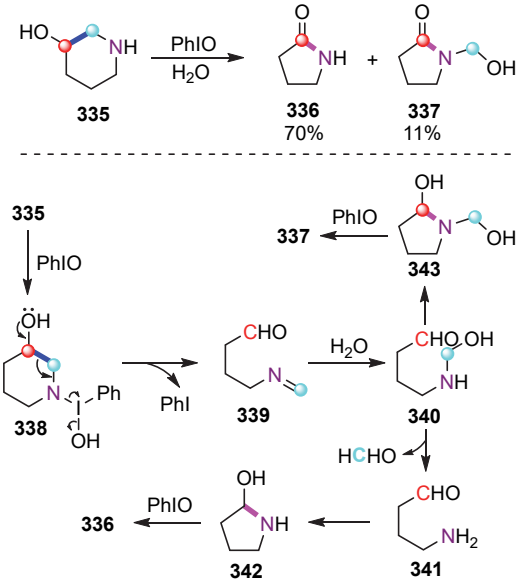
Scheme 67 Asymmetric ring contraction of cyclohexenes by utilizing HTIB in MeOH or CH_3CN



Scheme 68 Asymmetric ring contraction of cyclohexenes mediated by *in situ* formed chiral I(III) compound **332**

In addition to the ketone and alkene compounds described above, hydroxypiperidine could also undergo ring contraction upon treatment with hypervalent iodine reagent. For example, 3-hydroxypiperidine **335** could be converted to five-membered lactams **336** and **337** in the presence of iodosylbenzene and water, which was accomplished via a key intermediate **340**, a hydrolytic product of imino aldehyde intermediate **339**. The latter was probably generated from a ligand exchange on PhIO and the following rapidly oxidative Grob fragmentation of the resulting iodane **338**. Then, cyclization of aldehyde **341**, an one-carbon-shorter product of **340**, followed with the further oxidation of the resulting cyclic aminal **342** by PhIO, gave the lactam **336**. While **340** underwent a similar direct cyclization/oxidation process to provide lactam **337** through the intermediate **343** (Scheme 69).[75]

Another interesting reaction is the HTIB/NaN_3-promoted ring contractive cyanation of exocyclic *β*-enaminones **344**, enabling the synthesis of cyanocyclopentanone derivatives **345** under mild conditions, described by Das and co-workers[76] in 2017 (Scheme 70). Two possible pathways were proposed to explain this transformation. The first one initiates from the *in situ* formation of azido λ^3-iodane **346** with HTIB and NaN_3. Then, the released azido radical from **346** was trapped by *β*-enaminones **344**, leadig to the formation of intermediate **347**, which was further converted to the zwitterionic intermediate **348**,

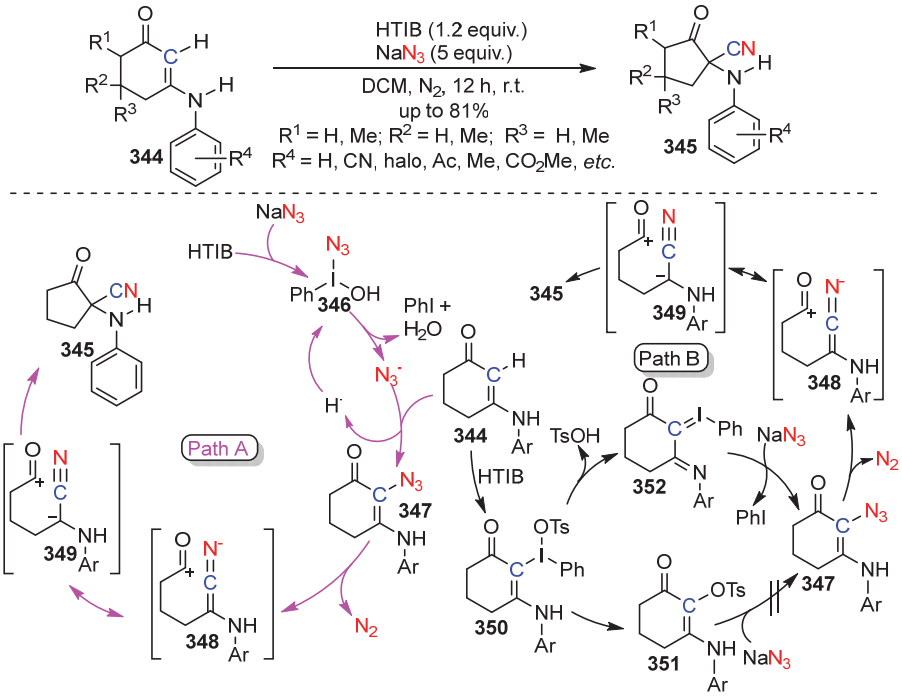


Scheme 69 Ring contraction of 3-hydroxypiperidine to lactams in the presence of PhIO and H_2O

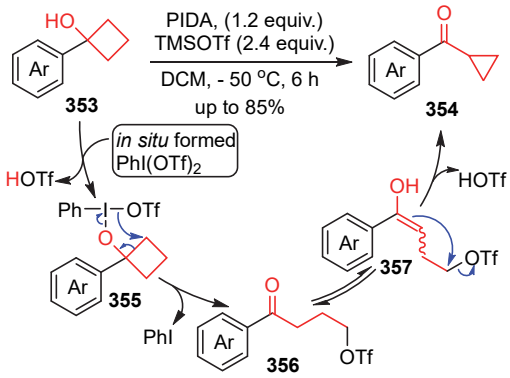
along with the release of nitrogen. Electrocyclic ring closing reaction of intermediate **349**, the resonance form of **348**, would generate the terminal product **345**. The second one starts from the ligand exchange reaction of HTIB with **344**, followed by conjugation as well as elimination of TsOH, giving **352** as a stable intermediate. The latter was identified by mass and NMR spectroscopy. While intermediate **351** could be also obtained and identified by mass and NMR spectroscopy upon prolonged stirring of **350** at room temperature. However, no conversion of **351** to the product was observed when it was further treated with NaN_3, revealing that the reaction does not react through intermediate **351**. While the desired **345** was formed in comparable yield by treating **352** separately with NaN_3, which probably occurred via a similar denitrogen/ring closing cascade as that described in path A.

In 2018, Peng and coworkers[77] found that cyclobutanols **353** could undergo PIDA-triggered oxidative ring contraction to give aryl cyclopropyl ketones **354**, mediated by $PhI(OTf)_2$ *in situ* formed from the reaction of PIDA and TMSOTf. This protocol initiated with the activation of **353** with $PhI(OTf)_2$, followed by the internal nucleophilic addition of OTf anion to the cyclobutyl ring of the resulting intermediate **355**, which afforded the ring-opening ketone **356**. Finally, enol **357** would yield the terminal ketone **354** via an intramolecular S_N2 procedure (Scheme 71).

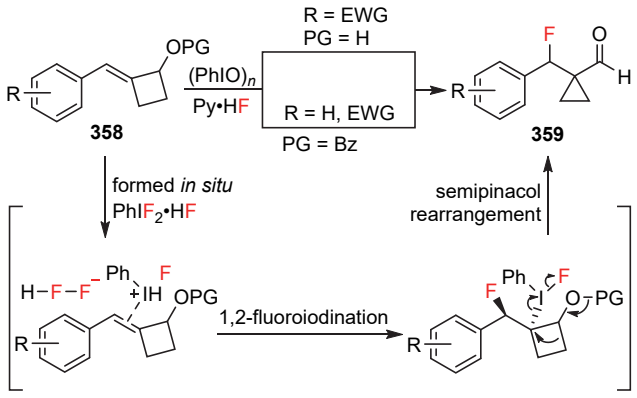
In 2021, Li and co-workers[78] reported an efficient access to *β*-monofluorinated cyclopropanecarbaldehydes **359** by treating 2-alkylidenecyclobutanol analogues **358** with iodosobenzene and Pyr•HF.[46-53,55] Mechanistically, the reaction of iodosobenzene and Pyr•HF in situ generated $PhIF_2$•HF, which enables the substrate to undergo fluorination/semipinacol rearrangement cascade to give the ring contraction product (Scheme 72).



Scheme 70 Ring contractive cyanation of exocyclic *β*-enaminones to prepare cyanocyclopentanone derivatives in the presence of HTIB and NaN_3



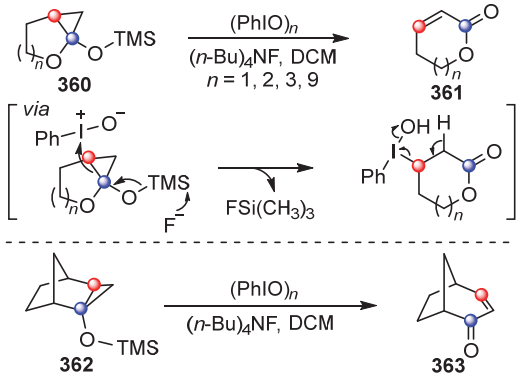
Scheme 71 Ring contraction of cyclobutanols to access aryl cyclopropyl ketones mediated by *in situ* formed $PhI(OTf)_2$



Scheme 72 Fluorination/semipinacol rearrangement cascade of 2-alkylidenecyclobutanol analogues triggered by *in situ* formed $PhIF_2$•HF

2.1.1.6 C to C ring expansion

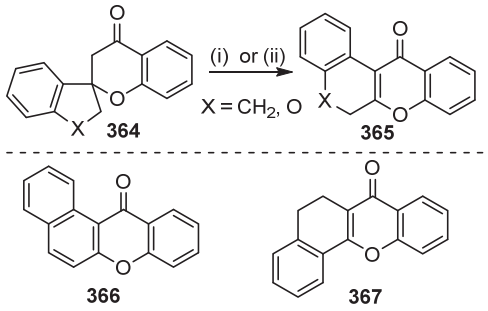
Compared to ring contractive reactions,[4d,9b,10f,40e,60-78] ring expansion reactions mediated by hypervalent iodine reagent are much more diverse. The substrates that could undergo the ring expansion reaction could be mainly classified into dicyclic[79-81] and monocyclic types.[11,43,82-94] In 1990, Moriarty's group[79] described the conversion of trimethylsilyloxycyclopropanols **360** to lactone **361** via oxidative ring expansion mediated by PhIO and tetrabutylammonium fluoride. Similarly, the reaction of compound **362** also could occur smoothly under the conditions to provide ketone **363** (Scheme 98). This one example transformation could be regarded as the earliest ring expansion enabled by hypervalent iodine reagent.



Scheme 73 Ring expansion of trimethylsilyloxycyclopropanols and oxysilane in the presence of PhIO and tetrabutylammonium fluoride

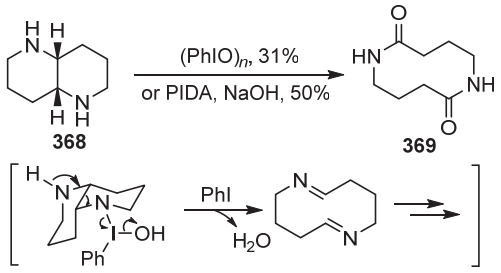
In 1998, Gabbutt and co-workers[80] reported the HTIB-

mediated oxidative ring expansion of spirocycles **364** could provide a simple approach for the preparation of key intermediate for assembling the natural compounds known as rotenoids (Scheme 74). When the X group of the starting material is methylene, aryl migration product **365** would be generated, accompanied by the formation of the subsequent aromatisation product **366** as well as the alkyl migration product **367**.



Scheme 74 Oxidative ring expansion of spirocycles mediated by HTIB

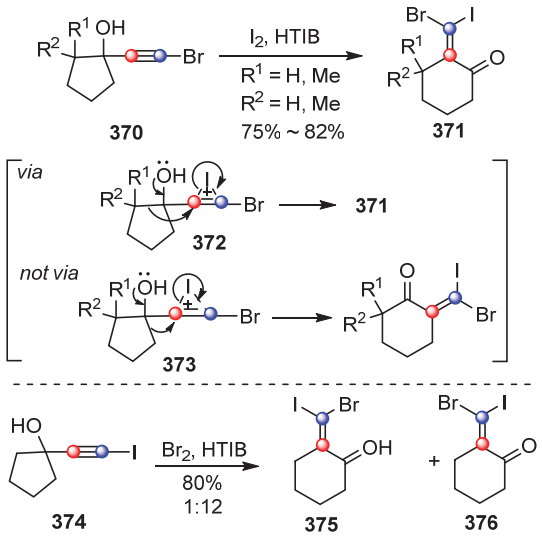
In 2002, Kozlowski *et al.*[81] discovered an exclusive rearrangement of 1,5-diazadecalin **368** and obtained ring-enlarged bislactam **369** in yield of 31%. This transformation undergoes an oxidation enabled by $(PhIO)_n$ or $(PhIO)_n$ *in situ* generated from the combination of PIDA and base, and a following ring opening/hydrolysis cascade. It is worth noting that the ring expansion of dicyclic compounds mediated hypervalent iodine reagent has been less explored so far (Scheme 75).



Scheme 75 Oxidative ring expansion of 1,5-diazadecalin to access bislactam triggered by (PhIO)n or (PhIO)n *in situ* generated from PIDA under base

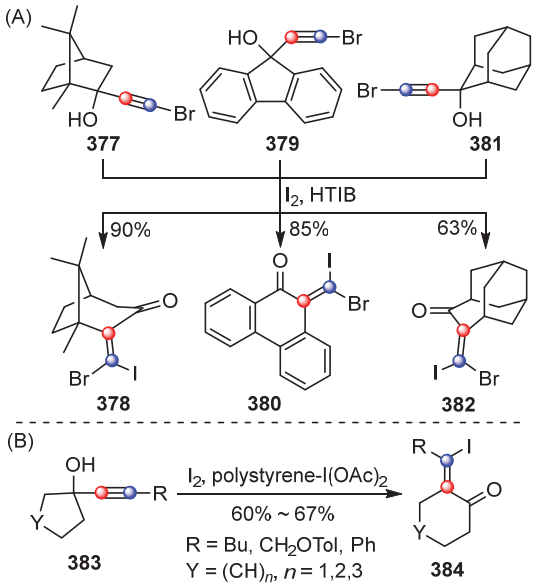
In 1992, McNelis *et al.*[82a-82b] demonstrated the earliest hypervalent iodine-mediated ring expansion of monocyclic substrate, namely, cyclopentyl bromoalkynols **370**, which could be converted into iodo-containing *α*,*β*-unsaturated ketone **371** by reacting with I_2 and HTIB. The reaction is postulated to undergo the 1,2 alkyl shift of intermediate **372**, rather than **373**. Similarly, cyclopentyl iodoalkynol **374** could also undergo this type of transformation when Br_2 and HTIB were applied, giving brominated products **375** and **376** (Scheme 76).

Additionally, other cyclic bromoalkynols including compounds **377**, **379** and **381**, when subjected to the



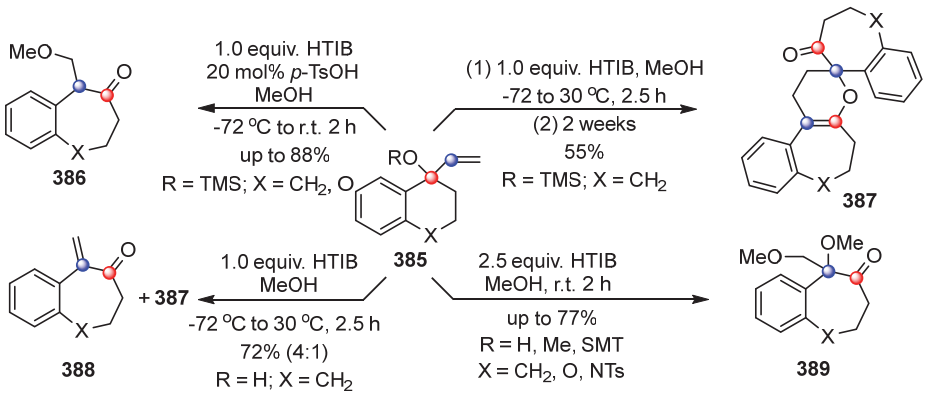
Scheme 76 Ring expansion of cyclopentyl bromoalkynols and cyclopentyl iodoalkynol involving HTIB

established conditions, could be converted to the ring-expanded *α*,*β*-unsaturated ketone **378**, **380** and **382**, respectively (Scheme 77A).[82c-82f] Meanwhile, Huang and co-workers[13] reported the similar ring expansion of 1-alkynylcycloalkanols **383** using poly[styrene(iodosodiacetate)] as the oxidant, which furnished a series of (*Z*)-2-(1-iodo-1-organyl)methylenecycloalkanones **384** (Scheme 77B).



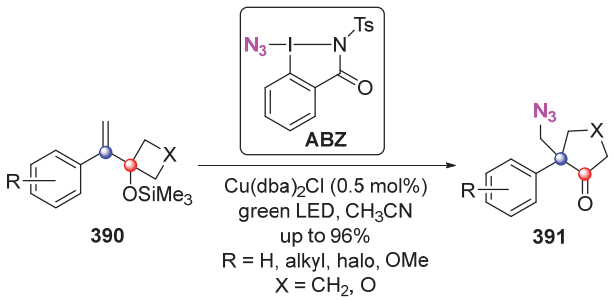
Scheme 77 Ring expansion of cycloalkynols involving hypervalent iodine reagent

In addition to alkynylcycloalkanols described above,[13,82] Silva's group[83-84] found that 1-vinylcycloalkanols (or the corresponding silyl or methyl ether **385**) could also participate the HTIB-mediated ring expansion to give different products **386** to **389** under the corresponding designated conditions (Scheme 78).



Scheme 78 Ring expansion of silyl or methyl ether mediated by HTIB

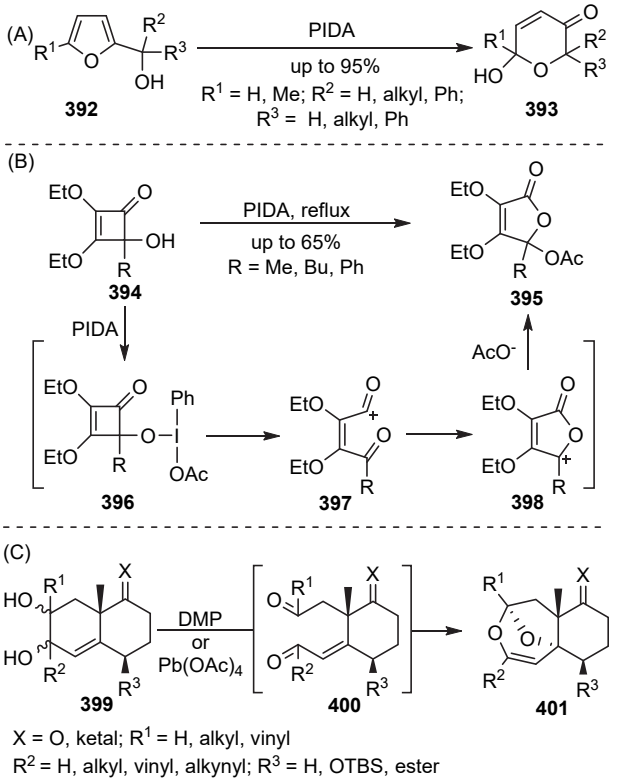
Another striking example is the photoredox-catalyzed azidation/ring enlargement reaction. In 2018, Waser and co-workers[85] treated silylated cyclobutanols **390** with ABZ (azidobenziodoxolone, Zhdankin reagent) in the presence of copper catalyst under irradiation of green LED, affording a variety of azidated cyclopentanones **391** in good to high yield (Scheme 79).



