Photochemistry of hypervalent iodine compounds

KUNFANG JIA and YIYUN CHEN

State Key Laboratory of Bioorganic and Natural Products Chemistry, Centre of Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China
e-mails: jiakunfang90@163.com; yiyunchen@sioc.ac.cn

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I. HYPERVALENT IODINE COMPOUNDS IN PHOTOCHEMISTRY

Hypervalent iodine compounds are environmental benign and nontoxic, which react under mild reaction conditions[1]. The most typical reactivity of hypervalent iodine compounds is the oxidation, accepting electrons to reduce from the oxidation state of +5 or +3 to −1. In addition, hypervalent iodine compounds show transition-metal-like reactivity similar to mercury(II), thallium(III), or lead(IV), such as ligand-exchange and substrate activation[2].

Light is green and renewable, and the utilization of light in chemistry has been an attractive research frontier[3]. As most organic small molecules absorb ultraviolet (UV) light, the direct photoexcitation with UV light is widely used[4]. Recently, the use of compact fluorescence lamp (CFL) and light emitting diode (LED) lamp has become prevalent and has reignited the research on visible-light-induced reactions by indirect photosensitization/photoredox catalysis[5]. The ruthenium(II) and iridium(III) metal complexes are the most widely used photosensitizers/photocatalysts, which upon visible light irradiation become efficient single-electron reductant or oxidant in the reaction.

The contents in this chapter are categorized by the photochemical role of hypervalent iodine compounds, including the substrates activation and the use as reagents in photochemical reactions (Figure 1). The carboxylic acids, alcohols, and amines can be activated by hypervalent iodine compounds, *in situ* or preformed, to generate hypervalent iodine-coordinated oxygen or nitrogen species (Section II). In contract, the hypervalent iodine-coordinated carbon and azide species such as iodonium salts, trifluoromethyl benziodoxoles, azido benziodoxoles, alkynyl benziodoxoles, and cyano benziodoxoles need to be used as reagents. For simplicity, the use of hydroxyl benziodoxoles or acetoxyl benziodoxoles as oxidative quencher in photoredox catalysis is included in the hypervalent iodine compounds as reagents (Section III).

As the direct photoexcitation and indirect photosensitization (photoredox catalysis) involve very different reaction mechanisms, they are discussed separately in this chapter (Figure 2). The direct photoexcitation typically involves the homolytic bond cleavage, while the indirect photosensitization/photoredox catalysis involves the single-electron transfer-enabled heterolytic bond cleavage reactions.

A. Direct Photoexcitation

The traditional photochemical reactivity of hypervalent iodine compounds is demonstrated with the direct photoexcitation. When the hypervalent iodine compounds form the hypervalent iodine-coordinated oxygen or nitrogen species, the bond energy of iodine–oxygen or iodine–nitrogen bond is significantly reduced compared to the strong hydrogen–oxygen or hydrogen–nitrogen bond. The weak iodine–oxygen or iodine–nitrogen bond can be homolytically cleaved to generate the (hypervalent) iodine radicals as well as the oxygen or nitrogen radicals with less energy and better chemoselectivity (Figure 2a).

B. Indirect Photosensitization (Photoredox Catalysis)

The indirect photosensitization (photoredox catalysis) is a recently discovered photochemical reactivity of hypervalent iodine compounds. When the hypervalent iodine compounds form the hypervalent iodine-coordinated oxygen or nitrogen species, the iodine–oxygen or iodine–nitrogen bond can undergo single-electron transfer reaction to generate the oxygen or nitrogen radicals (Figure 2b). Compared to the difficult oxygen–hydrogen bond in carboxylic acids and alcohols for oxidation, the oxidation potential of hypervalent iodine-coordinated oxygen species is significantly reduced so that oxidants with lower oxidation potential can

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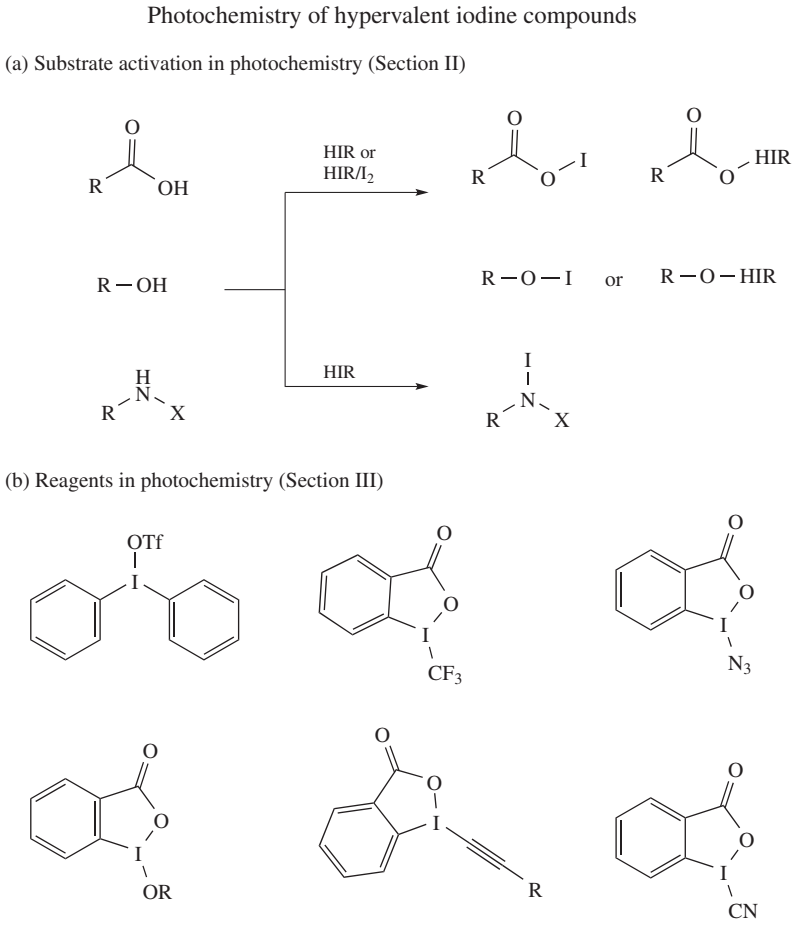

FIGURE 1. Photochemical roles of hypervalent iodine compounds.

be used. Hypervalent iodine-coordinated carbon and azide species such as iodonium salts, trifluoromethyl benziodoxoles, and azido benziodoxoles can undergo single-electron reduction reactions, while alkynyl benziodoxoles, azido benziodoxoles, and cyano benziodoxoles can undergo radical addition reactions.

II. HYPERVALENT IODINE COMPOUNDS FOR SUBSTRATE ACTIVATION IN PHOTOCHEMISTRY

Hypervalent iodine compounds undergo ligand exchange reactions with carboxylic acids, alcohols, and amines to generate hypervalent iodine-coordinated carboxylates, hydroxylates, and amines. As the iodine–oxygen and iodine–nitrogen bonds are weaker compared to hydrogen–oxygen and hydrogen–nitrogen bonds, they can undergo homolytic bond cleavage reactions under direct light irradiation to generate oxygen or nitrogen radicals, or undergo single-electron transfer reactions by photoredox catalysis to generate oxygen radicals.

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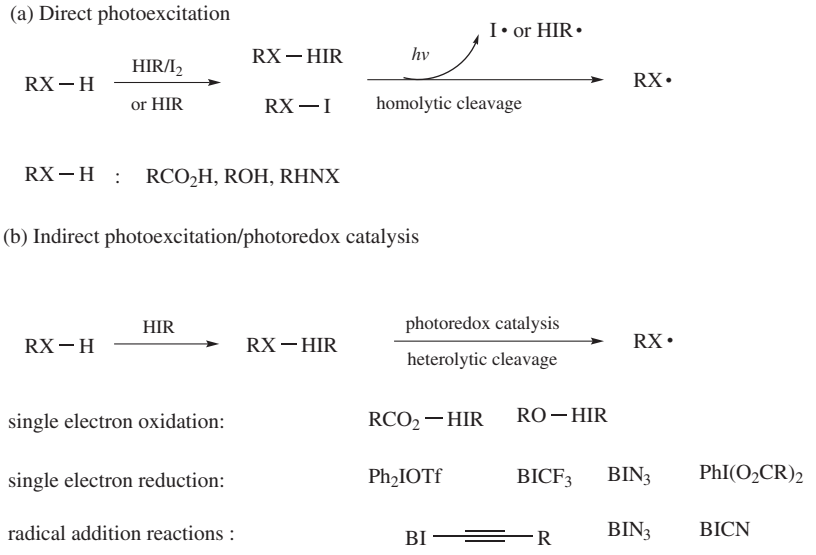

FIGURE 2. Direct photoexcitation and indirect photosensitization (photoredox catalysis).

A. Carboxylic Acid Activation

It is challenging to generate the carboxyl radicals from carboxylic acids either by homolytic bond cleavage or by single-electron oxidation reactions (Figure 3). The transition metals generate the transition-metal-bound carboxylates to activate carboxylic acids (Figure 3a); however, heating or strong oxidants are required for the carboxyl radical generation[6]. In contrast, the hypervalent iodine compounds generate the hypervalent iodine-coordinated carboxylates by ligand displacements[7], and the carboxyl radicals can be obtained under ambient conditions either by homolytic bond cleavage reactions under direct light irradiation (Figure 3b), or by single-electron transfer reactions under photoredox catalysis conditions (Figure 3c).

1. Direct irradiation

Togo, Yokoyama, and coworkers reported in 1991 the alkylation of aromatic heterocycles with bis(trifluoroacetoxy)iodo)benzene under UV light irradiation for the first time (Figure 4)[8]. The mechanistic investigations indicated the generation of hypervalent iodine(III)-coordinated carboxylates *in situ* from the alkyl carboxylate and bis(trifluoroacetoxy)iodo)benzene, which then underwent homolytic bond cleavage reaction with mercury light irradiation to yield the adamantyl carboxyl radical. The adamantyl carboxyl radical subsequently underwent decarboxylation to yield the adamantyl radicals after releasing the hypervalent iodine radical and carbon dioxide. The alkyl radical then did radical addition to heterocycles to form the alkyl-substituted heterocycles.

Togo, Yokoyama, and coworkers later reported the electronic effect of diacyloxyiodo-arenes with different substitutions on the aryl group for the alkylation reaction of heterocycles (Figure 5a)[9]. The unsubstituted diacyloxyiodo-arenes were the most efficient for the reaction, and neither the electron-rich substituents nor the electron-deficient substituents improved the alkylation reaction. The decarboxylative alkylation of (vinylsulfonyl)benzene was later

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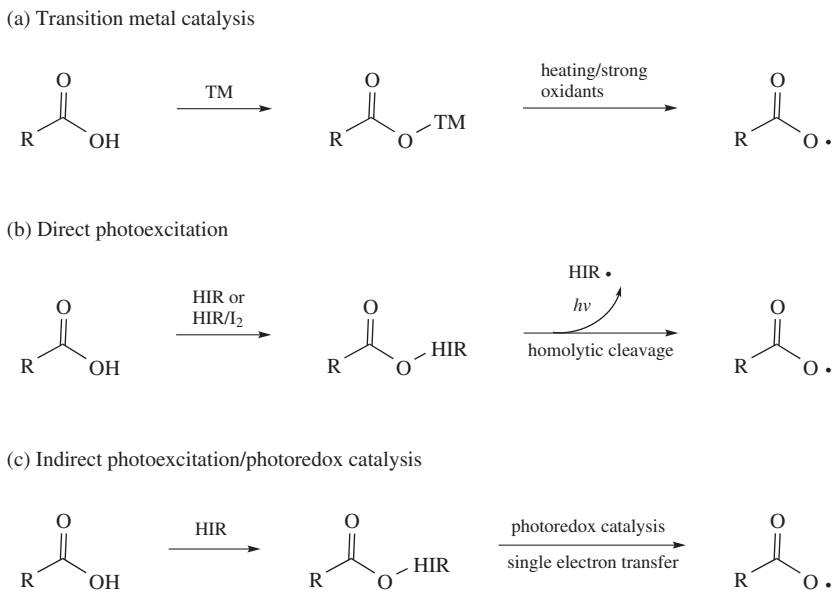

FIGURE 3. The hypervalent iodine activation of carboxylic acids.

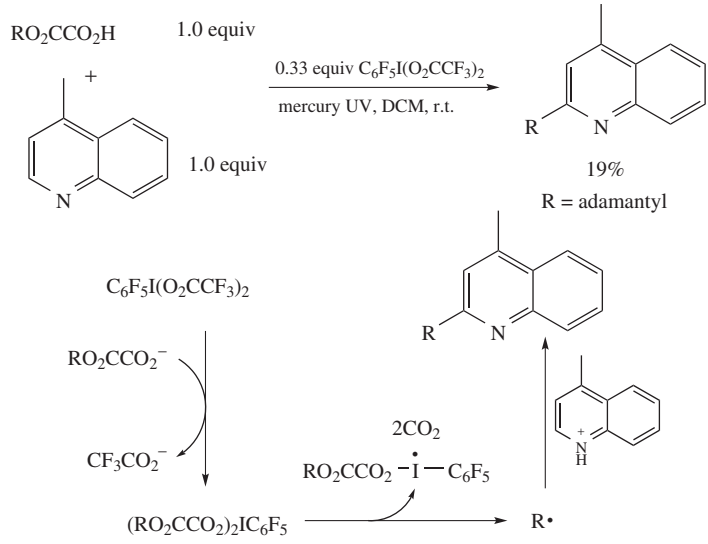

FIGURE 4. The alkylation of aromatic heterocycles with carboxylic acids.

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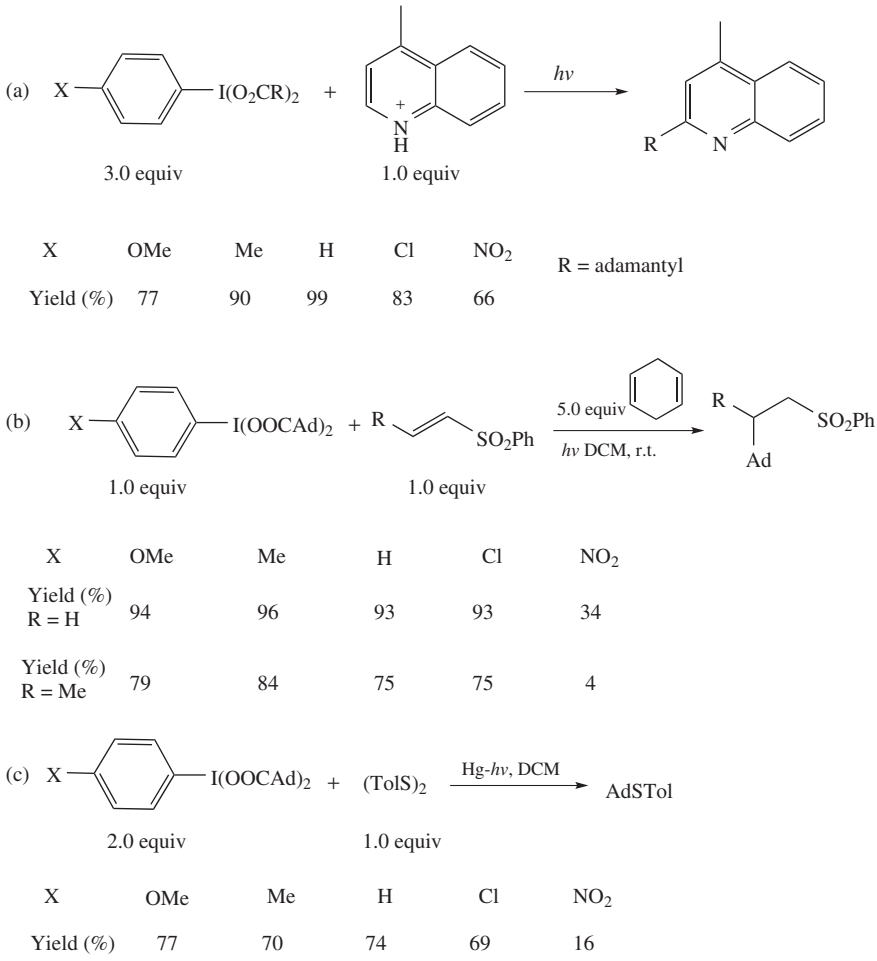

FIGURE 5. The electronic effect of diacyloxyiodo-arenes for alkylations.

achieved under similar conditions, and the substitution on aryl groups did not significantly affect the reaction except that the strongly electron-withdrawing nitro-substitution retarded the reaction (Figure 5b)[9, 10]. The decarboxylative sulfidation was also achieved using diacyloxyiodo-arenes under UV light irradiation in the presence of disulfides (Figure 5c)[11]. The corresponding adamantyl sulfide was obtained with a high-pressure mercury lamp irradiation and the substitution did not significantly affect the reaction except that the strongly electron-withdrawing nitro substitution retarded the reaction.

Wang and coworkers developed the decarboxylative alkynylation of keto acids in 2015 with cyclic iodine(III) reagent hydroxybenziodoxole under sunlight irradiation (Figure 6a)[12]. The mechanistic investigations suggested a benziodoxole-coordinated keto acid generated *in situ* from the hydroxybenziodoxole and keto acids, which decomposed to iodanyl radical and acyl radical under sunlight irradiation. The iodanyl radical reacted with bromoacetylene to give

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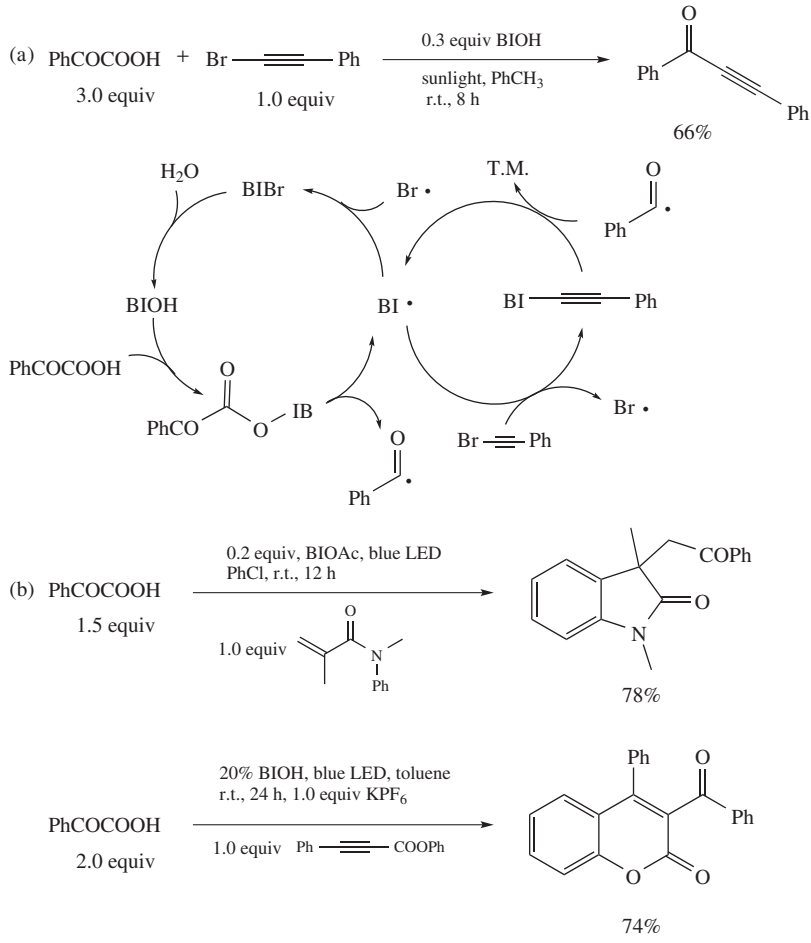

FIGURE 6. The acylation with keto acids.

alkynyl benziodoxole, and the benzoyl radical added to alkynyl benziodoxole after decarboxylation to yield the ynone. This acyl radical generation method was later applied to C−H activation cascade and cyclization reactions (Figure 6b)[13].