Scheme 79 Azidation/ring expansion of silylated cyclobutanols to prepare azidated cyclopentanones triggered by ABZ

Furthermore, many substrates containing hydroxyl group are prone to undergo hypervalent iodine-mediated ring expansion reaction. For example, in 1995, Piancateili and Mico *et al.*[86] described a special access to pyranones **393** with furan derivatives **392** via PIDA-mediated ring expansion through a plausible radical pathway (Scheme 80A). In 1999, Ohno and co-workers[87] presented a PIDA-mediated ring-expanded conversion of 4-hydroxy-2-cyclobutenone **394**, realizing the convenient synthesis of furanone **395** via the ring cleavage of intermediate **396**, the subsequent recyclization of the resulting cation **397** with a carbonyl oxygen and the following trap of the intermediate **398** by an acetate anion (Scheme 80B). Another interesting transformation reported by Arseniyadis *et al.*[88] was the Dess-Martin periodinane (DMP) triggered oxidative/pericyclic (glycol fission/intramolecular bis-hetero Diels-Alder) domino reaction of steroidal diols **399**, which allowed the preparation of **401** through intermediate ketone **400** with high yields. Meanwhile, this reaction also occurred smoothly when $Pb(OAc)_4$ was used as the oxidant (Scheme 80C).

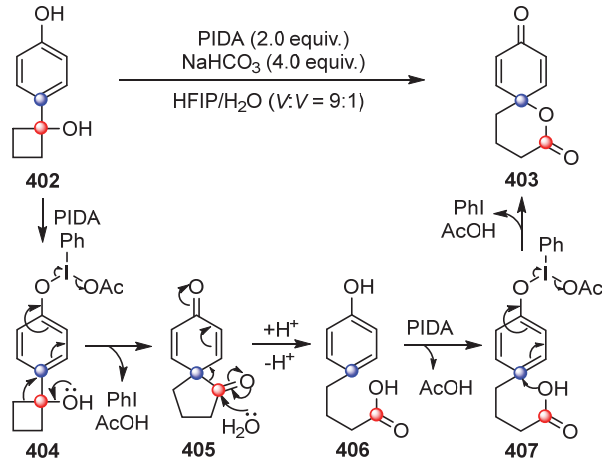
In 2010, Kita and Fujioka *et al.*[89] reported an interesting ac-



Scheme 80 I(III) compounds-mediated ring expansion of alcohols

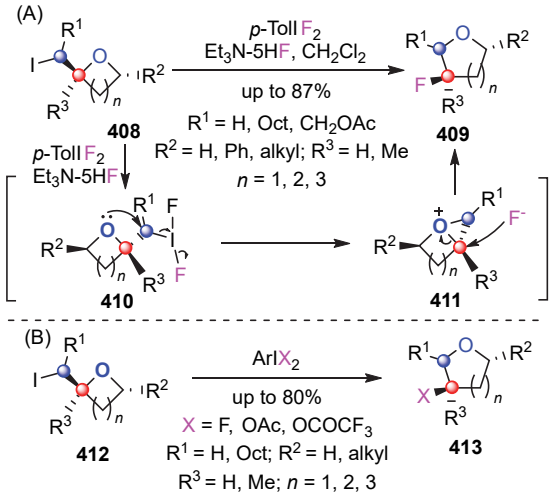
cess to spiro cyclohexadienone lactones **403** by reacting 1-(*p*-hydroxyaryl)cyclobutanols **402** with PIDA in the presence of $NaHCO_3$. This domino reaction initiates from the reaction of **402** and PIDA. The rearrangement of the resulting intermediate **404** gave the spiro cyclohexadienone ketone **405** as product as well as PhI and AcOH as byproducts. Nucleophilic attack to **405** by water followed the C—C bond cleavage and aromatization led to the formation of phenolic carboxylic acid **406**. Further oxidation of the latter by PIDA and the following ring closure/dearomatization afforded the terminal lactone **403** via intermediate **407** (Scheme 81).

Aside from the aforementioned alcohols that could be applied for synthesizing ring-expanded cyclic ethers, cyclic



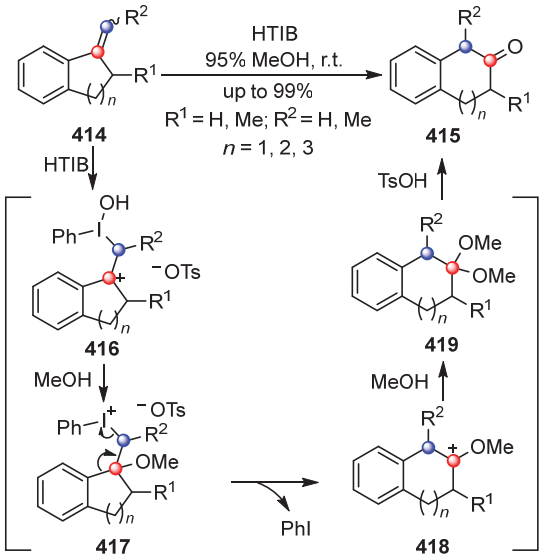
Scheme 81 Domino reaction of 1-(*p*-hydroxyaryl)cyclobutanols to prepare spiro cyclohexadienone lactones mediated by PIDA

ethers could also be used to prepare ring-enlarged cyclic ethers via hypervalent iodine-mediated oxidative ring expansion. In 2003, Hara and co-workers[90a] reported the synthesis of fluorinated ring-expanded cyclic ethers **409** from the reaction of the starting material **408** with *p*-TolIF$_2$. The process was postulated to initiate with the oxidation of **408** with *p*-TolIF$_2$, affording the *in situ* formed unstable I(III) species **410**. Quick decomposition of the later gave the deiodonative oxonium ion **411** and the following nucleophilic attack by fluoride ion would provide the terminal cyclic ethers **409** (Scheme 82A). Furthermore, they[90b] continued this research and found that similar transformations could occur smoothly when cyclic ethers **412** were applied as the starting material. Stereoselective fluoro-, acetoxy- or trifluoroacetoxy-substituted ring-enlarged products **413** could be generated when different hypervalent iodine compounds including *p*-TolIF$_2$, PIDA or PIFA, were utilized respectively (Scheme 82B).



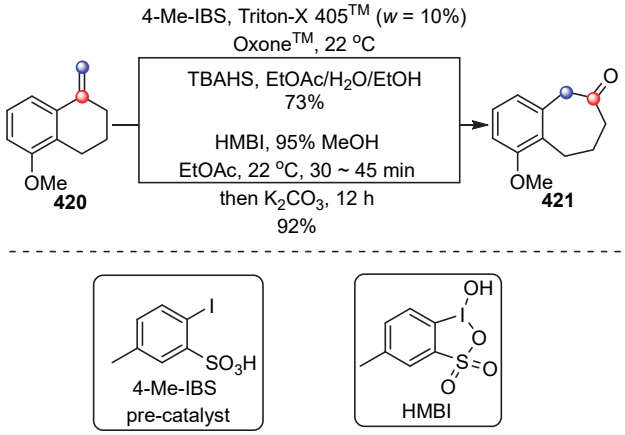
Scheme 82 I(III) species-mediated oxidative ring expansion of cyclic ethers

Exocyclic alkenes are another class of compounds that could undergo I(III) species-mediated oxidative ring expansion. In 2005, Koser and co-workers[91] described the oxidative ring expansion of alkylidenebenzocycloalkenes **414** to *β*-benzocycloalkenones **415** by using HTIB in 95% MeOH. It was presumed to be initiated from carbonium **416**, formed via the electronic attack to **414** by HTIB. Then nucleophilic attack to **416** by MeOH followed with 1,2-shift of the resulting iodonium **417** formed the six-membered carbonium **418** along with the release of PhI. Further nucleophilic attack to **418** by MeOH and the following acid hydrolysis of acetal **419** provided the final ketone **415** (Scheme 83).



Scheme 83 HTIB-mediated oxidative ring expansion of exocyclic alkenes to *β*-benzocycloalkenones.

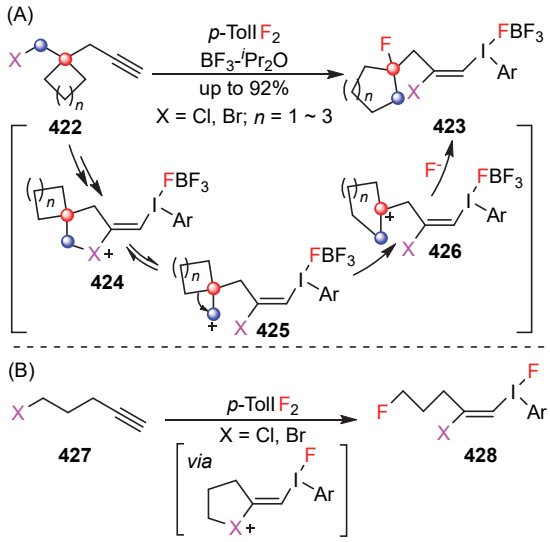
Similarly, Purohit's group[11] found that exocyclic alkenes **420** could be converted to ring-enlarged ketone **421** mediated by HMBI or I(III) species, *in situ* formed from the oxidation of pre-catalyst (4-Me-IBS) with oxone (Scheme 84).



Scheme 84 I(III) species-mediated oxidative ring expansion of exocyclic alkenes to ketone

In 2007, Ochiai's group[92a] reported an unusual *p*-TolIF$_2$-triggered domino λ^3-iodanation/1,4-halogen shift/

ring enlargement/fluorination of alkynes **422**. The reaction provided a series of (*E*)-*β*-halogenovinyl-(aryl)-λ^3-iodanes **423** via the following plausible mechanism. The addition to C≡C bond of **422** by tetracoordinated λ^3-bromane, formed *in situ* with the combination of *p*-TolIF$_2$ and BF$_3$, accomplishes with the halo shift forms the key five-membered halonium ions **424**. The following 1,2 alkyl rearrangement of carbonium **425**, the resonance form of **424**, affords carbonium **426**. Capture of the latter by fluoride releases the final olefins **423** (Scheme 85A). It is worth noting that this reaction was conducted smoothly on the basis of their own work reported in 2005 for preparing the stereo- and regioselective (*E*)-*β*-chloro and (*E*)-*β*-bromoalkenyl-λ^3-iodanes **428** via a *p*-TolIF$_2$-mediated λ^3-iodanation/1,4-halogen shift reaction of terminal alkynes **427** (Scheme 85B).[92b]

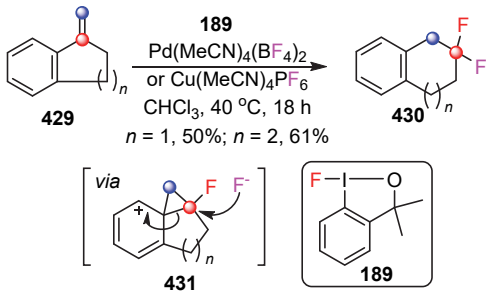


Scheme 85 Domino λ^3-iodanation/1,4-halogen shift/ring enlargement/fluorination of alkynes mediated by *p*-TolIF$_2$

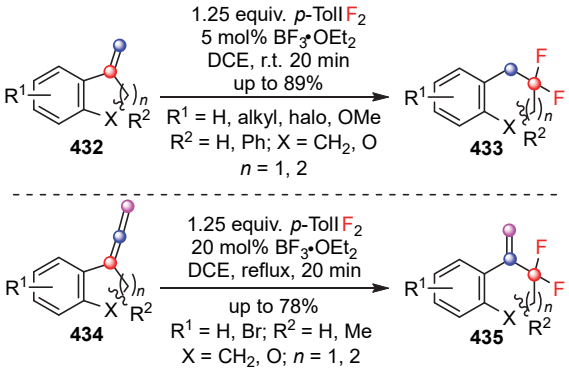
Another example is the *gem*-difluorination/ring expansion reaction of exocyclic alkenes **429** reported by Szabó and co-workers[43] in 2017. The method provided a useful approach for the synthesis of 2,2-difluoro-1,2,3,4-tetrahydronaphthalene **430** via *gem*-difluorination/ring expansion enabled by I(III) compound **189** and catalytic Pd(MeCN)$_4$(BF$_4$)$_2$ or Cu(MeCN)$_4$PF$_6$ (Scheme 86). The reaction was postulated to undergo carbonium **431** through a pathway similar to that shown in Scheme 38.

In 2019, Murphy's group[93] reported the conversion of benzo-fused carbocycles and heterocycles **432** to *gem*-difluoroalkyl arenes **433** via a *p*-TolIF$_2$-mediated difluorinative ring expansion. At the same time, allene-containing substrates **434** were also applicable to this conditions to yield allylic *gem*-difluorides **435**. Its key intermediate was similar to **436** (Scheme 87). Both of these approaches provided important fluorinated building blocks for construction of bioactive molecules.

In 2018, Li and co-workers[94] reported the synthesis of 2-arylbenzoxazinones **437** via a PIDA-triggered oxidative



Scheme 86 Difluorination/ring expansion of exocyclic alkenes induced by λ^3-iodane **189** and Pd(MeCN)$_4$(BF$_4$)$_2$ or Cu(MeCN)$_4$PF$_6$

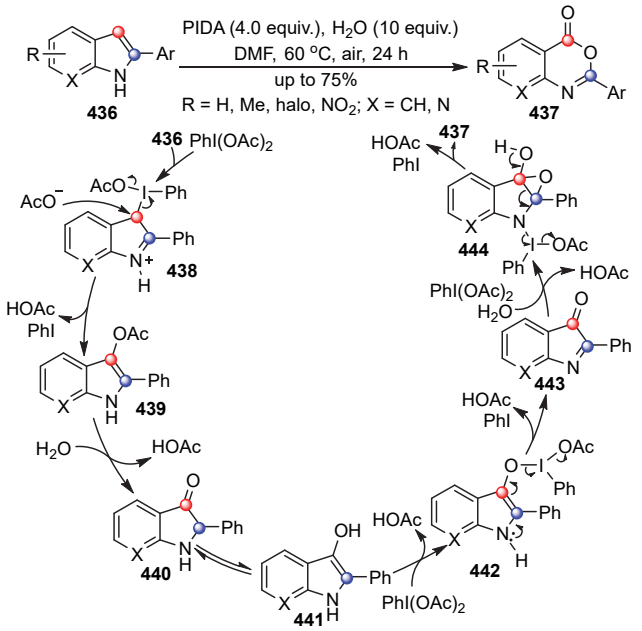


Scheme 87 *p*-TolIF$_2$-mediated difluorinative ring expansion of heterocycles and allene-containing substrates

reaction of 2-arylindoles **436** in one pot. Initially, ligand exchange reaction of PIDA with indole **436** followed by the nucleophilic attack to the resulting iminium salt **438** by acetate delivered indole **439**. Subsequently, hydrolysis of **439** gave 2-phenyl-3-oxindole **440**. Its enol tautomer **441** was further oxidized by PIDA to afford indolone **443** via the iodine(III) species **442**. Then, nucleophilic attack to **443** by H$_2$O and subsequent ligand exchange of PIDA afforded a novel Grob-type fragmentation intermediate **444**, furnishing the final ring-enlarged **437** along with the release of PhI and HOAc. It is worthy to note that H$_2$O played an important role in the reaction, which was identified by control reactions (Scheme 88).

2.1.1.7 Wagner-Meerwein rearrangement or Prins-pinacol tandem

The Wagner-Meerwein and pinacolic transpositions are also the well-known rearrangement reactions that could be realized by hypervalent iodine reagents.[95] In 2009, Canesi and co-workers[96a] found a usual PIDA-triggered homo-Wagner-Meerwein rearrangement, leading to a rapid synthesis of different types of highly functionalized dienones **446** from tertiary alcohols **445** containing a phenolic moiety (Scheme 89A). Similar to this 1,2-rearrangement, compounds **447** are also subjected to this condition to undergo a 1,3-rearrangement process (Scheme 89B).[96b] Substituted groups of **445** and **447** participating in these migration include aryl, alkyl, alkenyl and propargyl substituent. When the migratory group is an alkenyl or propargyl



Scheme 88 One-pot PIDA-triggered oxidative reaction of of 2-arylindoles leading to 2-arylbenzoxazinones

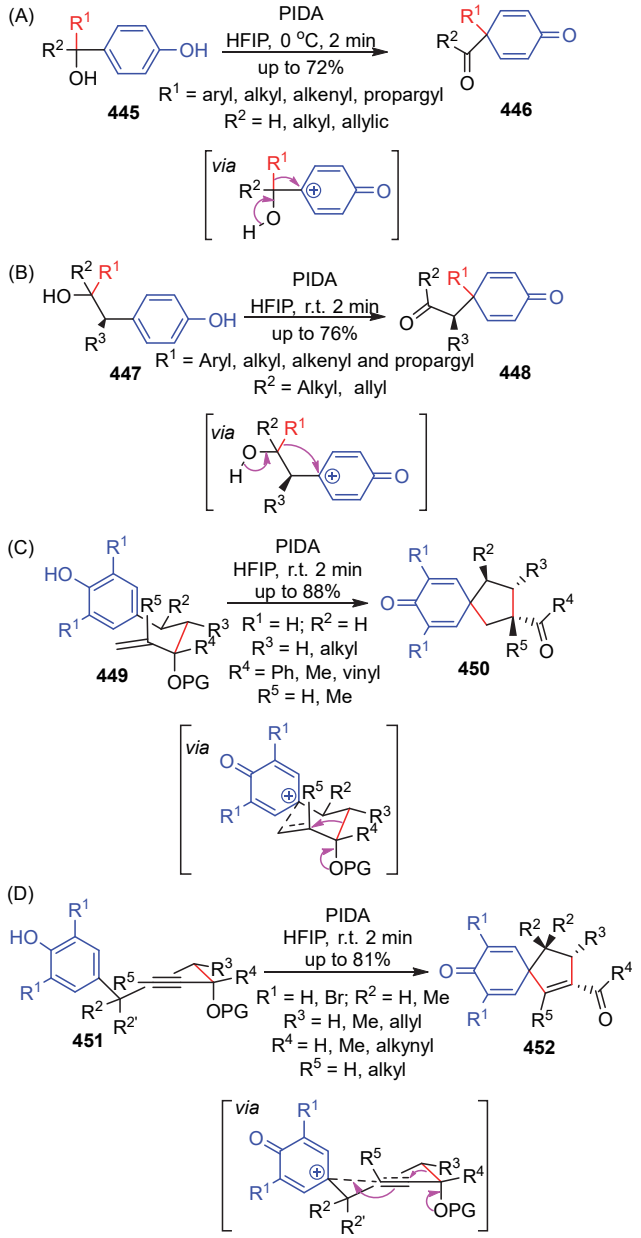
group, the reaction may also be regarded as a sigmatropic rearrangement, thus potential contraction may occur when bicyclic phenols was treated as the starting material. Additionally, via a PIDA-mediated oxidative Prins-pinacol tandem, substrates **449** and **451** are able to be converted to spiro[4.5]decanyl systems **450** and **452**, which have been found in several natural products possessing interesting biological properties (Scheme 89C, 89D).[97] Soon after, this effective method was applied for the rapid asymmetric synthesis of the main skeleton of kaurane diterpenes.[98] The successful realization of transpositions introduced above is initiated with the formation of the oxidative dearomatized intermediate from starting phenols.