Togo, Yokoyama, and coworkers reported in 1995 the generation of phenyl carboxyl radical from *ortho*-alkyl-substituted benzoic acids, which reacted with iodine and hypervalent iodine(III) reagents under UV light irradiation to yield the lactone (Figure 7)[14]. The mechanistic investigations indicated that the *in situ* generated iodine(I)-coordinated carboxylate decomposed to carboxyl radical and iodine radical under UV light irradiation. As the decarboxylation of the aromatic carboxyl radical was slower than the aliphatic carboxyl radical, the 1,5-hydrogen shift occurred and trapped by iodine with carboxylate attack to afford the lactone. Different hypervalent iodine(III) reagents were tested, and the noncyclic iodine(III) reagents were the most effective, among which the substituents on the phenyl group did not significantly affect the reaction.

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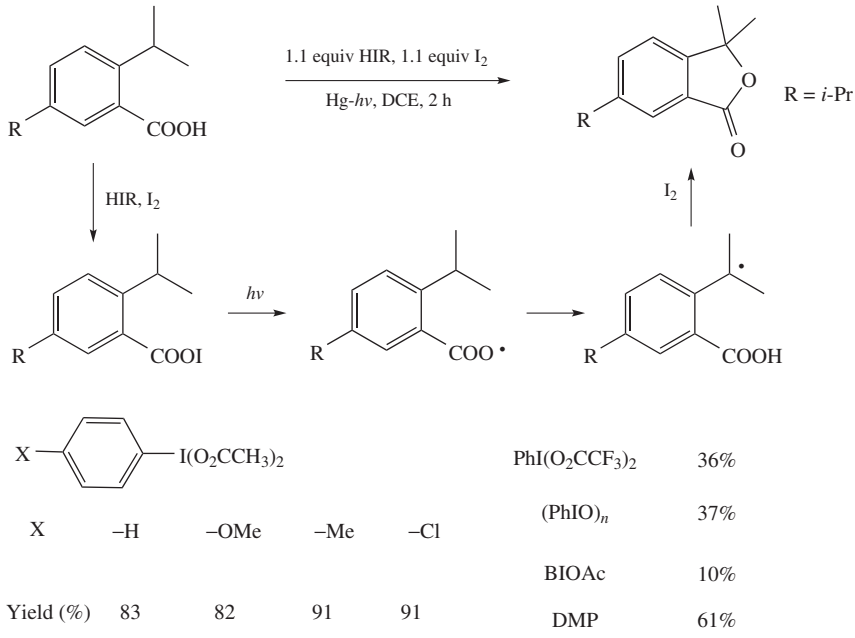

FIGURE 7. The lactonation with phenyl carboxylic acids.

In summary, the iodine(I)-carboxylate or hypervalent iodine(III)-carboxylate undergoes facile homolytic oxygen–iodine bond cleavage reaction to generate the carboxyl radical under direct light irradiation. The phenyl carboxyl radical undergoes hydrogen abstraction reaction and the aliphatic carboxyl radical undergoes decarboxylation reaction to generate the alkyl radical. The phenyl substitution on hypervalent iodine compounds does not significantly affect the reaction except for strongly electron-withdrawing groups.

2. Photoredox catalysis

Zhu and coworkers reported in 2014 that diacyloxyiodo-arene underwent decarboxylative C–H activation cascade to *N*-methyl-*N*-phenylmethacrylamides by photoredox catalysis (Figure 8a)[15]. This methodology was extended to various phenyliodine(III)-coordinated carboxylates to yield alkyl radicals for radical additions. The mechanistic investigations indicated that the diacyloxyiodo-arene was reduced by photoexcited $Ir^{III}*$ to afford the iodine(III)-coordinated carboxylate radical, which further underwent decarboxylation and radical C–H functionalization cascade to yield the product. The similar phenyliodine(III) activation method was later used by Jamison and coworkers to generate the alkyl radical for addition/cyclization to aryl isocyanides by photoredox catalysis (Figure 8b)[16]. The polycyclic compounds preparation by integrating the in-line isocyanide formation and photochemical cyclization was established in a three-step continuous flow system.

Chen and coworkers discovered in 2015 that the cyclic iodine(III) reagent acetoxyl benziodoxole (BIOAc) demonstrated transition-metal-like reactivity to enable the decarboxylative ynonylation by photoredox catalysis (Figure 9a)[17]. This reaction was initiated by the ligand exchange reaction between the ketoacid and the BIOAc to yield the BI-ketoacid intermediate.

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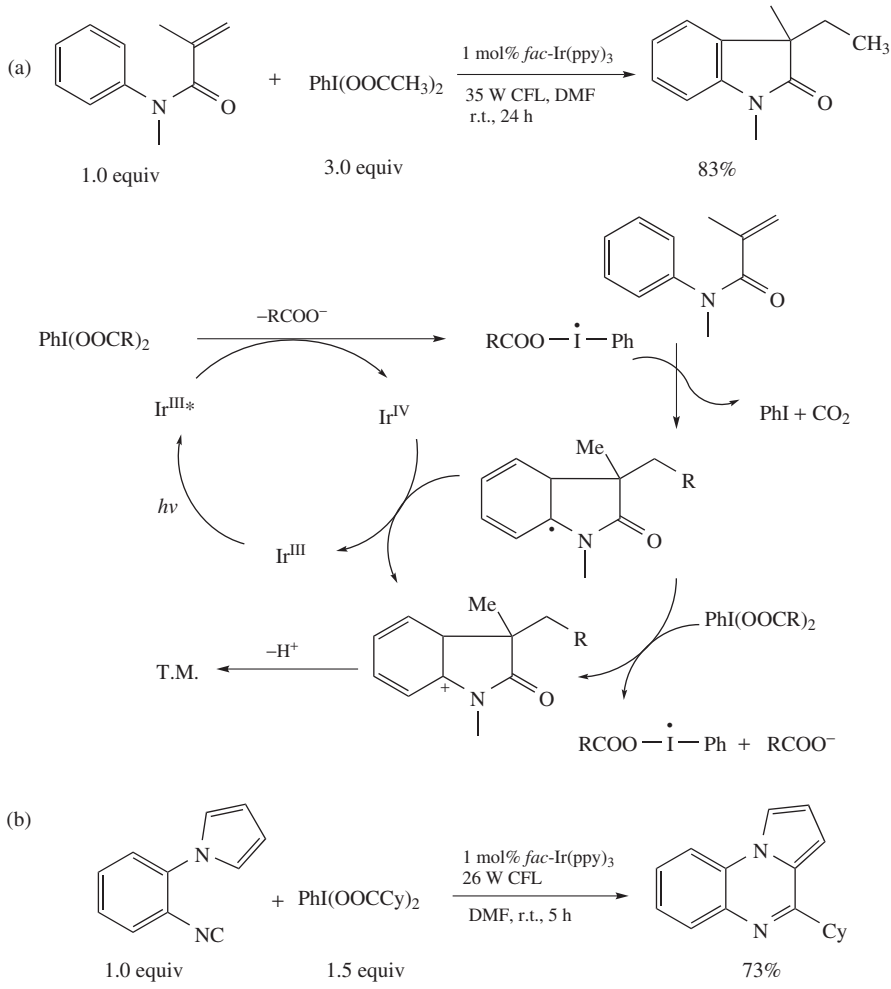

FIGURE 8. The alkylation with diacyloxyiodo-arene by photoredox catalysis.

This intermediate could be prepared independently and replaced the *in situ* generated mixture of ketoacid and BIOAc. In the photoredox catalytic cycle, the photoexcited Ru^{II}* was first oxidized by the benziodoxole radical to generate the Ru^{III} and the benziodoxole(III) cation. The benziodoxole(III) cation was then turned over for the new hypervalent iodine(III) catalytic cycle and the Ru^{III} further oxidized the BI-ketoacid intermediate to generate the acyl radical after decarboxylation. The alkyl- and aryl-substituted ketoacids, as well as carbamoyl ketoacids and alkoxycarbonyl ketoacids, were all applicable for the reaction. The decarboxylative semipinacol rearrangement was realized later by Duan and coworkers under similar reaction reactions with rhodamine as the photocatalyst (Figure 9b)[18].