2.1.2 C to N migration.

The hypervalent iodine reagents could also realize the C to N oxidative migration reactions, which can be classified into Hoffman rearrangement,[73a,99-119] Curtius rearrangement,[120-125] Beckmann rearrangement[126-127] and some other specific C to N migration reactions[128-137] including C to N migration/cyclization, ring expansion and 1,4-radical migration.

2.1.2.1 Hoffman rearrangement.

Hypervalent iodine reagents that could enable Hoffman rearrangement include λ^3-iodanes[73a,99-116] and λ^5-iodanes,[117-118] with the latter being relatively less investigated. The first I(III)-triggered Hoffman rearrangement reaction could be dated back to 1978, when Loudon and co-workers[99a] found the PIFA-mediated conversion of peptide amides **453** to isocyanates **454** and the following formation of its hydrolytic products **455** (Scheme 90A). Since then, plenty of Hoffman rearrangement of amides mediated by varied hypervalent iodine reagents have been reported, which proved that the protocol is a vital and effective

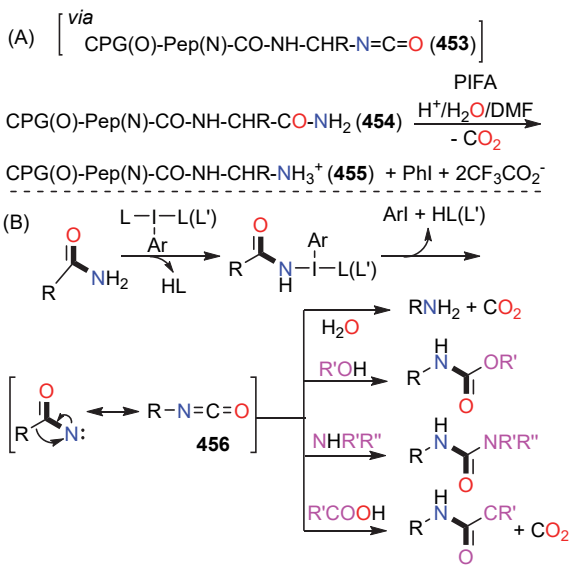


Scheme 89 PIDA-triggered Wagner-Meerwein rearrangement or Prins-pinacol tandem of tertiary alcohols containing a phenolic moiety

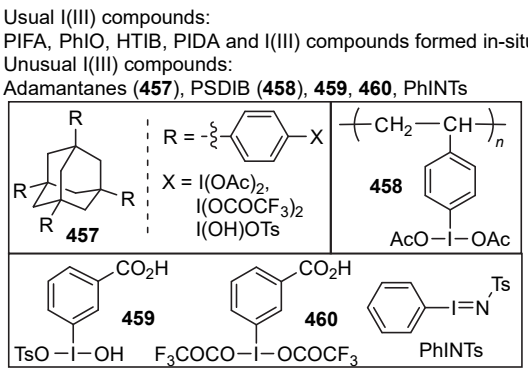
method for preparing different kinds of amines,[73a,99-105] ureas,[106-109] carbamates[109-110] and secondary amides,[105,111] as the formed isocyanate intermediate **456** from Hoffman rearrangement could continue to react with water, amine and alcohol and carboxylic acid, respectively (Scheme 90B).

Among these transformations, in addition to the commonly-used λ^3-iodanes, several unusual I(III) species, including compound **457**, **458**, **459**, **460** and PhINTs have also found application in various Hoffman rearrangement reactions (Scheme 91).[103,105,108]

Considering the limited examples of the reaction between isocyanates **456** and carboxylic acid, it necessary to introduce the specific Hoffman rearrangement/decarboxylation of primary amides **461** mediated by hypervalent io-

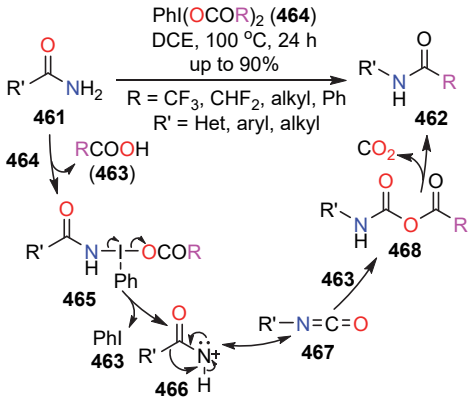


Scheme 90 General procedure of I(III)-mediated Hoffman rearrangement of amides



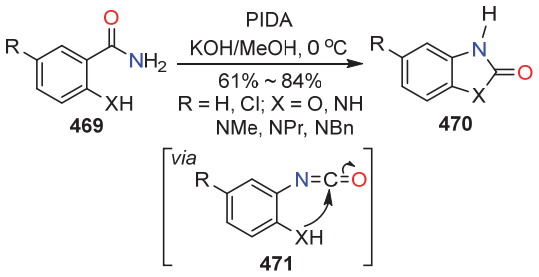
Scheme 91 Hoffman rearrangement of amides mediated by common and unusual λ^3-iodanes

dine(III) reagent **464**, in which the *in situ* formed carboxylic acid **463** took park and the secondary amides **462** was obtained (Scheme 92).[111] Initially, reaction of amides **461** with λ^3-iodanes **464** gives amidoiodane intermediate **465** as well as acid **463**. Then, reductive elimination of intermediate **465** occurs to generate a nitrenium cation **466** and releases PhI and acid **463**. Next, nitrenium **466** can be converted to isocyanate **467** via Hoffman rearrangement with the assistance of the carboxylate anion. The subsequent addition to isocyanate **467** by acid **463** affords carbamic anhydride **468**, whose decarboxylation delivers the terminal amides **462**, accompanied with extrusion of CO_2.



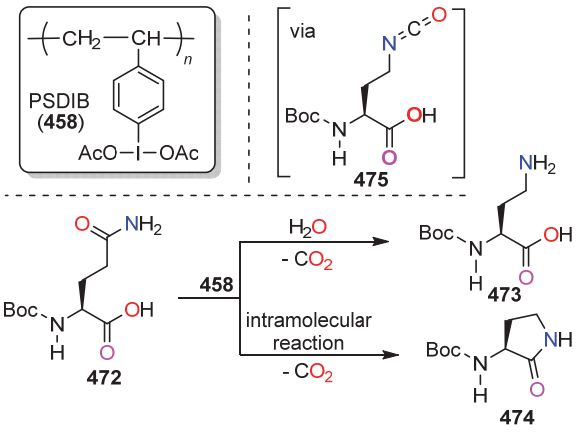
Scheme 92 Hoffman rearrangement of amides to terminal amides with I(III) compounds **464**

Furthermore, the protocol has also attracted much attention as a useful synthetic tool for synthesis of heterocyclic compounds[105,112-116] (Scheme 90B). For example, in 2001, Moriarty *et al.*[112] accomplished the synthesis of 2-benzimidazolones, 2-benzoxazolones and related compounds **470** from anthranilamides, salicylamides and some *β*-substituted amides **469**, respectively, using PIDA as the oxidant under basic conditions via an intramolecular cyclization of the isocyanate **471** formed *in situ* from the Hoffman rearrangement of **469**. The method provided a useful access to heterocyclic compounds **470** (R=4,6-di-phenyl, X=NH) possessing antibacterial activity (Scheme 93).



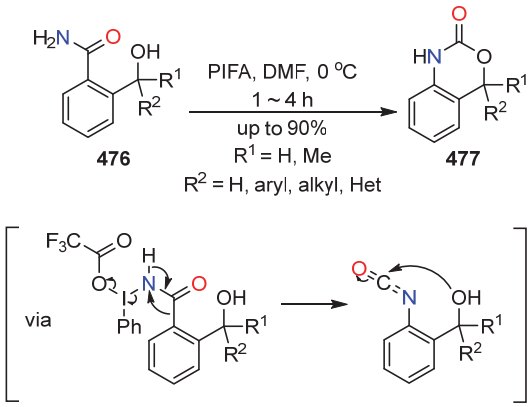
Scheme 93 Hoffman rearrangement of β-substituted amides with PIDA under basic conditions

In 2004, Yamada *et al.*[105] obtained two different Hoffman rearrangement products, *i.e.*, amino acid **473** and lactam **474**, by reacting amino acid **472** with PSDIB (**458**) via the same intermediate **475** (Scheme 94). This method once again proved one advantage of hypervalent iodine reagent-enabled Hoffman rearrangement reaction, as it permits many synthetic possibilities that were unavailable through the classical Hofmann reaction since many *N*-protecting groups and chiral substrates are sensitive to base.[102b]



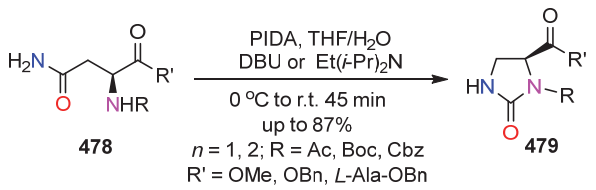
Scheme 94 PSDIB-mediated Hoffman rearrangement of amino acid

In 2007, Vlaar and co-workers[113] reported that the reaction of 2-hydroxymethylbenzamides **476** with PIFA underwent a Hoffman rearrangement/intramolecular addition tandem reaction, providing a useful access to benzoxazinone **477**, which may possess biological activities against human immunodeficiency virus or be used for the treatment of hormone-dependent cancers (Scheme 95).



Scheme 95 PIFA-mediated Hoffman rearrangement of 2-hydroxymethylbenzamides

In 2008, Tomasini's group[114] accomplished the synthesis of annular ureas **479** with protected asparagines and protected glutamines **478** through a PIDA-triggered Hoffman rearrangement under mild conditions. It is worth noting that the chirality of the substrate was kept intact during the transformation (Scheme 96).

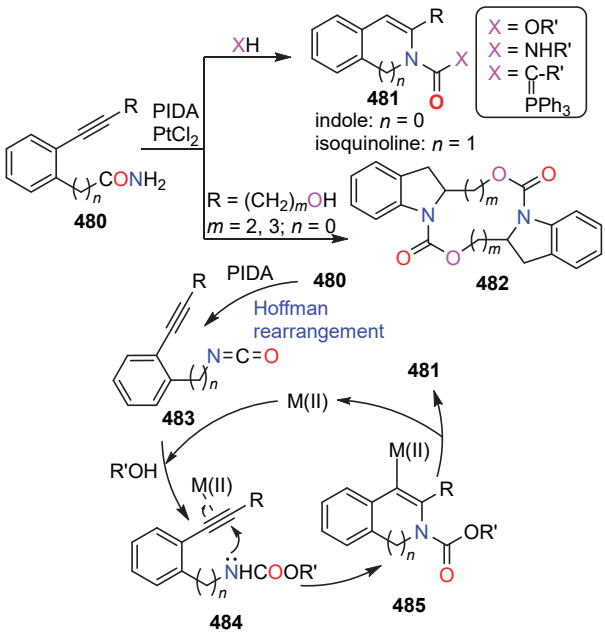


Scheme 96 PIDA-mediated Hoffman rearrangement of asparagines and glutamines

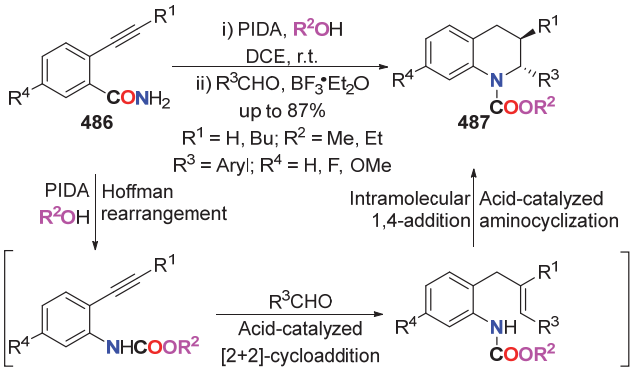
In 2009, Yanada and co-workers[115a] presented a concise access to isoquinolines **481** and indoles **482** by treating amides **480** with PIDA in the presence of catalytic $PtCl_2$. The mechanistic pathway involves a Hoffman rearrangement/cyclization tandem. Initially, isocyanate **483** was formed from the nucleophilic attack to PIDA by amide **480** and the following Hoffman rearrangement. Then, alcoholysis of **483** followed by activation of alkyne moiety by metal gave intermediate **484**. Finally, the hydrolytic product **481** was formed via an intramolecular cyclization process (Scheme 97).[115b]

In 2011, the same group[116] completed the synthesis of quinolones **487** from 2-alkynylbenzamides **486**, which was realized via a one-pot PIDA-triggered Hoffman rearrangement/acid-catalyzed [2+2]-cycloaddition/acid-catalyzed aminocyclization tandem (Scheme 98).

λ^5-Iodanes could also be utilized to realize the Hoffman



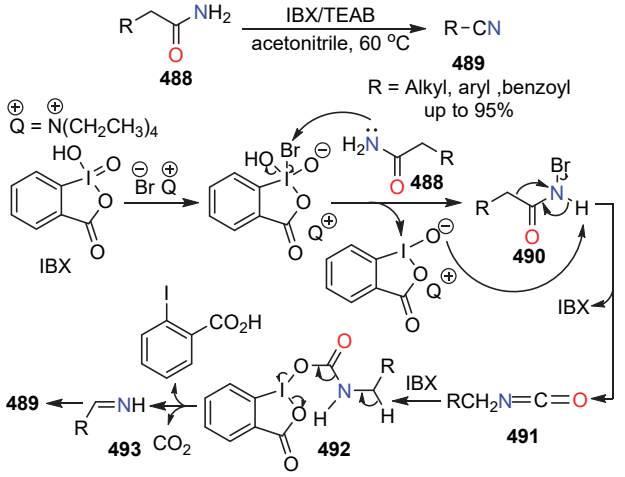
Scheme 97 A Hoffman rearrangement/cyclization tandem of amides to isoquinolines and indoles



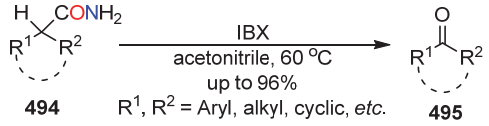
Scheme 98 Synthesis of quinolones from 2-alkynylbenzamides involving a PIDA-triggered Hoffman rearrangemen

rearrangement reaction.[117-118] In 2007, Akamanchi's group[117] reported a concise method for preparing one-carbon dehomologated nitriles **489** in moderate to high yields from the reaction of primary carboxamides **488** with IBX and TEAB under heat (Scheme 99). Mechanically, addition of TEAB to IBX followed with the oxidation of amide **488** led to the formation of *N*-bromoamide **490**, whose subsequent rearrangement formed isocyanate **491**. Nucleophilic attack to **491** by IBX provided the intermediate **492** along with the release of 2-iodobenzoic acid. Decomposes of the latter and the further rapid oxidation of the resulting imine **493** generated the final nitrile **489**.

Furthermore, they[118] realized the preparation of one-carbon-shorter ketones **495** using α,α-disubstituted acetamides **494** as substrate and IBX as oxidant, utilizing the same conditions via a similar pathway as above (Scheme 100).



Scheme 99 Synthesis of one-carbon dehomologated nitriles from primary carboxamides involving a IBX/TEAB-triggered Hoffman rearrangement

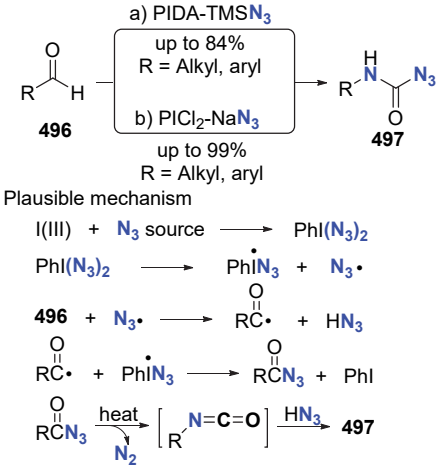


Scheme 100 Synthesis of one-carbon-shorter ketones from α,α-disubstituted acetamides involving a IBX-triggered Hoffman rearrangement.

2.1.2.2 Curtius rearrangement

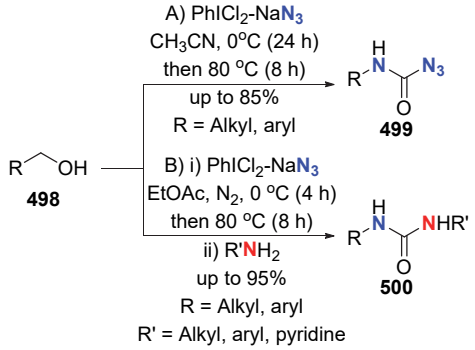
Curtius rearrangement triggered by combination of PhIO/$TMSN_3$ or PIFA/$TMSN_3$[120-123] can also generate the isocyano-containing species, as the one generated by the I(III)-triggered Hoffman rearrangement.[73a,99-116] Actually, the combination of λ^3-iodanes/$TMSN_3$ or λ^3-iodanes/NaN_3 was proved to be good alternative of IN_3 in azidation applications.[120-125] For example, in 2005, Bols and co-workers[120] found that the system of PIDA/$TMSN_3$ was capable of converting aldehydes **496** to carbamoyl azides **497** through an I(III)-mediated Curtius rearrangement/nucleophilic substitution (Scheme 101a). In 2008, Zhang's group[121] realized the same transformation of aldehydes **496** in the system of $PhICl_2$/NaN_3. A radical pathway and a following Curtius rearrangement were proposed for explaining this transformation (Scheme 101b). Initially, azido-hypervalent iodine reagent, formed *in situ* via the ligand exchange reaction of λ^3-iodanes and azido source, rapidly releases the iodo radical and azido radical. Subsequent trap of the latter by aldehydes **496** gives an acyl radical and hydrazoic acid. Bonding of the acyl radical with azido radical affords acyl azide, which further generates an isocyano intermediate under heat along with the release of nitrogen via a Curtius rearrangement. Finally, capture of the isocyano intermediate by the *in situ* formed hydrazoic acid furnishes the desired carbamoyl azides **497**.