The cyclic iodine(III) reagent (methoxyl benziodoxole (BIOMe)) was used by Qing and coworkers in 2016 for decarboxylative difluoromethylation with α,α-difluoroarylacetic acids,

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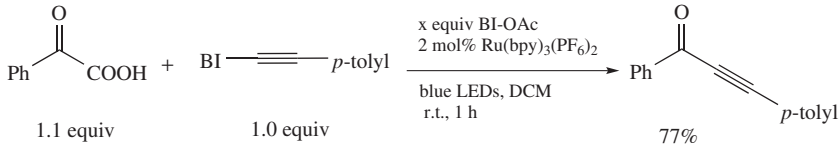
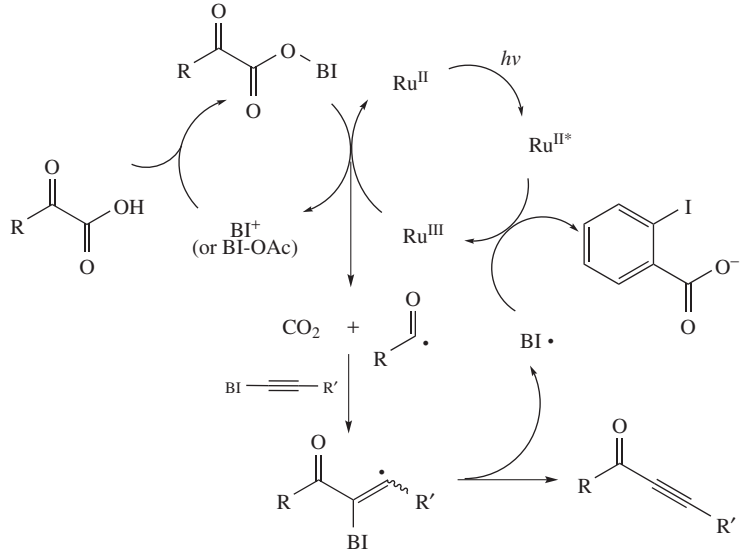
(a)



BI-OAc (equiv)	0	0.1	0.3	0.6	1.0	1.2
Yield (%)	2	59	68	79	86	85



(b)

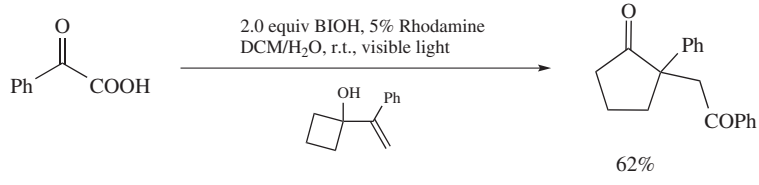


FIGURE 9. The acylation with cyclic iodine(III) reagents by photoredox catalysis.

which provided a facile entry to difluoroalkylated arenes by photoredox catalysis (Figure 10)[19]. The α,α-difluoroaryl acetic acid first reacted with BIOMe to form the BI-α,α-difluoroaryl acetic acid complex *in situ*, which was oxidized to generate the aryl difluoromethyl radical after CO_2 extrusion. This aryl difluoromethyl radical was then added to alkene for hydrodifluoromethylation reaction.

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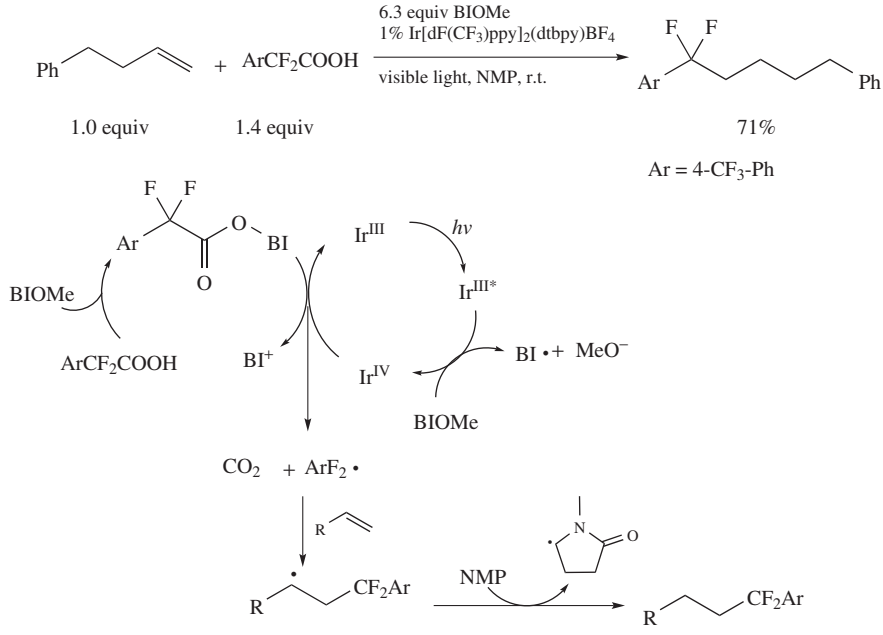

FIGURE 10. The difluoromethylation with cyclic iodine(III) reagents by photoredox catalysis.

Chen and coworkers discovered in 2015 a novel deboronative/decarboxylative alkenylation reaction with cyclic iodine(III) compounds by photoredox catalysis (Figure 11a)[20]. The mechanistic investigations indicated the formation of the benziodoxole-vinyl carboxylic acid complex, which was characterized by X-ray crystallography. The complex has an oxygen–iodine bond (2.12 Å) between the vinyl carboxylate and the benziodoxole moiety, which is similar to the oxygen–iodine bond (2.12 Å) in the benziodoxole moiety. The vinyl carboxylic acid and BIOAc generate the BI-vinyl carboxylate complex *in situ*, which can undergo alkyl radical addition from the oxidation of alkyl trifluoroborates. After the α-addition of the alkyl radical to the BI-vinyl carboxylate complex, the resulting alkyl radical intermediate undergoes benziodoxole-facilitated decarboxylation to release the benziodoxole radical and yields the alkene product. The radical addition to vinyl carboxylate was later utilized by Wang and coworkers in 2017 for the vinylation of 2,3-dihydrofuran in which the benziodoxole-vinyl carboxylic acid complex was the key reaction intermediate (Figure 11b)[21].

In summary, the hypervalent iodine(III)-coordinated carboxylates in photoredox catalysis undergo single-electron transfer reaction to generate carboxyl radicals via heterolytical bond-cleavage reaction of the oxygen–iodine bond, and the vinyl carboxylic acid can be activated for radical addition and subsequent decarboxylation reaction.

B. Alcohol Activation

It is challenging to generate the alkoxyl radicals from alcohols either from homolytic bond cleavage reaction or from single-electron oxidation reaction due to the strong bond dissociation energy of the oxygen–hydrogen bond and the high redox potential of alcohols (Figure 12)[22]. While transition metal catalysis has demonstrated alcohol activation applications for alkoxyl

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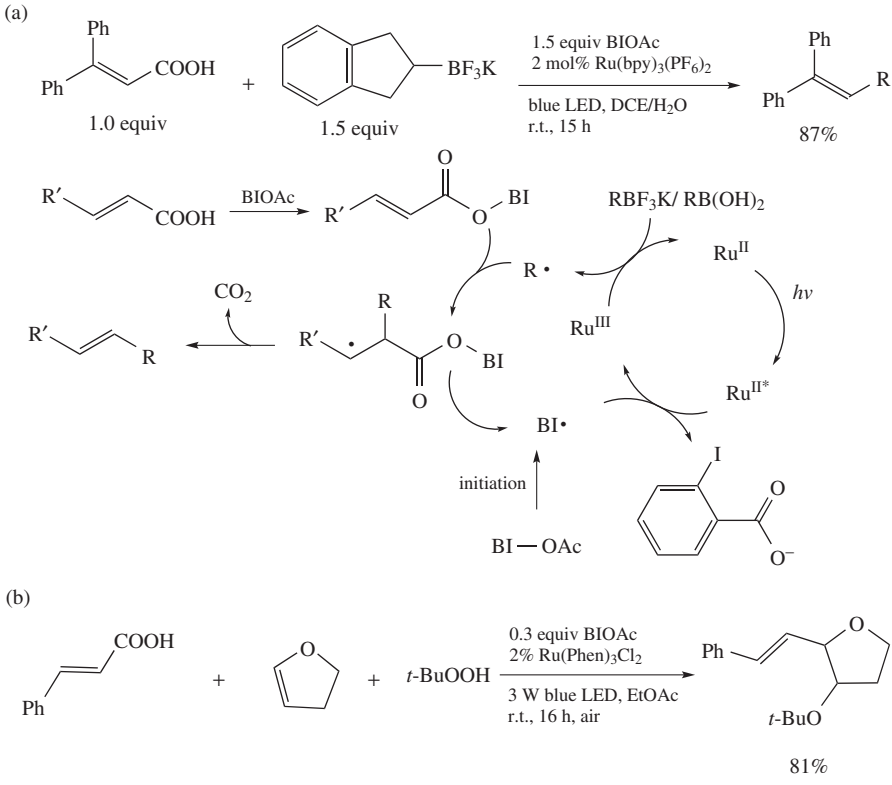

FIGURE 11. The alkenylation with cyclic iodine(III) reagents by photoredox catalysis.

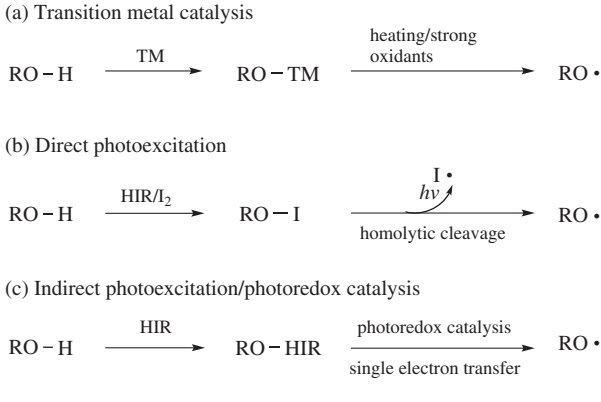

FIGURE 12. The hypervalent iodine activation of alcohols.

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radical generation (Figure 12a), heating and strong oxidants are required, offering to the hypervalent iodine compounds an attractive alternative[23]. Under light irradiation in the presence of iodosobenzene diacetate ($PhI(OAc)_2$) and iodine, the alcohol generates the iodine(I)-bound hydroxylate that can be homolytically cleaved to generate the alkoxyl radical (Figure 12b). Recently, the alcohol is reported to undergo ligand exchange with cyclic iodine(III) compounds to generate the cyclic iodine(III)-coordinated hydroxylate (Figure 12c)[24]. This cyclic iodine(III)-coordinated hydroxylate undergoes single-electron oxidation reaction under photoredox catalysis conditions to generate alkoxyl radicals, which can achieve the challenging inert C−H and C−C bond functionalizations.

1. Direct irradiation

Suárez and coworkers reported in 1984 the photolysis of alcohols with tungsten light for the synthesis of cyclic ethers in the presence of iodosobenzene diacetate ($PhI(OAc)_2$) and iodine (Figure 13a)[25]. The reaction mechanism involved the formation of the iodine(I)-bound hydroxylate, which led to the alkoxyl radical by homolytic cleavage upon irradiation. The alkoxyl radical underwent intramolecular hydrogen abstraction to generate the alkyl radical, then oxidized to the carbocation, and finally yielded cyclic ethers by nucleophilic alcohol attack. Baker and Brimble later reported the preparation of spiroacetals with similar reaction conditions via alkoxyl radical intermediate (Figure 13b)[26]. Suárez and coworkers reported in 1995 the synthesis of chiral spiroacetals from carbohydrates in pyranose or furanose forms in which both spiroacetal enantiomers were available from the same carbohydrate (Figure 13c)[27].

Millan and Galatsis reported in 1991 the photolysis of tertiary allylic alcohols with tungsten light leading to the epoxide formation in the presence of $PhI(OAc)_2$ and iodine (Figure 14a)[28]. The reaction mechanism involved the homolytic cleavage of the iodine(I)-bound hydroxylate to generate the alkoxyl radical upon irradiation. The alkyl group adjacent to the alkoxyl radical was required for the subsequent olefin addition and iodine trap to yield the alkyl iodide. Suárez and coworkers reported in 1995 the transannular cyclization of substituted cyclodecenones (Figure 14b)[29]. The reaction was initiated by the alkoxyl radical generation upon irradiation from the alcohol, $PhI(OAc)_2$, and iodine. The alkoxyl radical then added to the ketone to yield the ketyl radical and subsequently did transannular olefin addition to obtain the bicycle. Togo, Yokoyama, and coworkers reported in 1996 the intramolecular addition of alcohol to arenes for the cyclic ether synthesis (Figure 14c)[30]. The reaction mechanism involved the alkoxyl radical addition to the arene and the electron-rich or electron-deficient substituents on diacyloxyiodo-arenes that did not significantly affect the reaction.

Suárez and coworkers reported in 1986 the cleavage of steroidal alcohols with tungsten light in the presence of $PhI(OAc)_2$ and iodine (Figure 15a)[31]. Under argon atmosphere, the single carbon−carbon bond cleavage reaction was observed, while under oxygen atmosphere, the double carbon−carbon bond cleavage reaction occurred. Both the reactions involved the β-fragmentation of the alkoxyl radical, which was obtained from homolytic cleavage of the *in situ* formed iodine(I)-bound hydroxylate. Under argon atmosphere, the resulting alkyl radical was oxidized to the carbocation and eliminated proton to form the olefin. Under oxygen atmosphere, the alkyl radical was peroxidized by oxygen and further cyclized to ketone to generate the second alkoxyl radical. This newly formed alkoxyl radical underwent β-fragmentation to yield the alkyl radical, which was oxidized to yield the vinyl ketone. The same group later reported that the ketone was in equilibrium with hemiacetal, which could generate hemiacetal radical and undergo β-fragmentation to yield the ring-expansion product (Figure 15b)[31a,b]. Suárez and coworkers reported in 1992 the synthesis of chiral building blocks by fragmentation of the carbohydrates (Figure 15c)[32]. The reaction involved the formation of the alkoxyl radical and subsequent β-fragmentation to yield the alkyl radical, which was then oxidized to the carbocation and underwent nucleophilic acetate addition. Snyder and Chen reported in 1997

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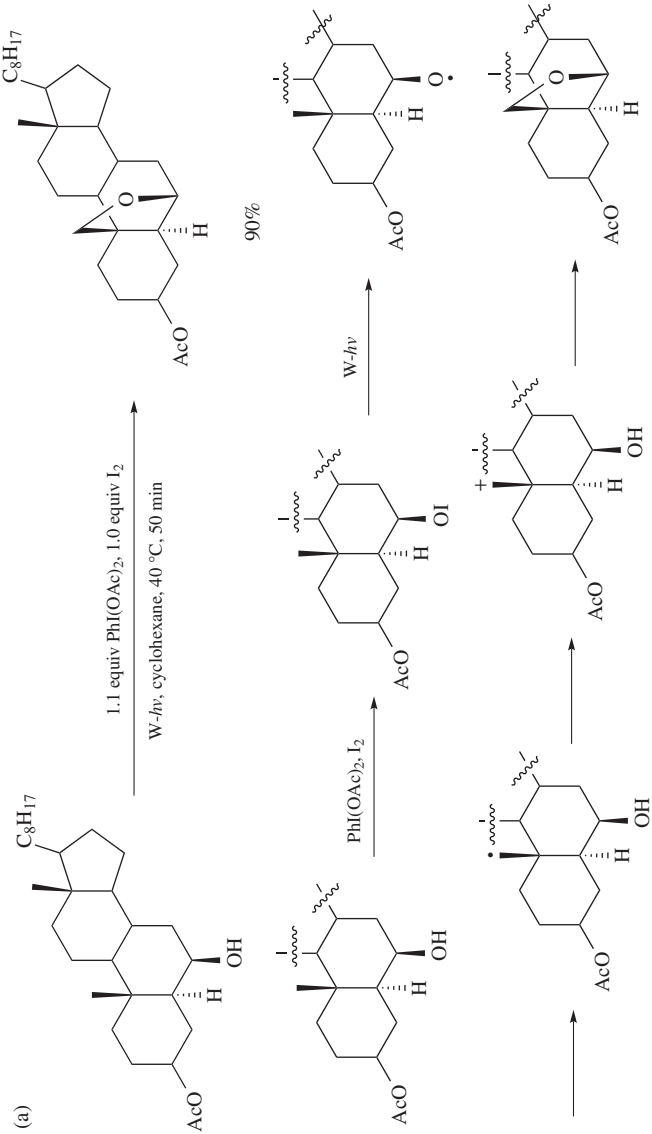

FIGURE 13. The cyclic ether formation with alcohols by intramolecular hydrogen abstractions.

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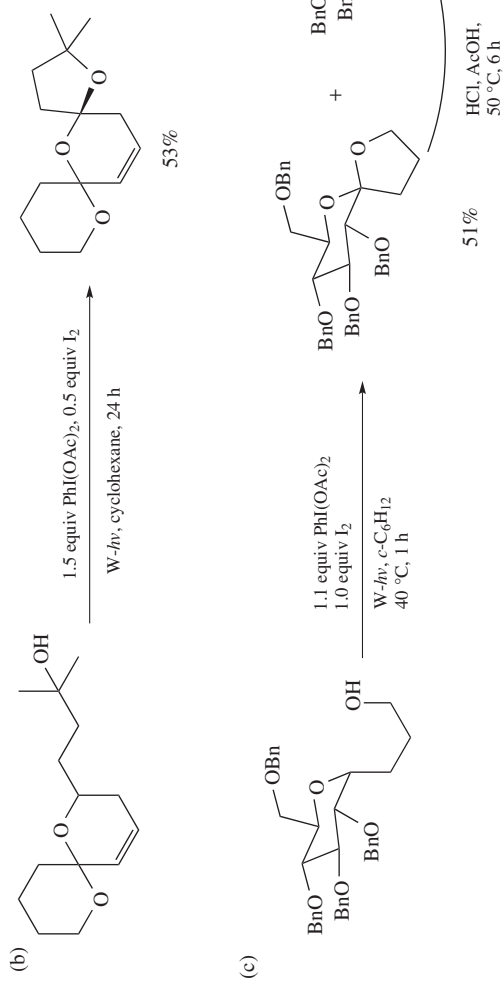

FIGURE 13. (*continued*)

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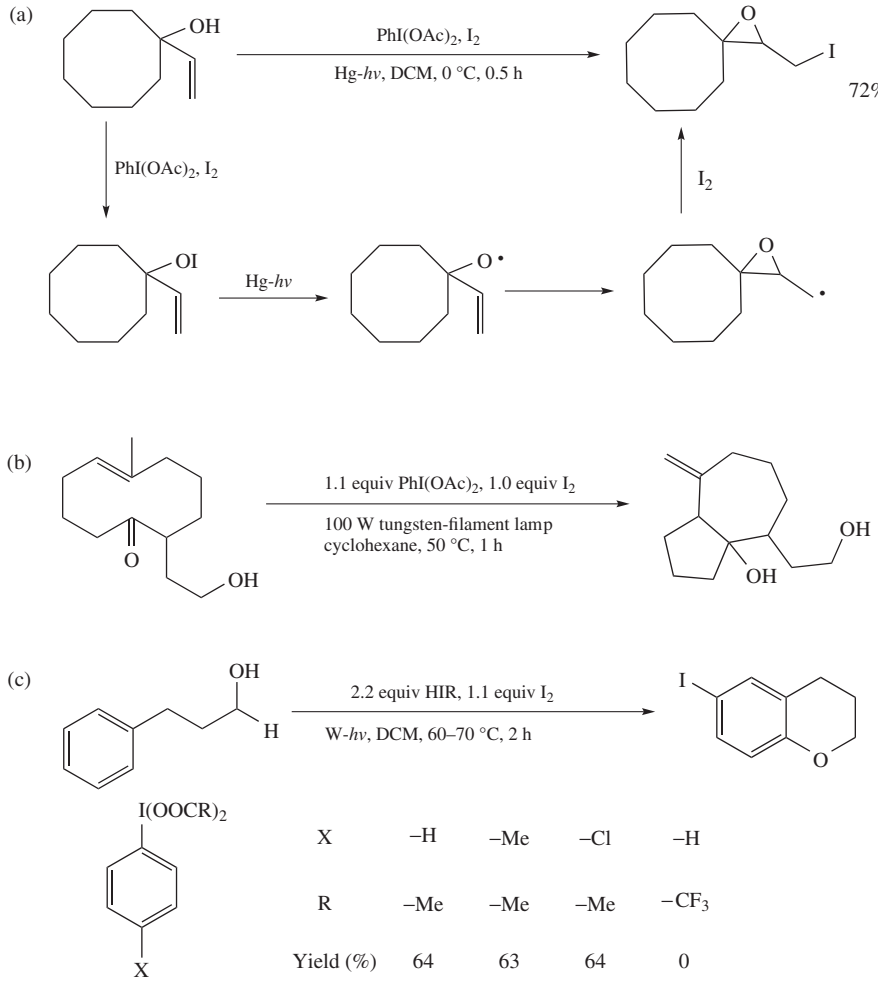

FIGURE 14. The cyclic ether formation with alcohols by alkene additions.

the photolysis of secondary alcohols to give bicyclic compounds with similar reaction mechanism (Figure 15d)[33].