Furthermore, Zhang's group[122] continued to realize the $PhICl_2$-mediated Curtius rearrangement of alcohols **498**. Corresponding carbamoyl azides **499** could be generated



Scheme 101 I(III)-Mediated Curtius rearrangement of azides leading to carbamoyl azides

smoothly in high yields (Scheme 102A). Interestingly, substituted ureas **500** were synthesized successfully when additional amine was added under the reaction conditions described above (Scheme 102B).[123]



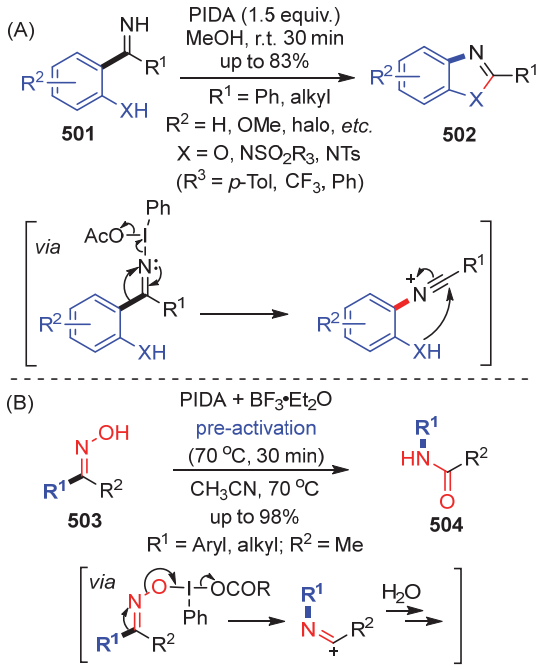
Scheme 102 $PhICl_2$-Mediated Curtius rearrangement of alcohols

2.1.2.3 Beckmann rearrangement.

The iodine-mediated Beckmann rearrangement of ketoximes delivering amides was reported by Ganguly[126a] and Liu[126b] in 2010 and 2012, respectively. Soon after, λ^3-iodane-triggered Beckmann rearrangement reaction was also realized. In 2015, Xiong and co-workers[127a] reported a Beckmann rearrangement/intramolecular cyclization cascade of imine **501** in the presence of PIDA, providing an alternative access to benzoxazoles and benzimidazoles **502** (Scheme 103A). In 2018, Miki *et al.*[127b-127c] described an I(III)-triggered Beckmann rearrangement/hydrolysis/elimination reaction of ketoximes **503** and successfully prepared amides **504** in high yields. The key λ^3-iodane is formed from the activation of PIDA by BF_3•Et_2O under heat (Scheme 103B).

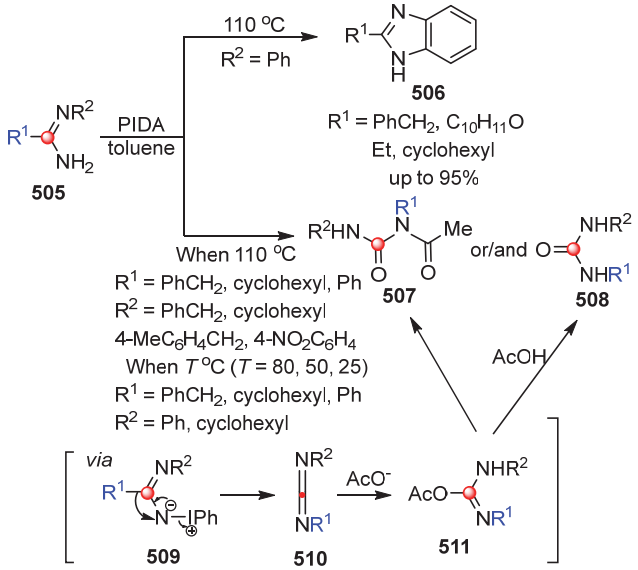
2.1.2.4 Other C to N migration.

In 1997, Ramsden[128] treated *N*-substituted amidines **505** with PIDA in toluene at 110 ℃ and obtained the nonmigratory 2-benzylbenzimidazoles **506** when the R^2 substituent of **505** is a phenyl group. While unexpected



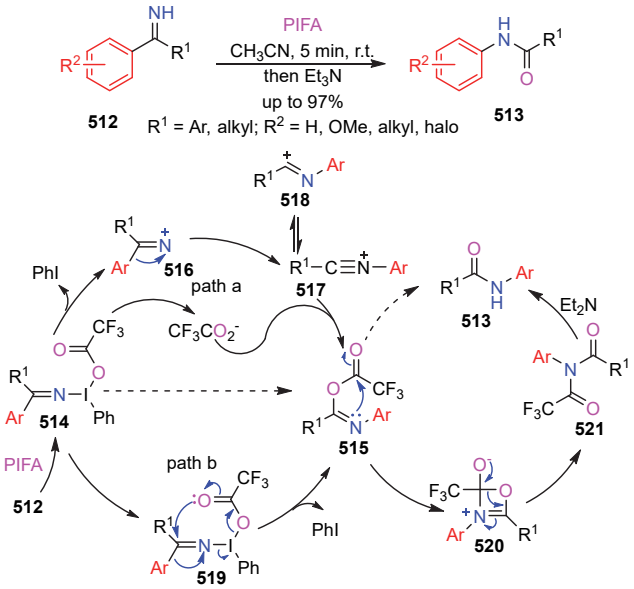
Scheme 103 Beckmann rearrangement mediated by λ^3-iodane

migration occurred to afford the *N*-acetylurea **507** or/and urea **508** derivatives under other conditions such as decreasing reaction temperature or changing R^1 and R^2 group of **505**. They postulated that the migration involved the C-N migration of an ylide intermediate **509**, leading to the formation of carbodiimide **510**. The latter was nucleophilically attacked by acetate anion, released from PIDA, to give intermediate **511** or/and the further migratory compounds **507** and **508**. Meanwhile, the application of PIFA in this transformation is feasible, too (Scheme 104).



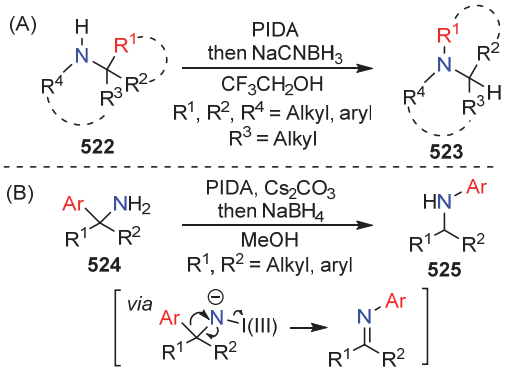
Scheme 104 C-N migration *N*-substituted amidines mediated by PIDA

Recently, Zhao and co-workers[129] successfully synthesized amides **513** with N-H ketimines **512** and PIFA through an PIFA-mediated C-N migration. Initially, ligand exchange reaction of PIFA with **512** gives species **514**. Then, elimination of PhI and the following 1,2-C to N migration of the resulting intermediate **516** leads to the formation of nitrilium **517**, the resonance form of iminium **518** (path a). Nucleophilic attack to **517** by *in situ* generated trifluoroacetic acid anion affords the key intermediate **515**. A subsequent 1,3 O to N trifluoroacetyl transfer, which is similar to Mumm rearrangement, furnished *N*-trifluoroacetyl amide **521** via the four-membered intermediate **520**. Finally, the trifluoroacetyl group of **521** could be selectively removed by further treatment with Et_3N and produces ketimines **513**. Another possible pathway involving a concerted elimination and an intramolecular rearrangement is also proposed for explaining the conversion of **514** into **515** (path b) (Scheme 105).



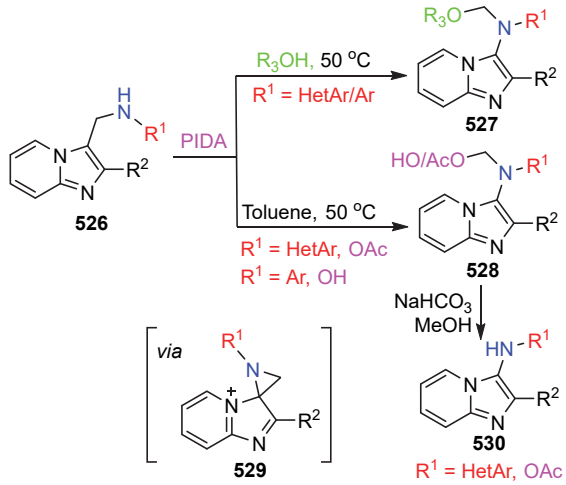
Scheme 105 C-N migration of N-H ketimines by employing PIFA

In 2018, Murai's group[130] reported a PIDA-triggered C-N migration/reduction and converted secondary amine **522** to ring-enlarged tertiary amines **523** (Scheme 106A). Additionally, primary amine **524** is also proved to be applicable to this transformation, affording secondary amine **525** as the product (Scheme 106B).[131]



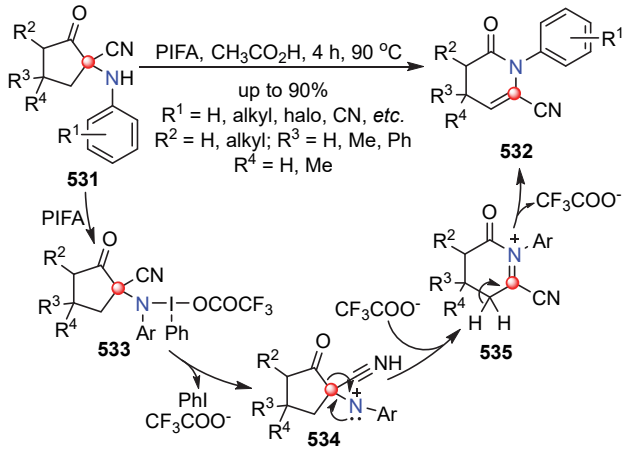
Scheme 106 C-N migration of primary and secondary amines triggered by PIDA

Another special I(III)-mediated C-N migration was the PIDA-mediated conversion of imidazo[1,2-*a*]pyridines **526** to imidazo[1,2-*a*]pyridin-3-amines **527** and **528** conducted in alcohol and toluene respectively, reported by Kumar and co-workers[132] in 2020. It was achieved successfully via the C-N migration of the key three-membered cyclic intermediate **529**. *N*-Acetoxymethyl group of **528** could be further removed to access 3-(pyridin-2-yl)aminoimidazo-[1,2-*a*]pyridines **530** in the presence of base (Scheme 107).



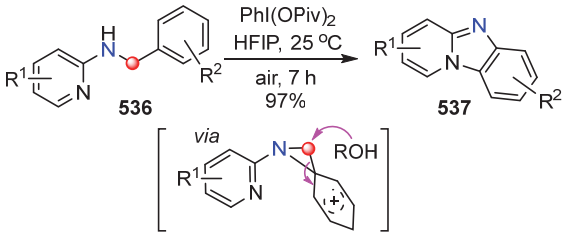
Scheme 107 C-N migration of imidazo[1,2-*a*]pyridines to prepare imidazo[1,2-*a*]pyridin-3-amines by employing by PIDA

In 2020, Das and co-workers[133a] reported a one-pot PIFA-induced ring expansion/lactamization of substituted cyclopentanones **531** on the basis of their previous work[76], providing a series of *N*-aryl-*δ*-valerolactams **532**. This reaction may initiate from the activation of **531** by PIFA to give intermediate **533**, followed by the generation of unusual nitrenium ion **534**.[133b] The rearrangement of the latter gave iminium intermediate **535** and the succedent tautomerization facilitated by conjugate base would release the final lactams **532** (Scheme 108).



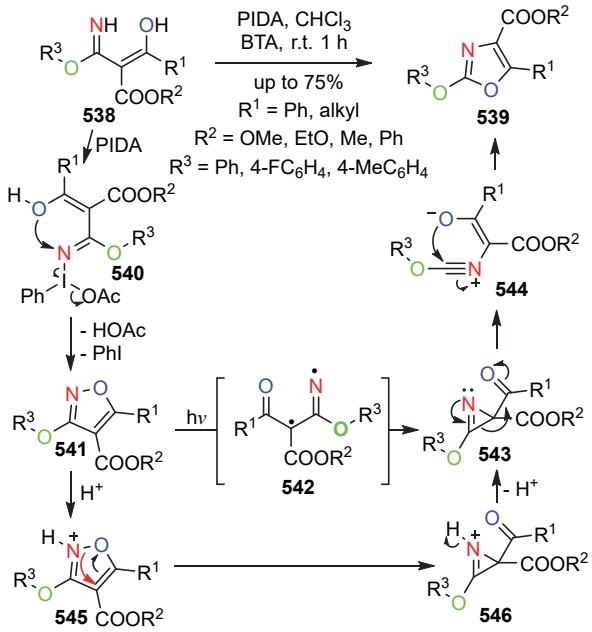
Scheme 108 One-pot PIFA-induced ring expansion/lactamization of cyclopentanones to *N*-aryl-*δ*-valerolactams

Some exclusive C-N migration/cyclization could also be realized by the hypervalent iodine reagent. In 2013, Zhu's group[134] demonstrated synthesis of pyrido[1,2-*a*]benzimidazoles **537** via a PhI(OPiv)$_2$-mediated C-N migration/cyclization of *N*-benzyl-2-aminopyridines **536**. This transformation occurred through an unusual *ipso* S_EAr reaction and subsequent solvent-assisted C—C and C—N bond cleavage (Scheme 109).



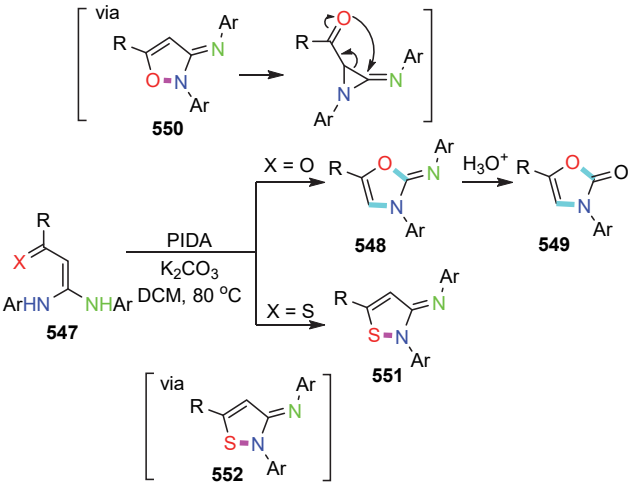
Scheme 109 PhI(OPiv)$_2$-mediated C-N migration/cyclization of *N*-benzyl-2-aminopyridines

In 2016, Xiong's group[135] reported an alternative approach for preparing cyclic compounds, 2,4,5-trisubstituted oxazoles **539** via a PIDA-mediated oxidative rearrangement of 3-hydroxybut-2-enimidates **538**, though the scope of substrates is limited (Scheme 110). Mechanically, the intramolecular nucleophilic attack of OH group on intermediate **540** to its nitrogen moiety, formed from the interaction of starting material **538** with PIDA, gave the cyclic product **541**. The latter could undergo two plausible pathways to afford the three-membered cyclic species **543**. One is protonation of **541** and subsequent *σ*-bond shift of resulting **545** and a following deprotonation of **546**. The other is a radical pathway of **541**, which would release free radical species **542** via homolytic cleavage of N—O bond and π-bond shift and then reached **543**. Intramolecular ring opening of **543** and nucleophilic attack of the resulting nitrile ylide **544** afforded the terminal oxazoles **539**.



Scheme 110 PIDA-mediated oxidative rearrangement of 3-hydroxybut-2-enimidates

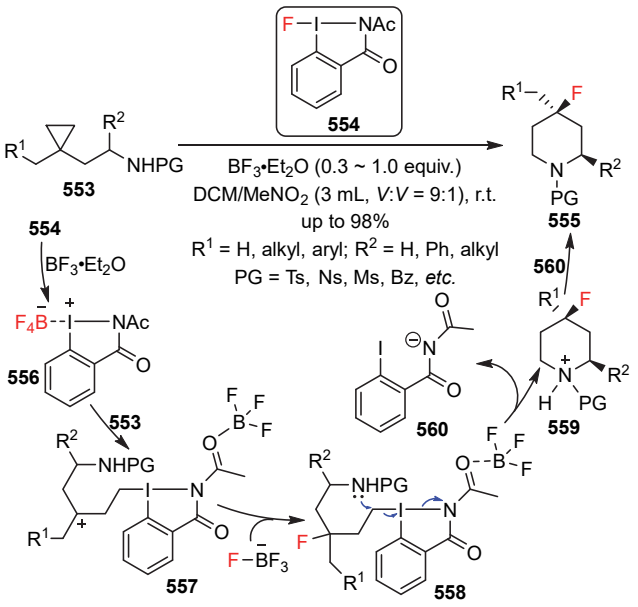
Additionally, in 2016, Yu and co-workers[136] synthesized a series of substituted oxazolines **548** and its subsequent hydrolytic products **549** with *α*-*oxo*-ketene *N*,*N*-acetals **547** through a PIDA-mediated Baldwin rearrangement. Differently, non-rearranged isothiazoline analogues **551** would be generated from *α*-*oxo*-ketene *N*,*S*-acetals **547** due to the better stability of N—S bond of intermediate **552** than the N—O bond of **550** under the reaction conditions (Scheme 111).



Scheme 111 Oxidative rearrangement of *α*-oxo-ketene *N*,*N*-acetals mediated by PIDA

It is worth noting that a ring expansion/fluorination of unactivated cyclopropanes **553** was found by Zhang's group,[137a] who utilized a new monofluoroiodane(III) reagent **554** as the fluorine source and provided a good protocol to medicinally relevant 4-fully substituted fluoropiperidines **555** with excellent regio- and diastereoselectivity. Mechanically, the activation of compound **554** by BF_3•Et_2O gives the λ^3-iodane **556**. Electrophilic attack to the sterically hindered C—C bond of **553** by activated λ^3-iodane **556** gives carbocationic species **557**. Then the tetrafluoroborate anion present in the system fluorinates the tertiary carbocation of **557**, and boron trifluoride activates the carbonyl oxygen of the acetyl group to generate intermediate **558**, which further polarizes the C—I(III) bond. Then, intramolecular nucleophilic attack to the C—I(III) bond of **558** by its amino group delivers the cyclic species **559** and imide anion **560**. The latter works as a base and captures a proton from 559 to give the termanal product **555** (Scheme 112).