Suárez and coworkers reported in 1987 the photolysis of the unsaturated lactol with tungsten light in the presence of $PhI(OAc)_2$ and iodine to yield the spirocycles. The reaction involved the alkyl radical formation from β-fragmentation of alkoxyl radicals, which underwent cyclization to vinyl ketones rather than being oxidized (Figure 16a)[34]. Pattenden and coworkers later reported in 1991 that the carbon-centered radical generated from β-fragmentation of alkoxyl radical underwent transannular cyclization cascade to yield the fused medium-sized rings (Figure 16b)[35].

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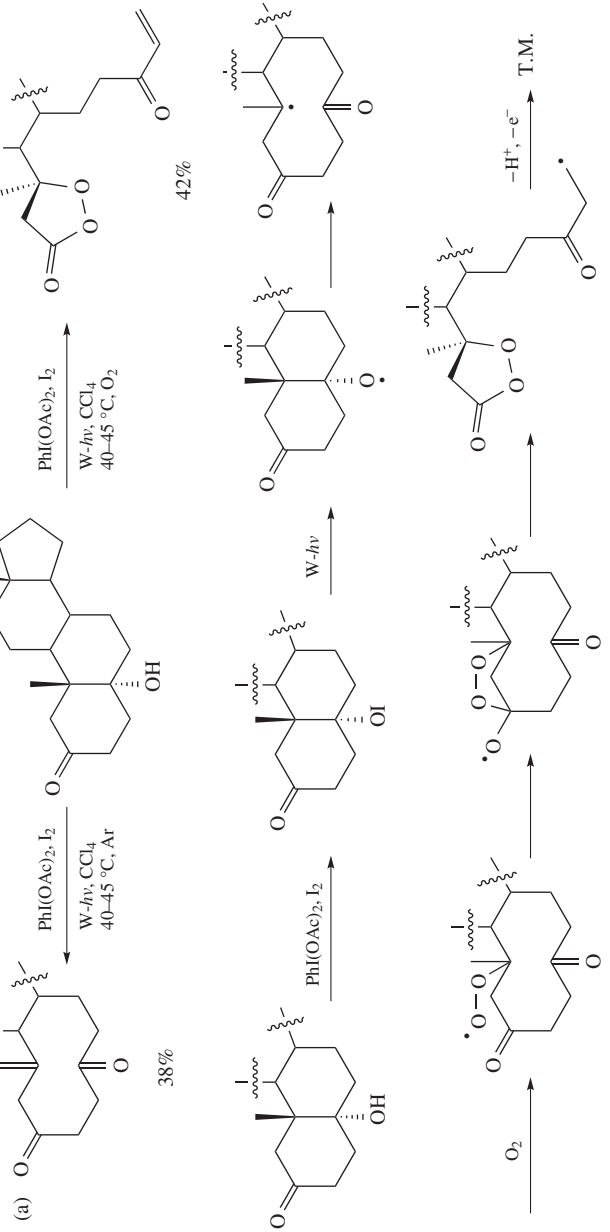

FIGURE 15. The cleavage of alcohols by β-fragmentation reaction.

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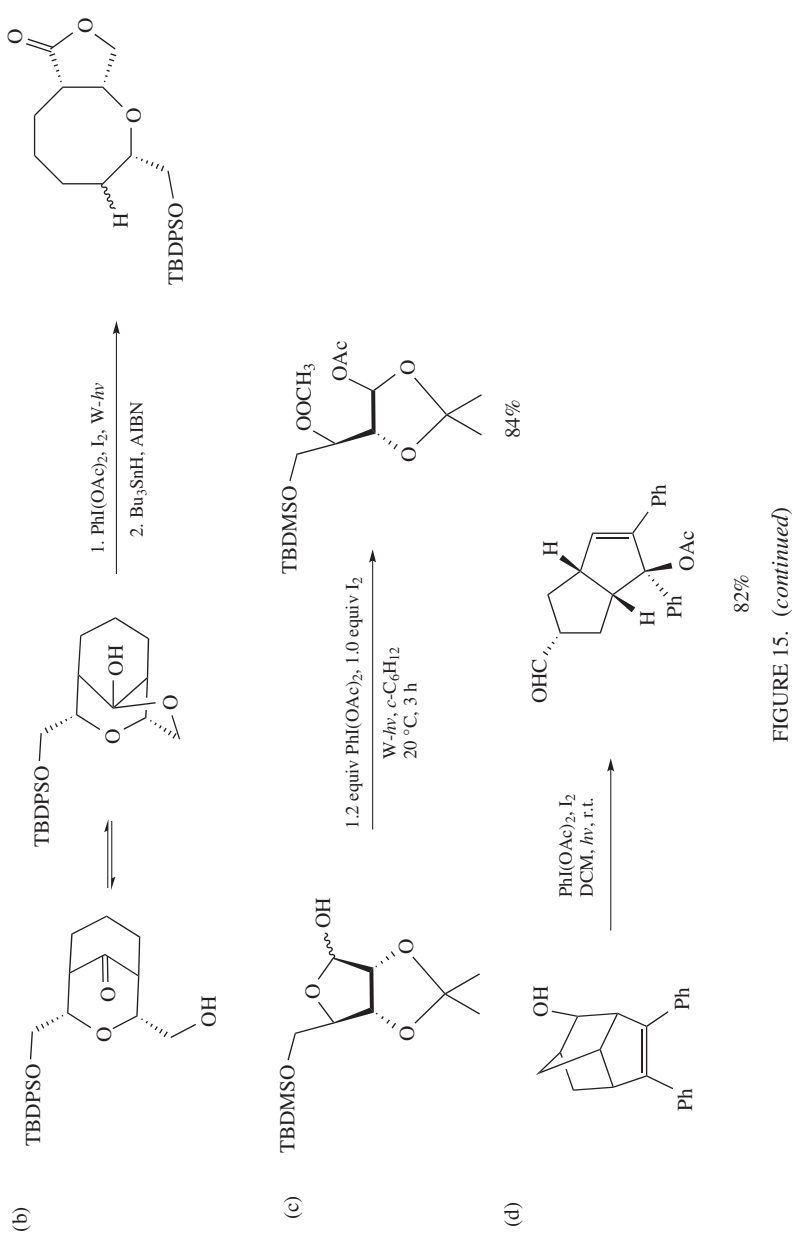

FIGURE 15. (*continued*)

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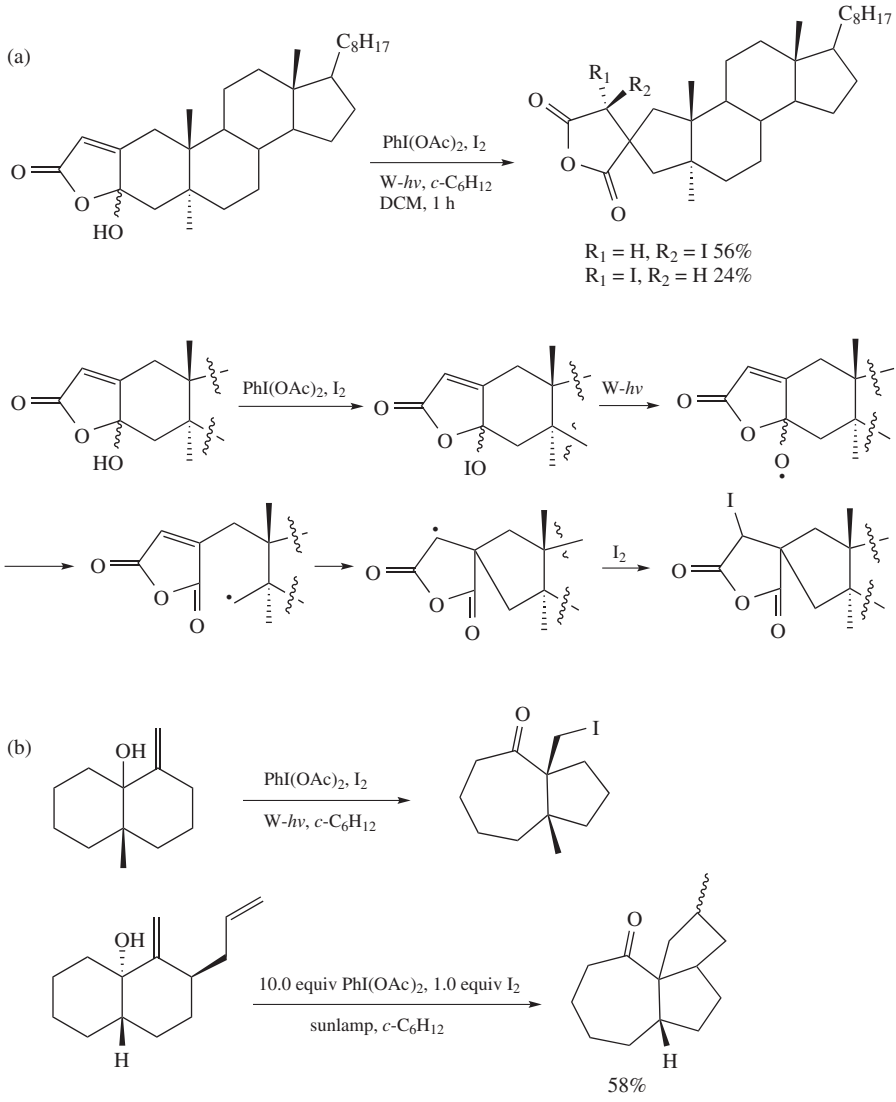

FIGURE 16. The fused ring formation with alcohols by β-fragmentation reaction.