In 2015, Shi and co-workers[137b] accomplished the conversion of *γ*,*γ*-disubstituted triflic amides **561** to C-N aryl migratory products **562** in the presence of PIFA and sliver catalyst via a 1,4-radical migration involving C—C bond cleavage and formation of new C—O/C—N bonds. Furthermore, γ-hydroxy amines and tetrahydroquinoline analogues were obtained from **562** in the subsequent transformations (Scheme 113). First, deprotonated product of **561** was coordinated to sliver catalyst and formed Ag



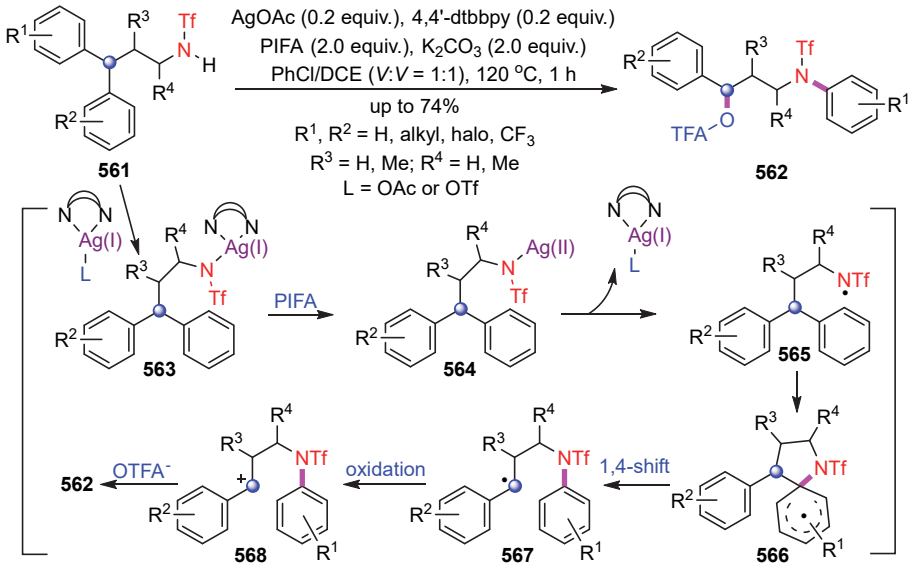
Scheme 112 Ring expansion/fluorination of cyclopropanes to fluoropiperidines triggered by I(III) reagent **554**

complex **563**, whose center became very electron-rich and thus was easily oxidized to Ag(II) complex **564** by PIFA. Subsequent homolytic cleavage of the N—Ag bond occurred to generate the electron-withdrawing *N*-centered radical **565** along with Ag(I) species. Intramolecular attack on the phenyl ring of the latter afforded an σ-complex intermediate **566** via dearomatization. A following 1,4-aryl migration of **566** generated a relatively stable benzylic radical **567**, which would be further oxidized to cation **568** via oxidation. Final reaction of trifluoroacetate with **568** delivered products **562**.

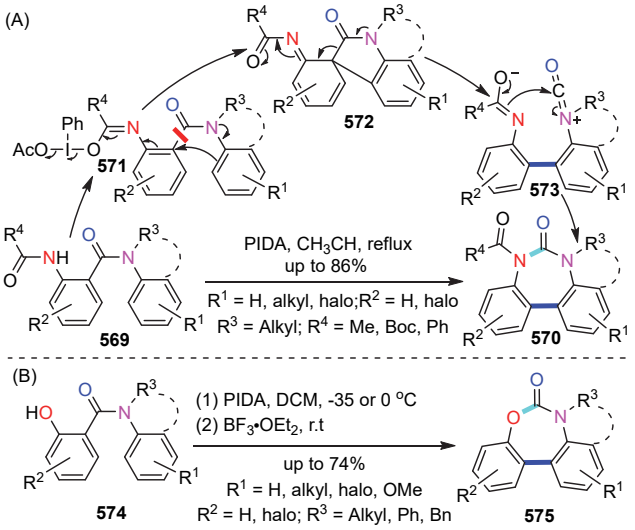
2.1.3 C to O migration

Despite the limited examples involving C to O migration by hypervalent iodine reagents, it is worth noting that in 2014, Zhao and Du *et al.*[138] reported an exclusive PIDA-triggered intramolecular oxidative cyclization of 2-substituted *N*-phenylbenzamides **569** and obtained a series of lactamization compounds **570**. Mechanically, reaction of **569** and PIDA gives intermediate **571** and acetic acid. Subsequently, nucleophilic *ipso*-attack of the aniline ring on the electron-deficient aromatic carbon atom of the anthranilic ring in **571** affords the *spiro*-intermediate **572**. Following ring opening of the latter gives rise to the intermediate **573** due to the presence of the electron-withdrawing acyl group on the imine N and the lone pair on the amide N. The final lactamization of **573** generates **570** (Scheme 114A). Similarly, amides **574** is also suitable for this intramolecular oxidative migration/cyclization reaction, leading to the synthesis of the corresponding lactonization compounds **575** at lower temperature (Scheme 114B).

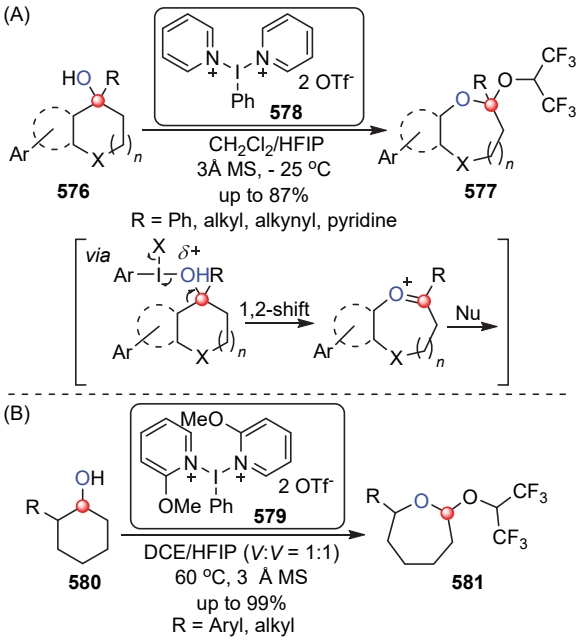
In 2016, Wengryniuk and co-workers[139a] reported the ring expansion of benzylic alcohols **576** in the presence of a novel bis(pyridinium) hypervalent iodine reagent **578** via



Scheme 113 1,4-Radical migration of γ,γ-disubstituted triflic amides mediated by PIFA and sliver catalyst



Scheme 114 Exclusive intramolecular oxidative migration/cyclization of *N*-phenylbenzamides and amides triggered by PIDA



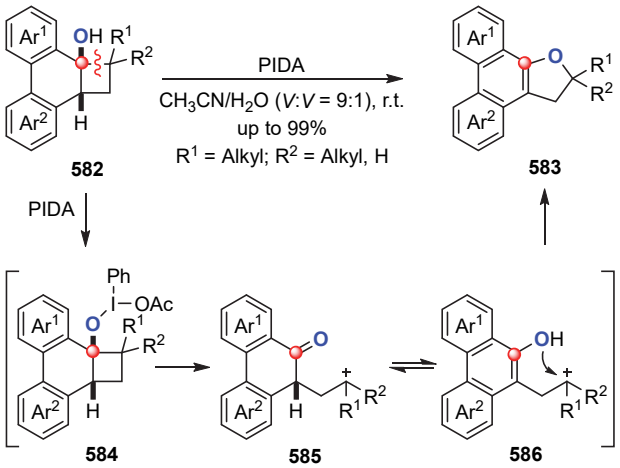
Scheme 115 Oxidative rearrangement of alcohols mediated by bis(pyridinium) hypervalent iodine reagent

an oxidative rearrangement, providing a facile access to seven- or eight-membered cyclic ethers **577**. It was regarded as the first synthetic application of this type of (poly)cationic λ^3-iodane (Scheme 115A). In 2018, another methoxy-containing bis(pyridinium) hypervalent iodine reagent **579** was prepared by them and further applied to the synthesis of ethers **581** via the similar oxidative rearrangement of secondary alcohols **580** (Scheme 115B).[139b]

In 2021, Takasu and co-workers[140] demonstrated the PIDA-mediated oxidative ring expansion of aryl-fused bicyclo[4.2.0]octanols **582**, providing a useful method for preparing dihydrofuran-containing polycyclic aromatic compounds **583**. The key steps of this transformation involve the generation of the Keto-type intermediate **585** as well as the intramolecular nucleophilic reaction of its tautomer **586** (Scheme 116).

2.2 X—C migration (X=N, O, S, Si or I)

Hypervalent iodine reagents are able to mediate not only C—C or C—N oxidative migratory transformation but also X—C migration (X=N, O, S, Si or I), though known examples of the latter are fewer than those of the former. In 2015, Gulder *et al.*[141] reported an interesting debenzoacylation/bromation of imides **587** and synthesized a series of *α*,*α*-dialkylated *α*-hydroxy carboxylamides **588**, which was accomplished via a N-C migration mediated by bromo-containing I(III) species **589** formed *in situ* from the combination of amide **590** with NBS. Initially, an electrophilic addition of I(III) species **589** to C=C bond of

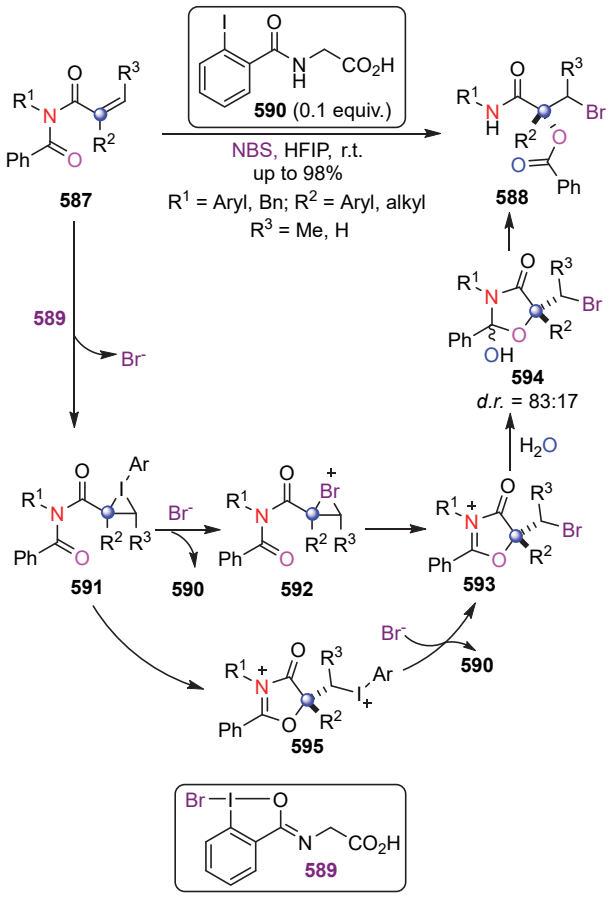


Scheme 116 PIDA-mediated oxidative ring expansion of bicyclo[4.2.0]octanols to access dihydrofuran-containing polycyclic aromatics

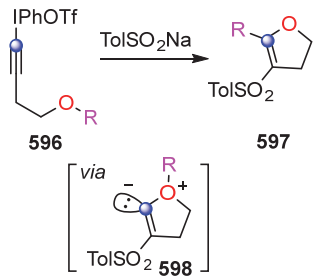
imides **587** gave the I(III) compound **591** as well as bromide. Subsequent nucleophilic ring opening by bromide generated the bromonium ion **592** along with amide **590**. An intramolecular nucleophilic attack of the carboxyl group in compound **592** opened the ring and afforded the five-membered cyclic iminium **593**. Alternatively, an intramolecular process of intermediate **591** and following substitution of the iodine(III) moiety of the resulting oxazolonium **595** by bromide gave rise to **590** and the key intermediate **593**, whose hydrate **594** was identified indirectly by isolation and characterization. Finally, the oxazolidin-4-one ring **594** was opened and gave the desired product **588** (Scheme 117).

So far, the only example of O-C migration mediated by λ^3-iodane compound was the 1,2-alkyl rearrangement of 1-hydroxybut-3-ynyliodonium ethers **596** mediated by sodium *p*-toluenesulfinate, reported by Feldman[142] in 2000. The transformation was accomplished via a five-membered cyclic ylide intermediate **598**, which could be also treated as an important part of Stevens rearrangement. It provides a convenient access to 2-substituted-3-*p*-toluenesulfonyldihydrofuran compounds **597** (Scheme 118).

In 2013, Nevado and co-workers[143] reported a radical pathway to access oxindoles **600** or indolones **601** from conjugated tosyl amides **599**, utilizing Togni's reagent and copper catalyst via a trifluoromethylation/S-C migration/desulfonylation cascade. Mechanically, Togni's reagent and copper catalyst first formed the Cu^{II} calalyst **602** *in situ*. Treatment of the latter with conjugated tosyl amides **599** generated the key intermediates **603**, which were converted to amide radicals **605** via the cyclic radical **604** followed with a subsequent release of a molecular SO_2. Hydrogen abstraction of **605** yielded the trifluoromethylation/migration/desulfonylation product **600** when R^1 of **599** is an aryl group, while trifluoromethylation/migration/desulfonylation/cyclization product **601** were formed via intermediate **606** when R^1 is an alkyl group (Scheme 119).

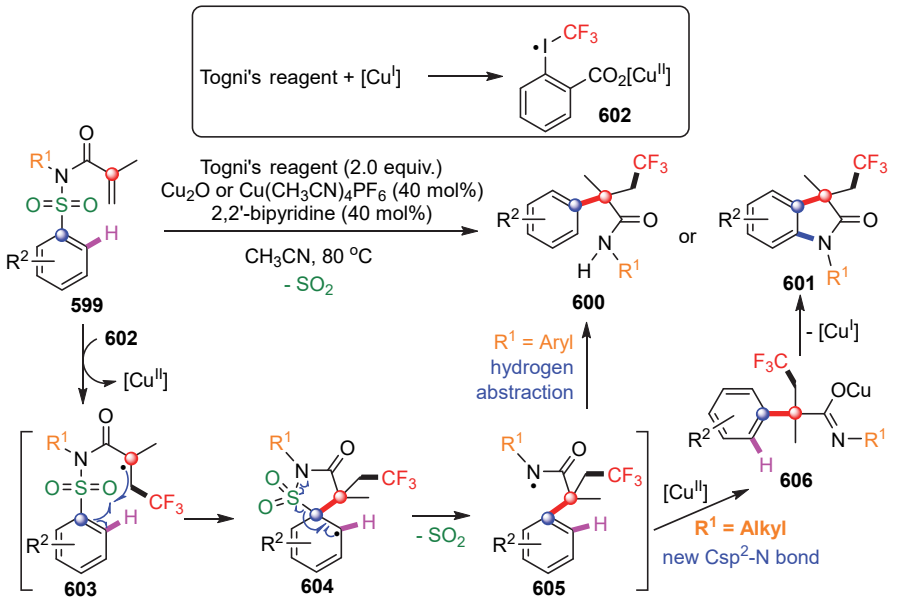


Scheme 117 N-C migration of imides to *α*,*α*-dialkylated *α*-hydroxy carboxylamides triggered by bromo-containing λ^3-iodane **575** formed *in situ*

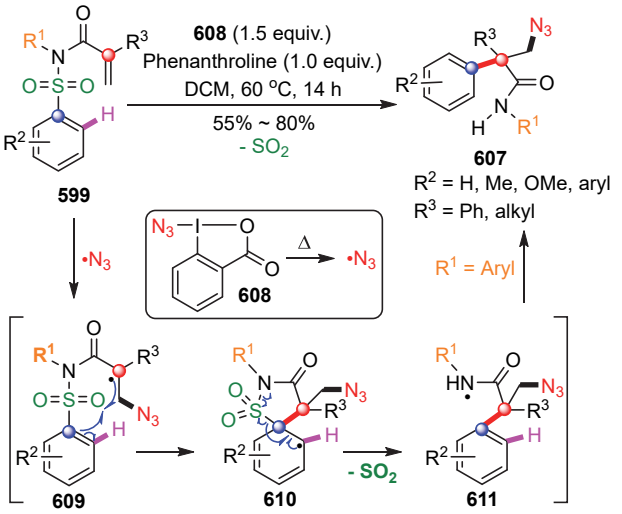


Scheme 118 Stevens rearrangement of ethers to 2-substituted-3-*p*-toluenesulfonyldihydrofurans involving λ^3-iodane compound

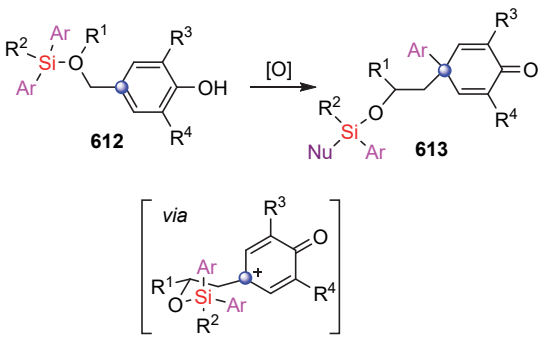
Furthermore, it is necessary to note that they also employed a similar protocol to access *α*-aryl-*β*-azido amides **607** with conjugated tosyl amides **599** mediated by azido-containing λ^3-iodane **608** via a radical azidation/S to C migration/desulfonylation pathway (Scheme 120)[144]. Differently, azido radical was generated directly by heat, without the participation of metal catalyst. The proposed mechanism is that the azide centered radical interacted with the activated alkene to give a new C(sp^3)—N bond and an *α*-alkyl radical intermediate **609**. A 5-*ipso* cyclization then took place on the aromatic ring generating aryl radical **610**, which led to amidyl radical **611** upon re-aromatization with concomitant desulfonylation.



Scheme 119 Radical trifluoromethylation/migration/desulfonylation cascade of tosyl amides mediated by the combination of Togni's reagent and Cu^{I} calalyst



Scheme 120 Radical azidation/aryl migration/desulfonylation cascade of ascade of tosyl amides mediated mediated by λ^3-iodane **608**



Scheme 121 PIDA-mediated aryl *ipso*-rearrangement of phenolic derivatives to ketones.