In summary, under UV light irradiation in the presence of $PhI(OAc)_2$ and iodine, the alcohol generates the iodine(I)-bound hydroxylate *in situ*, which undergoes homolytic bond cleavage reaction to yield the alkoxyl radical. This alkoxyl radical undergoes hydrogen abstraction, olefin addition or β-fragmentation to generate the alkyl radical, which is usually intramolecularly trapped or oxidized to carbocation. However, the subsequent intermolecular carbon–carbon formation remains elusive with this approach.

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2. Photoredox catalysis

Chen and coworkers reported in 2016 the first visible-light-induced alcohol oxidation to generate alkoxyl radicals by cyclic iodine(III) reagent catalysis under mild photoredox catalysis conditions (Figure 17a)[24a]. The reaction involved the key benziodoxole/alcohol complex formation *in situ*, which enabled the alkoxyl radical generation by significantly reducing the oxidation potential of alcohols (Figure 17b–d). The alkoxyl radical underwent β-fragmentation to yield the alkyl radical, which did radical addition to the alkynyl or vinyl carboxylate-bound benziodoxole for alkynylation or alkenylation. Various strained cycloalkanols, and for the first time linear alcohols, underwent the selective $C(sp^3)$–$C(sp^3)$ bond cleavage and intermolecular C–C bond formation reactions.

Chen and coworkers reported in 2017 the first alkoxyl-radical-enabled carbonyl–$C(sp^3)$ bond cleavage/alkynylation reaction by photoredox catalysis (Figure 18a)[24b]. The reaction was initiated by the oxidation of the photoexcited $Ru(bpy)_3^{2+*}$ to $Ru(bpy)_3^{3+}$ by either the CIR or its decomposing CIR radical adduct. The $Ru(bpy)_3^{3+}$ then oxidized the β-carbonyl alcohol/CIR complex formed *in situ* and released the CIR cation (CIR^+) for the new CIR catalytic cycle. The alkoxyl radical underwent β-carbonyl–$C(sp^3)$ bond-cleavage reaction to yield the carbamoyl, alkoxylcarbonyl, or acyl radical and finally formed ynamides, ynoates, or ynones by radical addition to alkynyl benziodoxoles (Figure 18b). β-Amide, β-ester, and β-ketone alcohols yielded ynamides, ynoates, and ynones, respectively, for the first time, with excellent regio- and chemo-selectivity under mild reaction conditions. The use of novel cyclic iodine(III) reagents was essential for β-carbonyl alkoxyl radical generation from β-carbonyl alcohols (Figure 18c).

In summary, the cyclic iodine(III) reagents in photoredox catalysis significantly reduce the oxidation potential of alcohols to generate alkoxyl radicals via cyclic iodine(III)-coordinated alcohols. Compared to alkoxyl radicals generated from direct irradiation, the photoredox catalysis conditions are mild, and the resulting alkyl radical or acyl radical from β-fragmentation undergoes selective intermolecular carbon–carbon formation reactions.

C. Amine Activation

Compared to photochemical transformation of carboxylic acids and alcohols using hypervalent iodine compounds, its related reports on amines are far less (Figure 19)[36]. In the presence of $PhI(OAc)_2$ and iodine, the protected amine generates iodine(I)-bound amines and is homolytically cleaved to generate the nitrogen radical under direct light irradiation. In contrast, the hypervalent iodine activation of amines by photoredox catalysis remains elusive.

1. Direct irradiation

Suárez and coworkers reported in 1985 the photolysis of nitro-substituted amines with tungsten light leading to cyclic amines in the presence of $PhI(OAc)_2$ and iodine (Figure 20)[37]. The reaction mechanism involved the formation of the iodine(I)-bound amines whose homolytic cleavage upon irradiation led to the nitrogen radical. The nitrogen radical then underwent intramolecular hydrogen abstraction to generate the alkyl radical, which was trapped by iodine or further oxidized to carbocation for cyclic amine formation.

Togo, Yokoyama, and coworkers reported in 1998 the preparation of saccharin skeleton via sulfonyl-protected nitrogen radical intermediate (Figure 21a)[38]. Different hypervalent iodine(III) reagents were tested, and the phenyl substituents decreased the reaction yields. Muñiz and Martinez reported in 2015 the photolysis of sulfonamides with visible light leading to cyclic sulfonamides with iodosobenzene di-*m*-chlorobenzoate ($PhI(mCBA)_2$) and catalytic amount of iodine (Figure 21b)[39]. Herrera and coworkers reported in 2015 the similar reaction in the presence of $PhI(OAc)_2$ and iodine, and the amide was obtained with the addition

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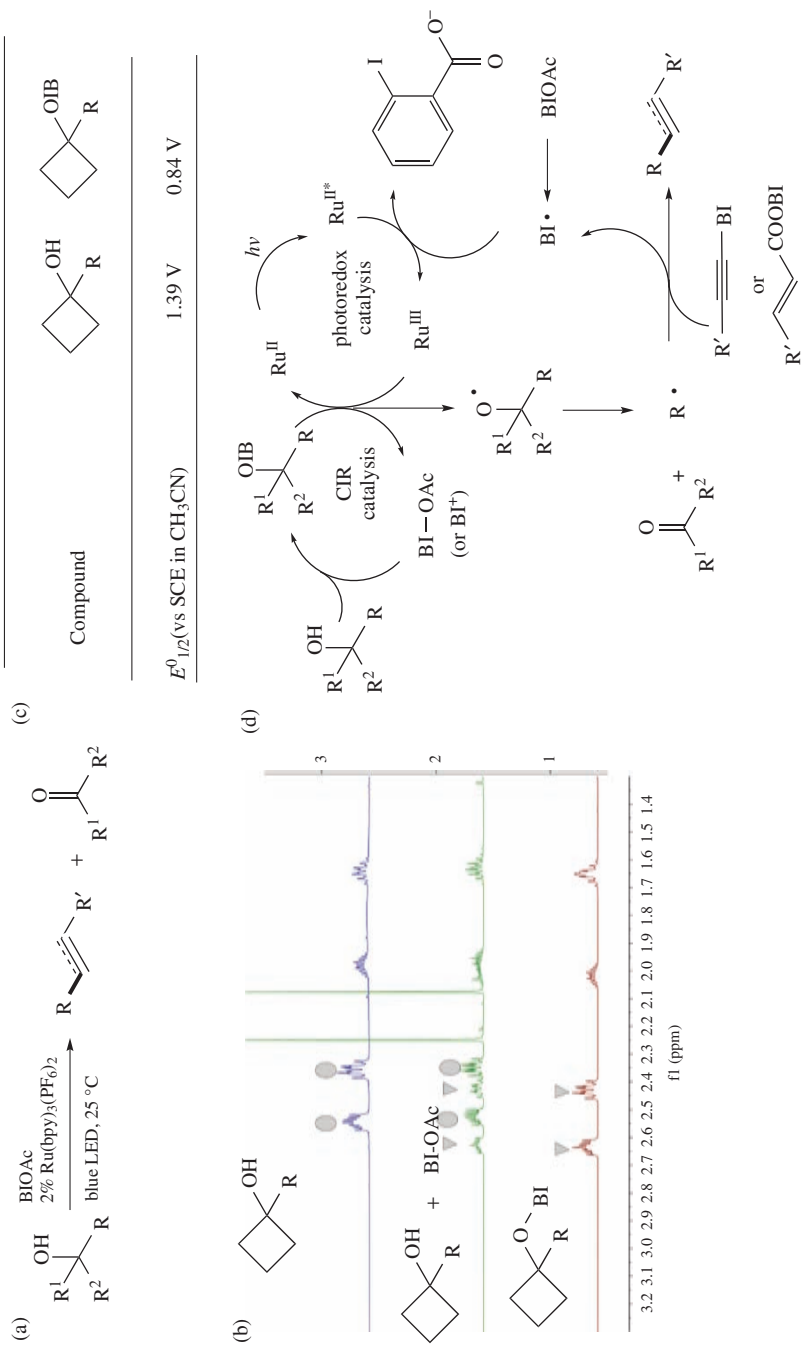

FIGURE 17. The $C(sp^3)$–$C(sp^3)$ bond cleavage/functionalization with cyclic iodine(III) reagents by photoredox catalysis.