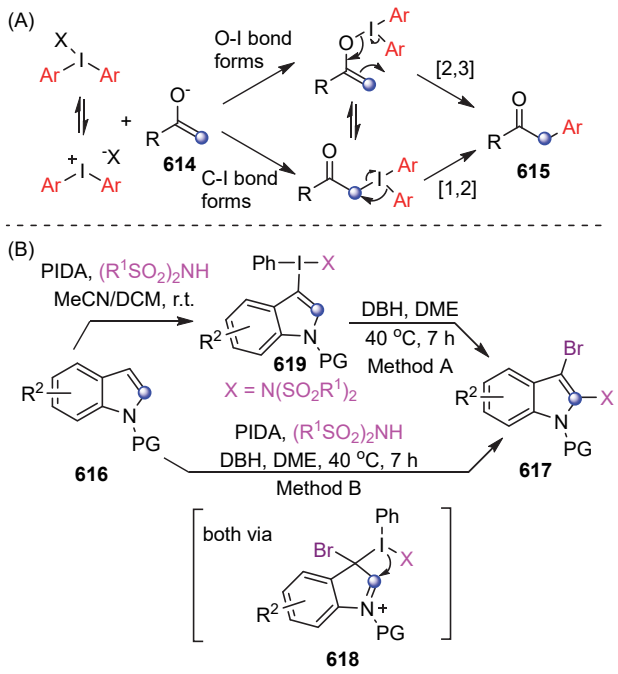
Functionalized oxindoles **607** were obtained in a completely regioselective fashion. In addition, similar transformations for accessing other functionalized heterocyclic scaffolds were reported by them in 2015.[145]

In 2012, Canesi's group[146] reported a PIDA-mediated long-distance aryl *ipso*- Si to C rearrangement of phenolic derivatives **612** containing a lateral chain of silyl segment to synthesize ketones **613** under mild conditions (Scheme 121). This reaction was regarded as a potent access to natural products.

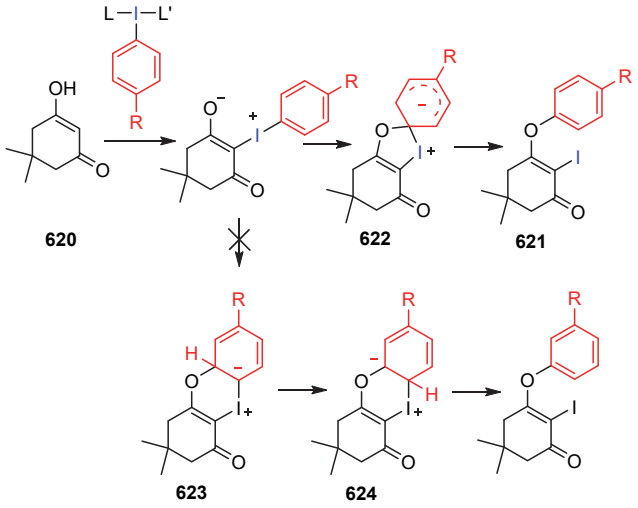
Aside from the *α*-arylation of enolates **614** accessing ketones **615** via two plausible I to C migratory pathways (*i.e.* 1,2- or 2,3-migration) described by Norrby's group[147] in 2010 (Scheme 122A), the other interesting example of I — C migratory transformations is the one-pot PIDA-triggered bromination/1,3-migration/amination of indoles **616** with sulfamides, delivering dual functionalized indoles **617**, reported by Moriyama and Togo[148] in 2015. It was achieved via the I — C migration of indolyl(phenyl)iodonium imides intermediate **618** (method B). Alternatively, I(III) species **619** was prepared and isolated first via the ligand exchange reaction of indoles **616** with the *in situ* formed sulfamide-containing I(III) compound from the combination of PIDA and sulfamide. Finally, bromination of compound **619** in the presence of DBH could also generate indoles **617** (Scheme 122B).

2.3 I to X migration(X=O or N)

In 1970, Takaku *et al.*[149] reported a PIDA-mediated Smiles-type rearrangement of 3-hydroxy-5,5-dimethylcyclohex-2- en-1-one **620** and obtained the I to O migratory product 2-iodo-5,5-dimethyl-3-phenoxycyclohex-2-en-1-ones **621** (Scheme 123). Given the obtained migratory iodides **621**, this 1,4-migration was believed to undergo



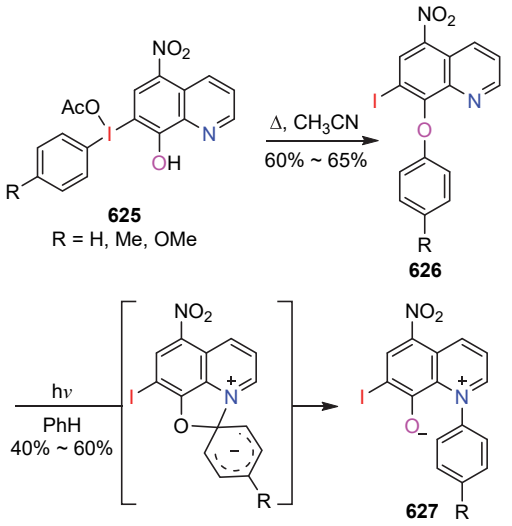
Scheme 122 Hypervalent iodine-mediated I-C migratory transformations



Scheme 123 Smiles rearrangement of allyl alcohol to access ether mediated by λ^3-iodane species

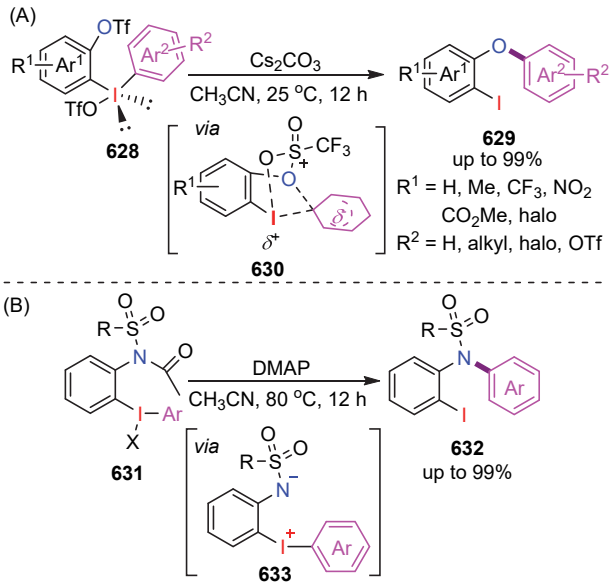
through a five-membered cyclic intermediate **622** but not the six-membered intermediate **623** or the subsequent species **624**. Furthermore, Kappe, Moriarty, Spyroudis and Kim *et al.* respectively employed this protocol to prepare heterocyclic compounds and found that this reaction was preferable under heat.[150]

Interestingly, Spyroudis *et al.*[151] reported the similar I to O migration of aryliodonio-quinoline-8-olates **625** and obtained the migratory product **626**, which could be further converted to the O to N migratory product 7-iodo-5-nitro-1-phenylquinolin-1-ium-8-olates **627** under irradiation (Scheme 124). 4-Aminocoumarin could also be applied as a good substrate for this transformation.[152]



Scheme 124 Smiles rearrangement of aryliodonio-quinoline-8-olates involving λ^3-iodane species

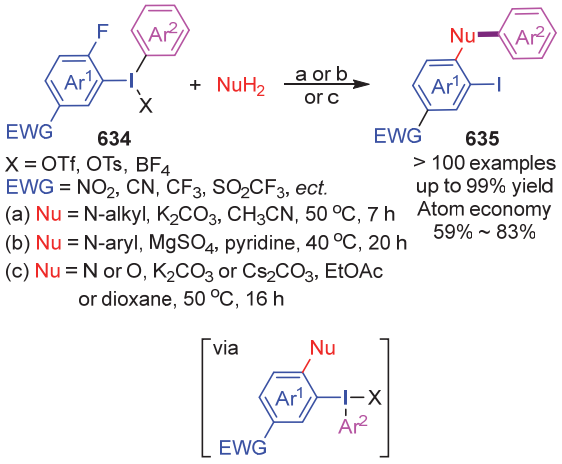
In recent years, Han, Wang and Olofsson have refreshed this type of transformations. In 2018, Han and Wang *et al.*[153] described an intramolecular I to O aryl-migration of *ortho* OTf-containing diaryliodonium salts **628** promoted by base, accessing *ortho*-iodo diaryl ethers **629** smoothly via intermediate **630**, originated from the sulfonyl directed nucleophilic aromatic substitution (Scheme 125A). Similarly, in 2020, they[154] further reported the deacetylative/I-N aryl-migration of diaryliodonium salts **631** and obtained *ortho*-iodo *N*-aryl sulfonamides **632** in the presence of 4-dimethylaminopyridine (DMAP) via the zwitterionic iodoniums **633** (Scheme 125B). Both these reactions expend the application of diaryliodonium salts.



Scheme 125 Intramolecular aryl-migration of diaryliodonium salts

In 2022, Olofsson *et al.*[155] reported a one-pot metal-free diarylation of *N*- and *O*-nucleophiles of diaryliodonium

salts **634**, accessing a series of di- and triarylamines and diaryl ethers **635** in one single step (>100 examples). Aliphatic amines, anilines, ammonia, and even water are suitable for this diarylation under mild conditions, revealing its good functional group tolerance. The transformation proceeds smoothly through the first unique pathway where the iodine(III) moiety and the EWG together activate the aryl group sufficiently for a S_NAr with concomitant loss of the fluorine atom to out-compete the usual ligand coupling pathway and the following I to X (X=N and O) aryl migration. Additionally, the retained iodide increases the atom economy and facilitates downstream transformations (Scheme 126).



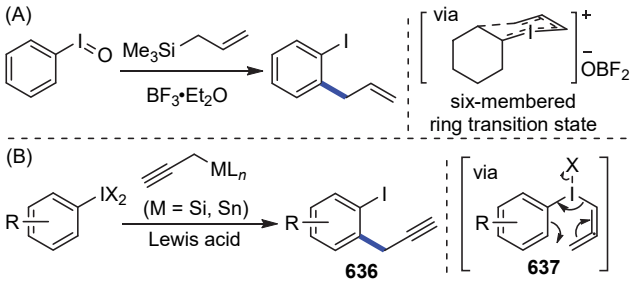
Scheme 126 Diarylation of *N*- and *O*-nucleophiles in the presence of diaryliodonium salt **634** via aryl rearrangement

2.4 Sigmatropic rearrangement

Recent years, significant progress has been achieved with I(III)-mediated sigmatropic rearrangement transformation, especially the reductive "iodonio-Claisen" rearrangement (RICR),[156-169] [3,3]-sigmatropic rearrangement of diaryliodonium,[170-178] alkenyl-containing or alkynyl-containing λ^3-iodanes,[179-180] IBX[181] and *in situ* formed I(III) species.[182-184] Additionally, reactions involving I(III)-mediated [2,3]-, [1,3]- or [5,5]-sigmatropic rearrangement also have been described.[185-187] The progress of this field in the near future is believed to be great given the existing iodane-directed C—H functionalization and thus as a very useful method for accessing important building blocks in organic synthesis.[1k,1l,1p]

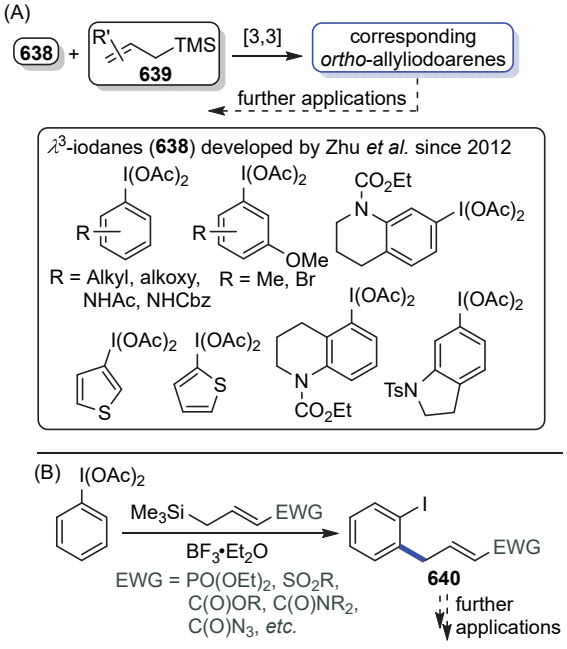
2.4.1 [3,3]-Sigmatropic rearrangement

In 1988, Oh's group[156] found an unexpected generation of *ortho*-allyliodobenzene when conducting the reaction of a mixture of PhIO and BF_3•Et_2O with allyl(trimethyl)-siliane. A plausible six-membered ring transition state was proposed to explain for the experimental results (Scheme 127A). A few years later, Ochiai *et al.*[157] and Norton *et al.*[158] independently proposed the term, [3,3]-sigmatropic rearrangement and reductive "iodonio-Claisen" rearrangement (RICR), to described their closely related reaction of λ^3-iodanes with silyl- and stannyl-propagylic species to access to the same **636** via a hypervalent allenyl(aryl)iodinanes **637** (Scheme 127B).



Scheme 127 Earliest examples of the iodonio-Claisen manifold

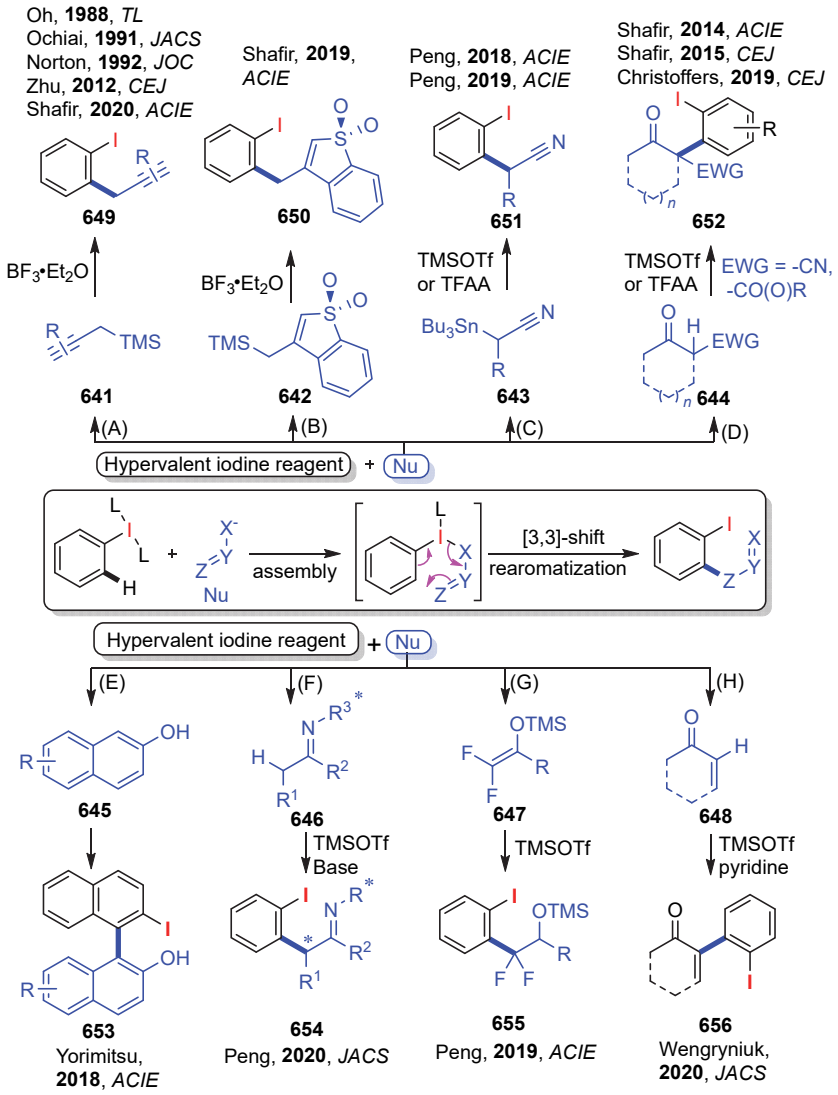
The development of RICR has gone through a short period of silence perhaps due to its limited scope at the time.[1o] Soon after, however, it attracted renewed attention as a vital synthetic tool, leading to a rapid renaissance of this type of reaction. For example, since 2012, Zhu and co-workers[159a-159c] have developed a series of complex *ortho*-allyliodoarenes via the reductive "iodonio-Claisen" rearrangement of allyl(trimethyl)silianes **639** with substituted λ^3-iodanes **638** (Scheme 128A). Furthermore, the obtained *ortho*-allyliodoarenes could participate the further derivatization applications (Scheme 128A). In 2020, Shafir and co-workers realized the iodane-directed C—H allylation of PIDA with allylsilanes containing electron-withdrawing groups, providing viable access to olefins **640** as well as a broader range of molecules (Scheme 128B). Density functional theory (DFT) calculations were also utilized to explain the [3,3]-sigmatropic rearrangement pathway in the reaction mechanism.[160]



Scheme 128 Recent developments of [3,3]-sigmatropic rearrangement of substituted λ^3-iodanes with substituted allyl(trimethyl)silianes

In addition to the [3,3]-sigmatropic rearrangement of

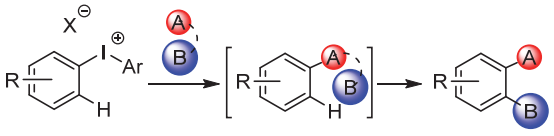
substituted λ^3-iodanes with C-C double and triple bond **641** described above, more and more nucleophiles were proved to be prone to undergo this type of reaction. Examples include benzothiophene dioxide-based silane naphthols **642**,[161] α-stannyl nitriles **643**,[162] carbonyl compounds **644**,[163] naphthols **645**,[164] 2-oxazoline **646**,[165] difluoroenol silyl ethers **647**[166] and α,β-unsaturated ketones **648**[167](Scheme 129). As can be seen from these successful transformations (Scheme 129), so important is the proper nucleophile that it can trap the electrophilic aryl iodane to assemble a key λ^3-iodanes intermediate and undergo the subsequent [3,3]-sigmatropic rearrangement to afford the corresponding *ortho*-functionalized aryliodanes **649** to **656**, which could be utilized as useful building blocks in the continue transformations (Scheme 129). Carbonyl compounds **644** can be converted into their enol form under acidic conditions to promote the rearrangement transformation.[163] It was worth noting that the necessity of the addition of acids (Lewis or Brønsted) was studied in 2016 by Shafir *et al.*[168] who found that acids (Lewis or Brønsted) can further enhance the reactivity of λ^3 iodanes and provide evidence from a structural and electronic (DFT) points of views. Also, Yorimitsu *et al.*[164a] treated 4-*tert*-butylphenol as a substrate in their study, which was found to be prone to undergo RICR and following double aromatization to give the expected biaryl product as well as the unexpected more aromatic benzene ring species via the aromatization/intramolecular nucleophilic reaction and the following elimination of hydriodic acid. As for the substrate of Peng's research, there was an additional deprotonation by base before the formation of the precursor of the [3,3]-rearrangement. This is also an interesting example of asymmetric [3,3]-sigmatropic rearrangement involving hypervalent iodine compound.[165] Peng and co-workers[166] described a new cross-coupling reaction between aryliodanes and difluoroenol silyl ethers **647** in which aryliodanes not only serve as an oxidant but also act as a coupling partner, providing a novel metal-free access to *ortho*-iodo difluoroalkylated arenes. Furthermore, Wengryniuk *et al.*[167] utilized β-pyridinium silyl enol ethers,



Scheme 129 Nucleophiles proved to be suitable for reductive "iodonio-Claisen" rearrangement (RICR)

formed *in situ* from *α*,*β*-unsaturated ketones **648** and pyridine in the presence of TMSOTf, to obtain a series of *α*-arylation enones **656**. At the same time, the pyridinium moiety is important for the generation of the desired product, which could electronically promote the [3,3]-rearrangement but also sterically block the formation of the α-oxidation by-product. It is worth noting that an alternative iodane- directed *para*-selective C—H benzylation of PIDA or *in situ* formed PIFA with benzyl metalloids has been also reported by Hyatt[1f,169] and Shafir[161] since 2018. So far, twice consecutive [3,3]-sigmatropic rearrangements, [5,5]-sigmatropic rearrangement[182] and other pathways[169] have been proposed for the mechanism of this transformation, though its exact mechanism is unclear yet.

Aside from the reductive "iodonio-Claisen" rearrangement mentioned above, it is worth noting that diaryliodonium salts were used in various double functionalization reactions, wherein the C—I(III) and *ortho* C—H bonds are converted to C-heteroatom or C—C bonds via stepwise bond formation (Scheme 130).[170-178] These transformations construct highly functionalized arenes from relatively simple diaryliodonium salts, providing vital accesses to complicated skeletons present in organic functional materials and natural products.



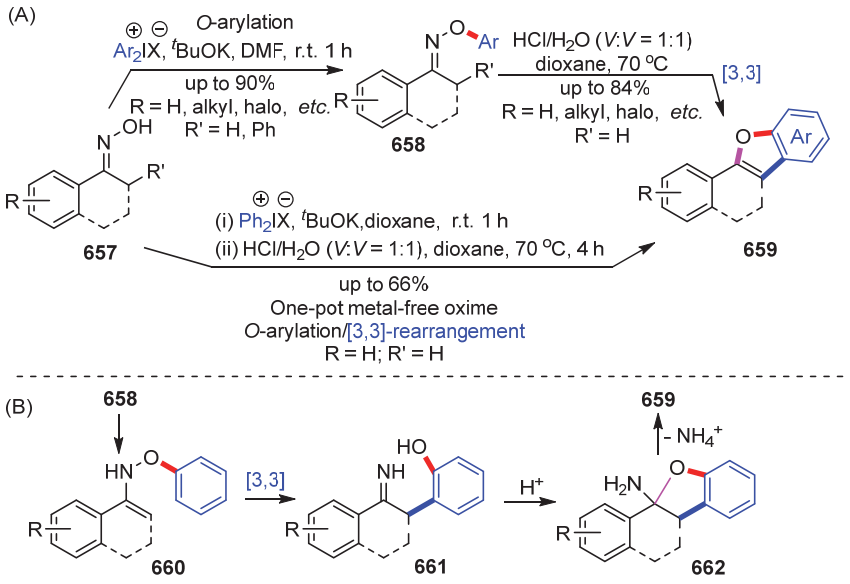
Scheme 130 Double functionalization of C—I(III) and/or *ortho* C—H bonds with diaryliodonium salts

In 2014, Kürti and co-workers[170] described two simple accesses to benzo[*b*]furans **659** with the oximes **657** and diaryliodonium salts. Oximes **657** can be converted to *O*-aryloximes **658** with diaryliodonium salts first, and then **659** was generated under acidic conditions via the [3,3]-rearrangement/cyclization of **658**. Alternatively, **659** could be directly prepared via the one-pot *O*-arylation/[3,3]-rearrangement/cyclization tandem of **657** with diaryliodonium salts (Scheme 131A). Intermediate **660**, the tautomer of enamine **658**, underwent a [3,3]-rearrangement to lead to the formation of aryl-rearranged enamine **661**. Intramolecular nucleophilic addition of the latter under acidic conditions gave the five-membered intermediate **662**. The following elimination of **662** afforded the terminal benzo[*b*]furans **659** along with the release of ammonia (Scheme 131B).

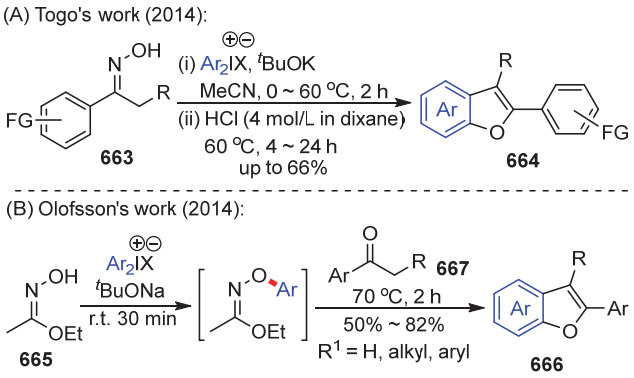
In the same year, Togo *et al.*[171] reported a similar one-pot two-step *O*-arylation/[3,3]-shift of oximes **663** with diaryliodonium salts, proving a series of benzo[*b*]furans **664** (Scheme 132A). In addition, Olofsson and co-workers[172] also obtained the corresponding benzo[*b*]furans **666** via a one-pot two-step *O*-arylation/[3,3]-shift of ethyl acetohydroxamate **665**, diaryliodonium salts and ketone **667** (Scheme 132B).

Similarly, *N*-hydroxyindole **668** was proved to be applicable to this diaryliodonium salts-employed *O*-arylation/[3,3]-shift/cyclization cascade by Vincent[173] in 2015. The reaction led to the formation of benzofuroindoline **669** (44%) along with another migratory product pyrroloindoline **670** (20%). The former was generated due to the intramolecular nucleophilic addition to the imine moiety of [3,3]-rearranged imine **672** by its amide moiety with the aid of K_2CO_3 (Scheme 133, path a), while alike addition by phenolic hydroxyl on **672** followed a further *O*-arylation gave the pyrroloindoline **670** (Scheme 133, path b).

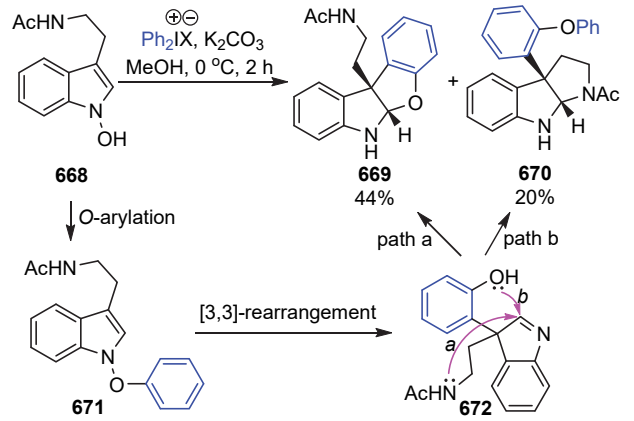
In 2017, Mo *et al.*[174] prepared a series of benzoxazoles **675**, accomplished via a two-step *O*-arylation [3,3]-shift/cyclization reactions of amidoximes **673** and diarylio



Scheme 131 *O*-arylation/[3,3]-rearrangement tandem of oximes to benzo[*b*]furans

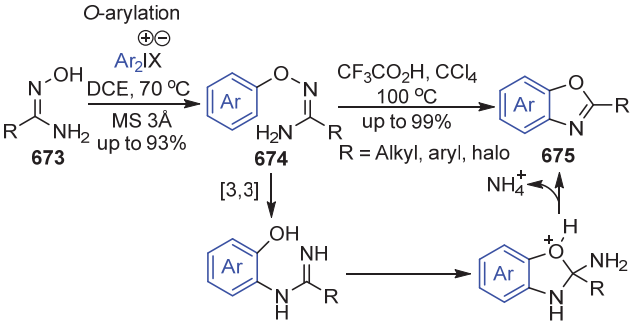


Scheme 132 Access to benzo[*b*]furans via the one-pot two-step *O*-arylation/[3,3]-shift of oximes with diaryliodonium salts



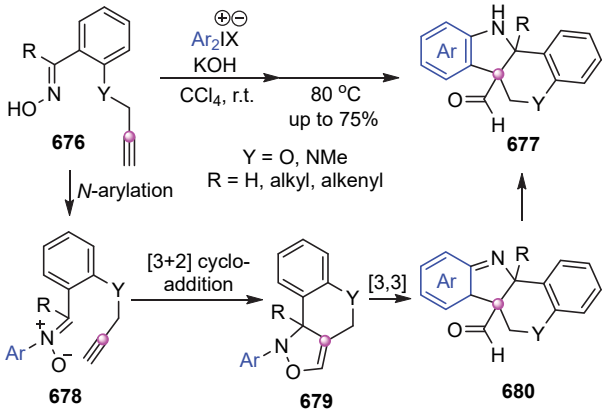
Scheme 133 Access to benzofuroindoline and pyrroloindoline via the *O*-arylation/[3,3]-shift/cyclization cascade of *N*-hydroxyindole with diaryliodonium salts

donium salts (Scheme 134). Differently, *O*-arylation of **673** was promoted by 3Å molecule in the absence of base, delivering *O*-arylated amidoximes **674** in good yields. The process of this TFA-mediated [3,3]-rearrangement/cyclization was similar to the one displayed in Scheme 131.



Scheme 134 Access to benzoxazoles via the two-step base-free *O*-arylation/[3,3]-shift/cyclization of amidoximes with diaryliodonium salts

In the same year, Mo *et al.*[175] further synthesized a series of 2,3-quaternary fused indolines **677** via a one-pot two-step *N*-arylation/[3 + 2] cycloaddition/[3,3]-shift of alkynyl tethered oximes **676** and diaryliodonium salts in the presence of KOH. It is worth noting that *N*-arylation, rather than *O*-arylation described above occurred, and the resulting alkynyl tethered nitrones **678** then went through an intramolecular [3 + 2] cycloaddition, leading to the generation of intermediate **679**. Following [3,3]-sigmatropic rearrangement and subsequent deprotonation of the resulting **680** gave the terminal indolines **677** under heat. The method features easily available cheap materials, multiple bond formation, gram scalable preparation and diversity of fused indoline scaffolds (Scheme 135).

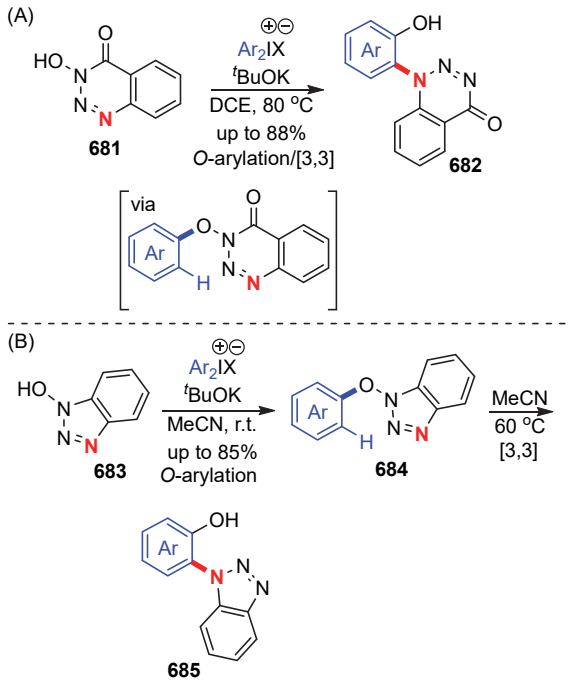


Scheme 135 Access to indolines via a one-pot two-step *N*-arylation/[3 + 2] cycloaddition/[3,3]-shift of alkynyl tethered oximes and diaryliodonium salts

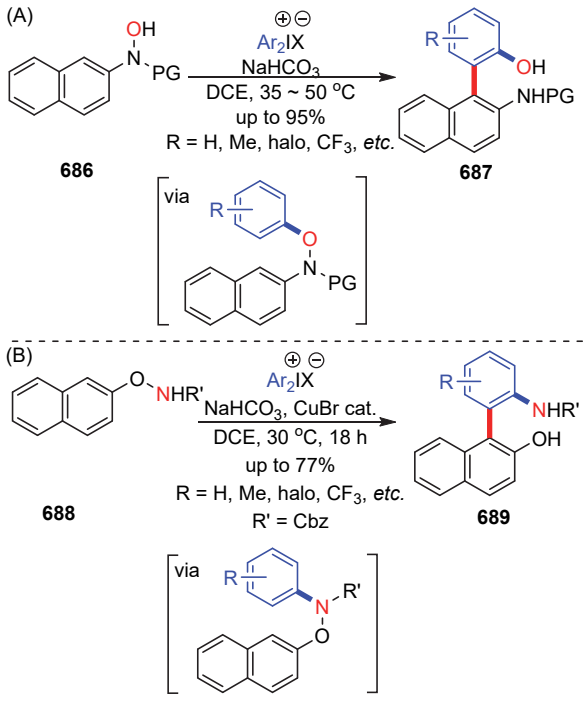
In addition to the above-mentioned *O*- or *N*-arylation/[3,3]-shift/cyclization tandem involving diaryliodonium salts, several examples of simple *O*- or *N*-arylation/[3,3]-sigmatropic rearrangement utilizing diaryliodonium salts also have been reported. For instance, *N*-aryl benzo[1,2,3]-triazin-4(1*H*)-ones **682** were prepared from *N*-hydroxy benzo[1,2,3]triazin-4(3*H*)-ones **681** and diaryliodonium salts in one pot by Mo and co-workers[176a] in 2015 (Scheme 136A). Then they[176b] further synthesized *N*-(2-hydroxyaryl)benzotriazoles **685** via a similar *O*-arylation/[3,3]-rearrangement of *N*-hydroxybenzotriazoles **683** with diaryliodonium salts. Differently, it is a two-step process and aryl-substituted products **684** were obtained first under mild conditions and further isolated and identified (Scheme 136B).

In 2020, Gao *et al.*[177a] realized the synthesis of a series of NOBIN analogues **687** via a one-pot *O*-arylation/[3,3]-rearrangement tandem of arylhydroxylamines **686** and diaryliodonium salts under mild conditions (Scheme 137A). Furthermore, *O*-arylhydroxylamines **688** were also proved to be suitable for the similar *N*-arylation/[3,3]-rearrangement, leading to the formation of biaryls **689** (Scheme 137B).[177b]

In 2020, Tan *et al.*[178a] synthesized a series of privileged NOBIN structures **691** through an arylation/[3,3]-sigmatropic rearrangement tandem of diarylhalonium salts with benzyl (naphthalen-2-yloxy)carbamates **690** in the presence of cesium carbonate at room temperature (Scheme

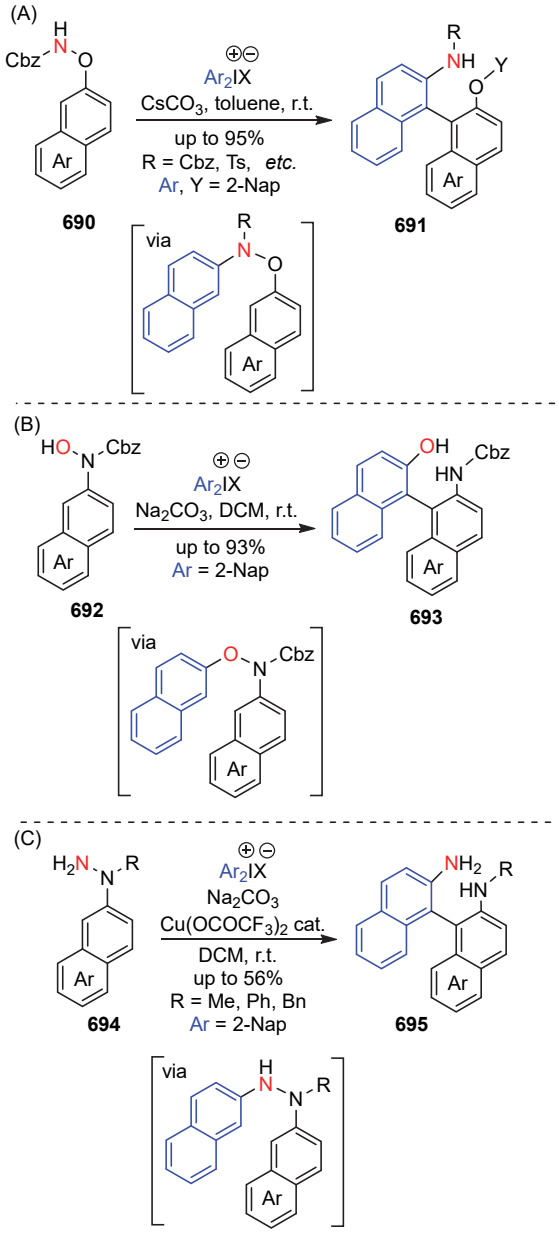


Scheme 136 *O*-arylation/[3,3]-shift tandem of **667** and **668** involving diaryliodonium salts



Scheme 137 [3,3]-Sigmatropic rearrangement involving diaryliodonium salts

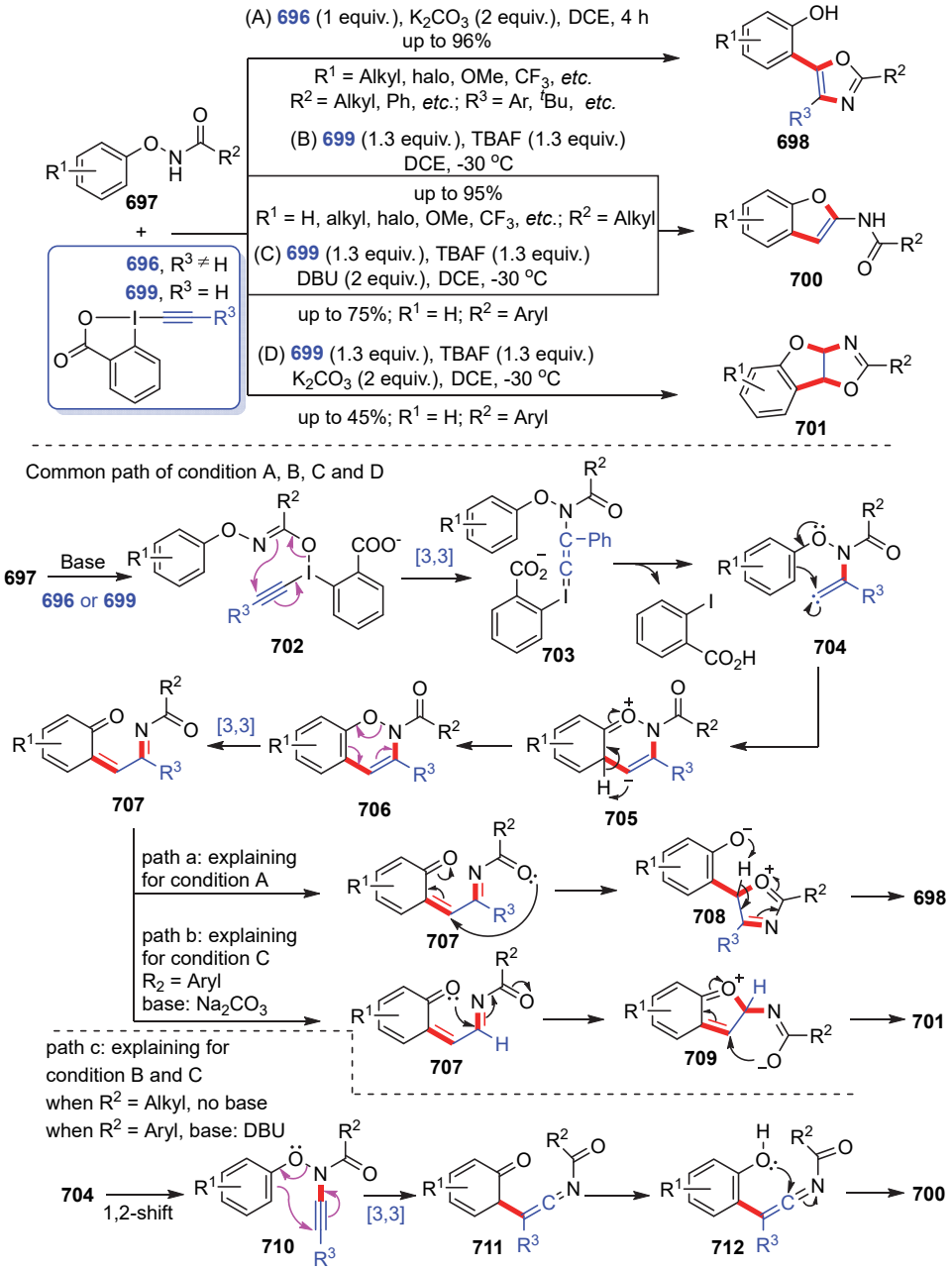
138A). Benzyl hydroxy(naphthalen-2-yl)carbamates **692** were also applicable to the reaction systems and afforded substituted NOBINs **693** in high yields, wherein sodium carbonate was used as the base (Scheme 138B). It is worth noting that several BINAMs **695** could be obtained in moderate yields when a catalytic amount of copper(II) trifluoroacetate was added to the *N*-arylation/[3,3]-rearrangement system of *N*-arylhydrazines **694** with diaryliodonium salts (Scheme 138C).[178] The protocol also provides vital strategy for constructing binaphthyl skeletons.



Scheme 138 Access to NOBIN or BINAMs via the one-pot two-step arylation/[3,3]-shift of (naphthalen-2-yloxy)carbamates or *N*-arylhydrazines with diaryliodonium salts

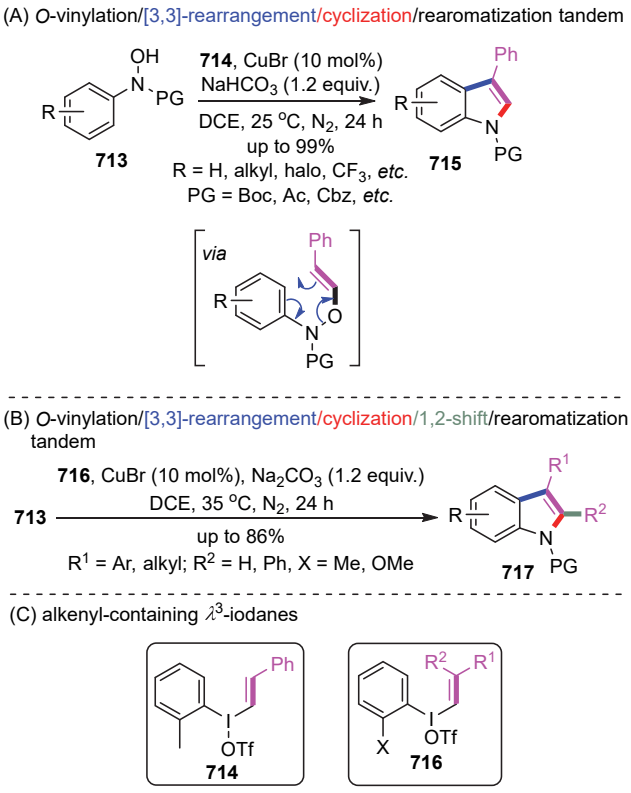
Another striking λ^3-iodane participating [3,3]-sigmatropic rearrangement was realized by alkynyl-containing λ^3-iodanes, *i.e.*, alkynylbenziodoxolones **696**, which was applied by Wen's group[179a] in 2018 for the synthesis of 2-(oxazol-5-yl)phenols **698** via a [3,3]-rearrangement/cyclization tandem of *N*-phenoxyamides **697** (Scheme 139A). In 2019, they[179b-179c] continued to conduct the reaction of TIPS-protected alkynylbenziodoxolones **699** with *N*-phenoxyamides **697** under different base conditions and obtained different products, benzofurans **700** and dihydrobenzofuro[2,3-*d*]oxazoles **701** (Scheme 139B～139D). It is

worth noting that the formation of these products underwent multiple [3,3]-rearrangement, as reflected in their plausible pathways. Initially, deprotection of bench-stable alkynyl-containing λ^3-iodanes **696** in the presence of base occurred and gave a more active I(III) species, which was nucleophilically attacked by the deprotonated tautomer of **697** and generated intermediate **702**. [3,3]-Rearrangement of the latter furnished vinyliodonium ylide **703**, from which 2-iodobenzoic acid was removed to afford the first key intermediate alkylidene carbene **704**. The following intramolecular alkylidene carbene insertion of **704** gave cyclization intermediate **705**, whose isomer **706** underwent another [3,3]-rearrangement and led to the cleavage of the N—O bond as well as the formation of the second key intermediate **707**. Intramolecular nucleophilic attack on the olefinic bond of **707** by its amide carbonyl group provided a cyclization intermediate **708** (Scheme 139, path a). The product **698** was formed after the aromatization of **708**. While a cyclization intermediate **709** was observed when the ketone carbonyl group of **707** participated in an intramolecular nucleophilic attack on its imine moiety (Scheme 139, path b). Biscyclization by-products **701** were obtained via the attack of amide carbonyl group in **709** to the olefinic bond. On the other hand, alkylidene carbene **704** could be easily converted to the terminal alkyne intermediate **710** through a 1,2-hydride shift. Finally, products **700** were obtained after a [3,3]-rearrangement and cyclization via intermediates **711** and subsequent **712** (Scheme 139, path c).



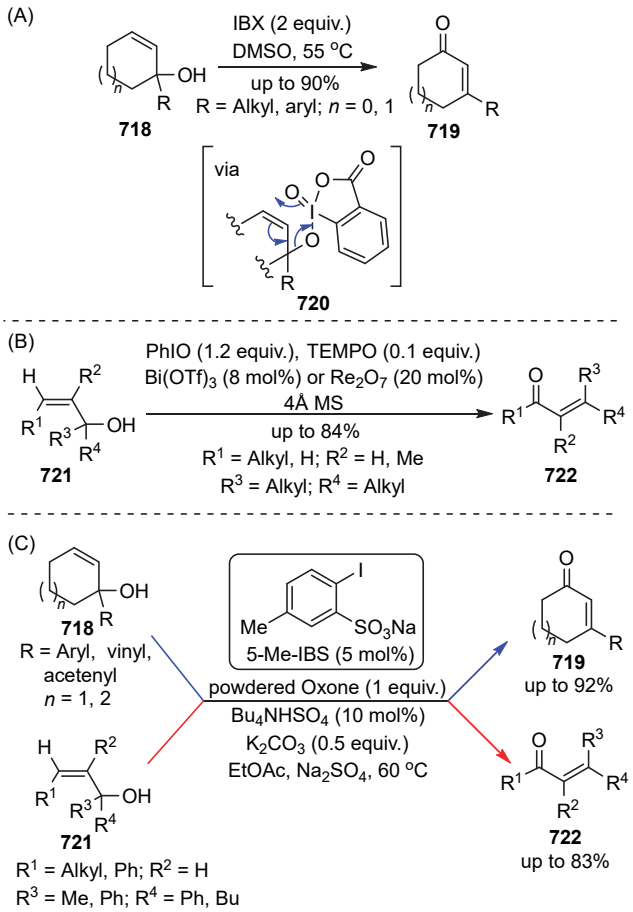
Scheme 139 Multiple [3,3]-rearrangement of *N*-phenoxyamides in the presence of alkynylbenziodoxolones

Alkenyl-containing λ^3-iodanes were also proved to be able to undergo [3,3]-rearrangement by Gao *et al.*[180] In 2018. They successfully conducted the *O*-vinylation/[3,3]-rearrangement/cyclization/rearomatization tandem of arylhydroxylamines **713** with alkenyl-containing λ^3-iodanes **714** (Scheme 140C), providing a vital protocol for the synthesis of indole derivatives **715** in good yields (Scheme 140A). Likewise, a sequential *O*-vinylation/[3,3]-rearrangement/cyclization/1,2-shift/rearomatization of **713** occured to give a series of highly substituted indoles **717** when λ^3-iodanes **716** (Scheme 140C) was utilized in this system (Scheme 140B).



Scheme 140 Tandem reactions involving [3,3]-rearrangement of arylhydroxylamines with alkenyl-containing λ^3-iodanes

In 2004, Iwabuchi and co-workers[181a] reported the preparation of β-disubstituted α,β-unsaturated ketones **719** via the metal-free oxidative rearrangement of cyclic tertiary allylic alcohols **718** mediated by IBX in DMSO (Scheme 141A). Similar to the known mechanism of Cr(VI)-mediated oxidative rearrangement of tertiary allylic alcohols to enones,[181b-181f] this reaction occurs smoothly through a [3,3]-rearrangement of the key intermediate **720**. Furthermore, they realized the same transformation by utilizing the combination of 2,2,6,6-tetramethylpiperidinooxy (TEMPO)/$NaIO_4$-SiO_2 in 2008[181g]. Soon after, Vatèle refreshed this reaction and converted allylic alcohols **721** to α,β-unsaturated ketones **722** by employing the combination of TEMPO/Lewis acid/PhIO (Scheme 141B).[182] Alternatively, Ishihara employed 5-Me-IBS, *in situ* prepared by oxone, and oxidized allylic alcohols **718** and **721** to the corresponding α,β-un- saturated ketones **719** and **722** via the similar I(III)-mediated [3,3]-rearrangement process (Scheme 141C).[183]

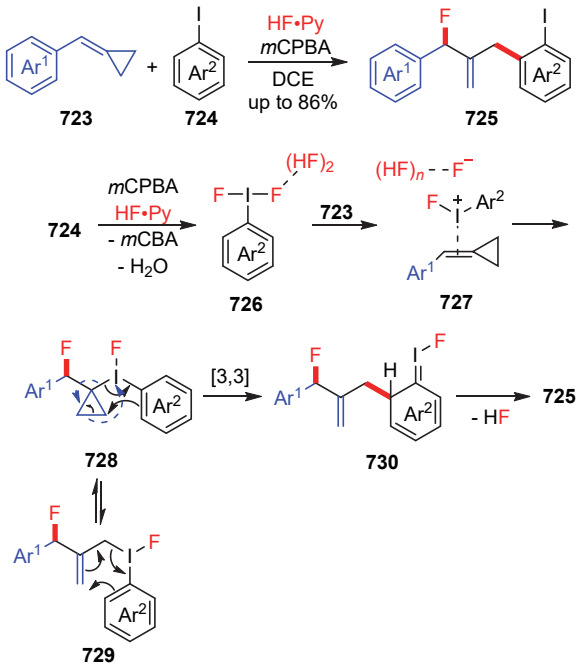


Scheme 141 Access to enones via I(III)-oxidized [3,3]-rearrangement of tertiary allylic alcohol

It is necessary to mention the oxidative fluoroarylation of benzylidenecyclopropanes **723** with aryl iodides **724** and HF•Py, conducted by Li's group[184] in 2022, providing a series of monofluorinated 1,1-bis-benzyl-alkenes **725** via a regioselective 1,2-fluoroiodination/[3,3]-rearrangement tandem. In this transformation, aryl I(III) spices **726** was formed *in situ* via the oxidation of aryl iodides **724** by *m*CPBA and the following activation by HF•Py. Interaction of I(III) spices **726** with benzylidenecyclopropanes **723** and the following regioselective 1,2-fluoroiodination delivered the key intermediate **728**. Then, direct iodonio-[3,3]-rearrangement of **728** occurred and released the intermediate **730**. Final elimination of **730** provided product **725**. The formation of **730** was also assumed to undergo a [3,3]-rearrangement of I(III) intermediate **729**, a pathway that could not rule out at present, though comparison experiments suggest that it is less likely from **729** (Scheme 142).

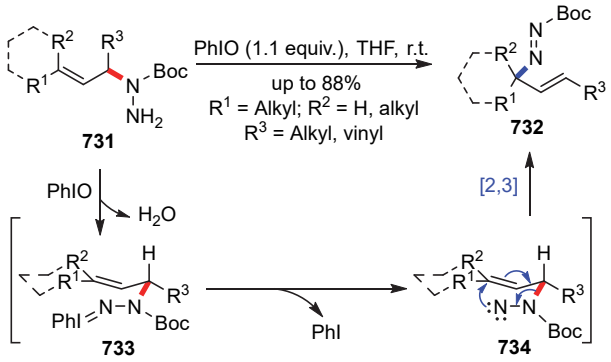
2.4.2 Other sigmatropic rearrangement

In 2011, Thomson's group[185] provided an interesting access to allylic amines **732** via a PhIO-mediated [2,3]-sigmatropic rearrangement of allylic hydrazides **731**, which was shown to be a useful protocol for preparing precursors



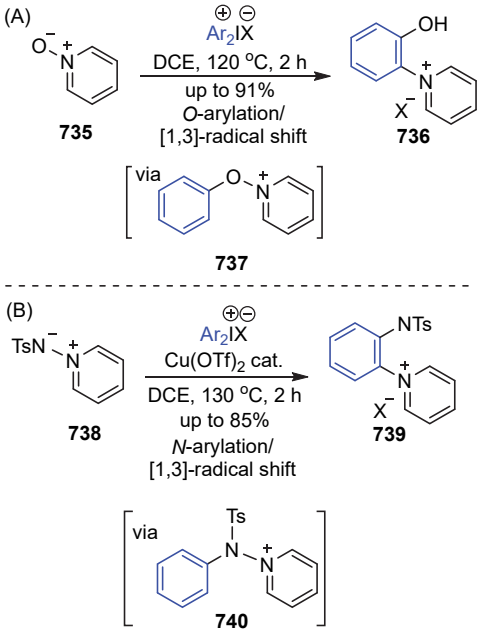
Scheme 142 Oxidative fluoroarylation of benzylidenecyclopropanes with aryl iodides and HF•Py triggered by *in situ* formed aryl I(III) spices **726** via [3,3]-rearrangement

of a variety of compounds. Presumably, reaction of hydrazide **731** with iodosobenzene first generated aminoiodinane **733**, which further formed the free singlet *N*-nitrene **734** along with losing iodobenzene. Then [2,3]-sigmatropic rearrangement of the latter released the terminal allylic amines **732**. This is one of the limited examples of an exclusive type of sigmatropic rearrangement employing hypervalent iodine species (Scheme 143).



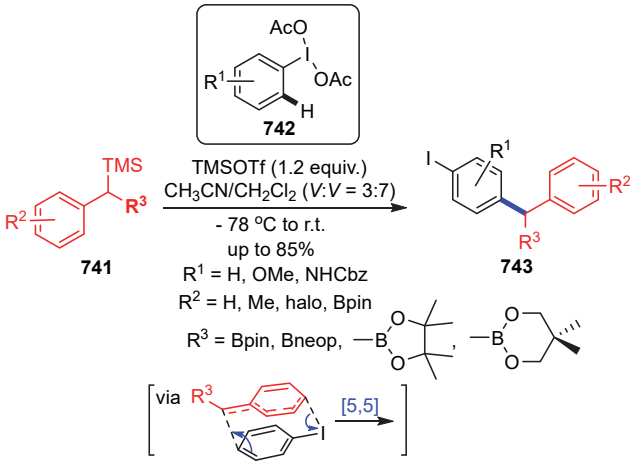
Scheme 143 PhIO-mediated [2,3]-sigmatropic rearrangement of allylic hydrazides to amines

In 2013, Chen and co-workers[186a] employed pyridine *N*-oxides **735** as hydroxylamines and achieved a double functionalization transformation of diaryliodonium salts under heat, delivering a series of pyridinium phenols **736**. This reaction was accomplished via an *O*-arylation/1,3-radical rearrangement cascade of the intermediate **737** (Scheme 144A). Likewise, the authors also realized the reactions of various diaryliodonium salts and pyridinium *N*-amidate **738** in the presence of a copper catalyst to afford 2-pyridinium aniline derivatives **739** (Scheme 144B).[186b]



Scheme 144 Arylation/1,3-radical rearrangement cascade involving diaryliodonium salts

In 2021, Shafir and co-workers[187] described an unusual iodane-directed *para*-selective C—H (*α*-borylbenzylation) of λ^3-iodane **742** with *gem*-*α*,*α*-dimetalloid-substituted benzylic compounds **741** under acidic conditions, delivering a series of aryl iodide **743**. Given the result of DFT calculations, a [5,5]-sigmatropic rearrangement driven by the high-energy iodine(III) species was proposed to explain for its mechanism (Scheme 145), which was also used to explain for the iodane-directed *para*-selective C—H benzylation mentioned above.[169] In a word, transformations described above expand the platform of sigmatropic rearrangement mediated by hypervalent iodine reagents.



Scheme 145 *para*-Selective C—H (*α*-borylbenzylation) of benzylic compounds and λ^3-iodane **742** via a plausible [5,5]-sigmatropic rearrangement

3 Conclusions

In conclusion, various oxidative rearrangement reactions mediated by hypervalent iodine reagents were summarized and discussed in this review paper. These metal-free transformations have not only enriched the development of rearrangement reactions, but also provided useful synthetic building blocks in organic synthesis. We hope that the review will provide useful reference and provoking insights to the researchers working in the field. It can be envisaged that more interesting rearrangement reactions enabled by hypervalent iodine reagents will be developed in the future.

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