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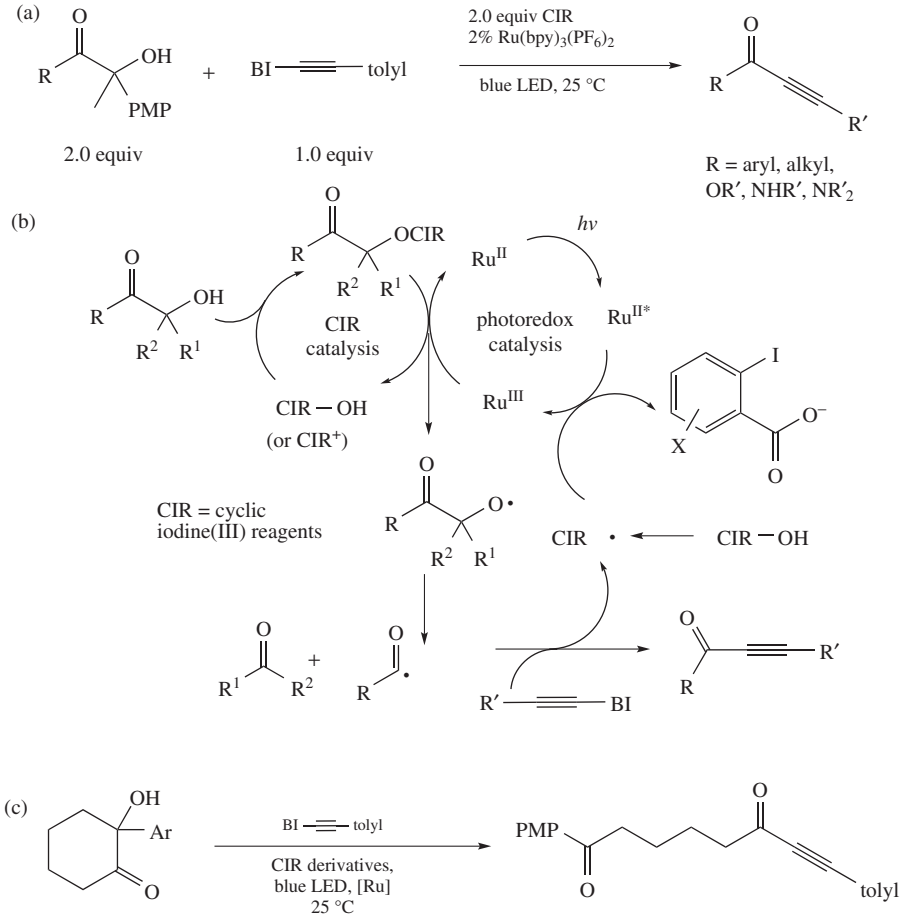

CIR	Alcohol	BIOAc/ alcohol	3,4-F-BIOAc/ alcohol	3,4-OMe-BIOAc /alcohol	2,3,4,5-F- BI-OH /alcohol
Alcohol /CIR(E_p) (V)	1.69	1.06	0.93	1.21	N/A
Yield (%)	0	48	53	41	77 (74)

FIGURE 18. The carbonyl−C(sp^3) bond cleavage/functionalization with cyclic iodine(III) reagents by photoredox catalysis.

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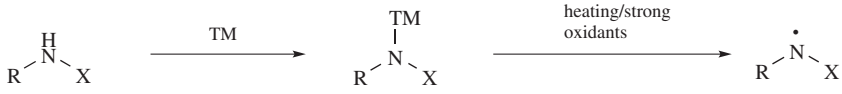
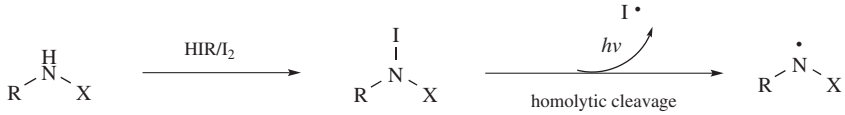
(a) Transition metal catalysis



(b) Direct photoexcitation



(c) Indirect photoexcitation/photoredox catalysis

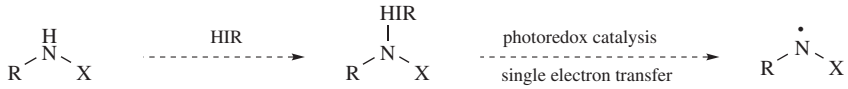


FIGURE 19. The hypervalent iodine activation of amines.

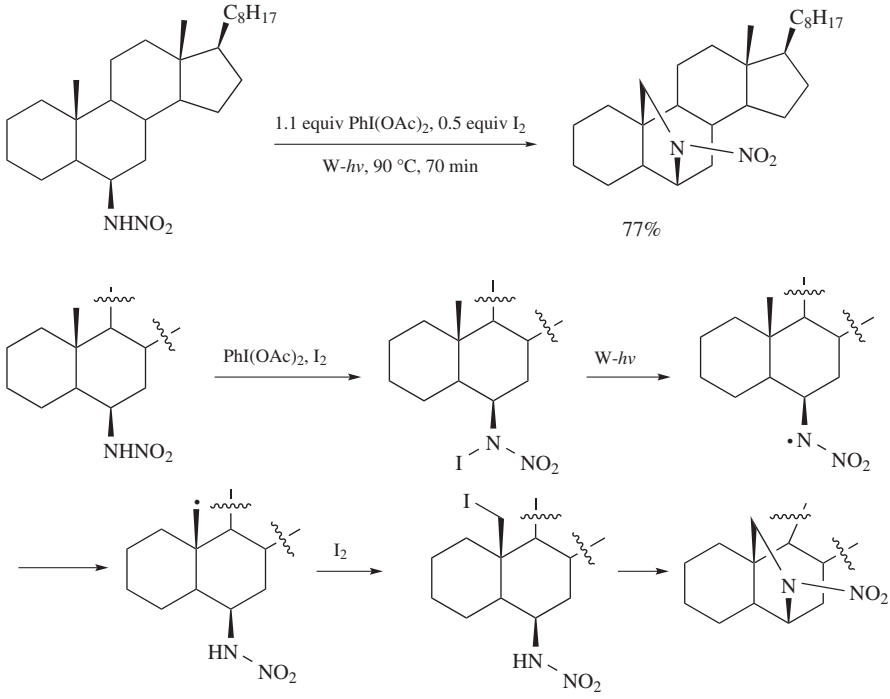


FIGURE 20. The cyclic amine formation with amines by intramolecular hydrogen abstractions.

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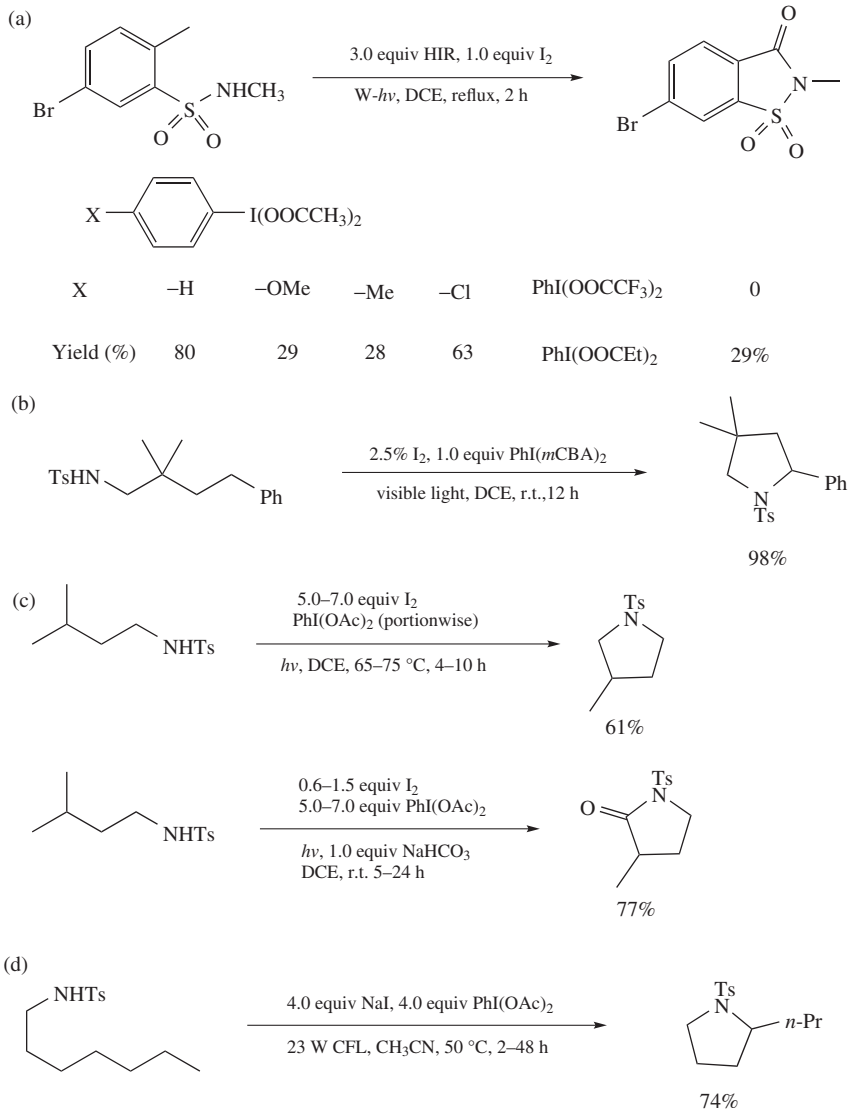

FIGURE 21. The cyclic amine formation with amines by intramolecular hydrogen abstractions.

of bases (Figure 21c)[40]. Nagib and coworkers reported in 2016 the sulfonamide cyclization reaction with visible light in the presence of $PhI(OAc)_2$ and sodium iodide (Figure 21d)[41].

Togo, Yokoyama, and coworkers reported in 1998 the intramolecular addition of sulfonyl-protected amine to arenes for the synthesis of cyclic phenyl amine (Figure 22a)[42]. The reaction mechanism involved the nitrogen radical addition to the arene to yield the radical intermediate, which further underwent oxidation and elimination to yield the cyclic aniline product.

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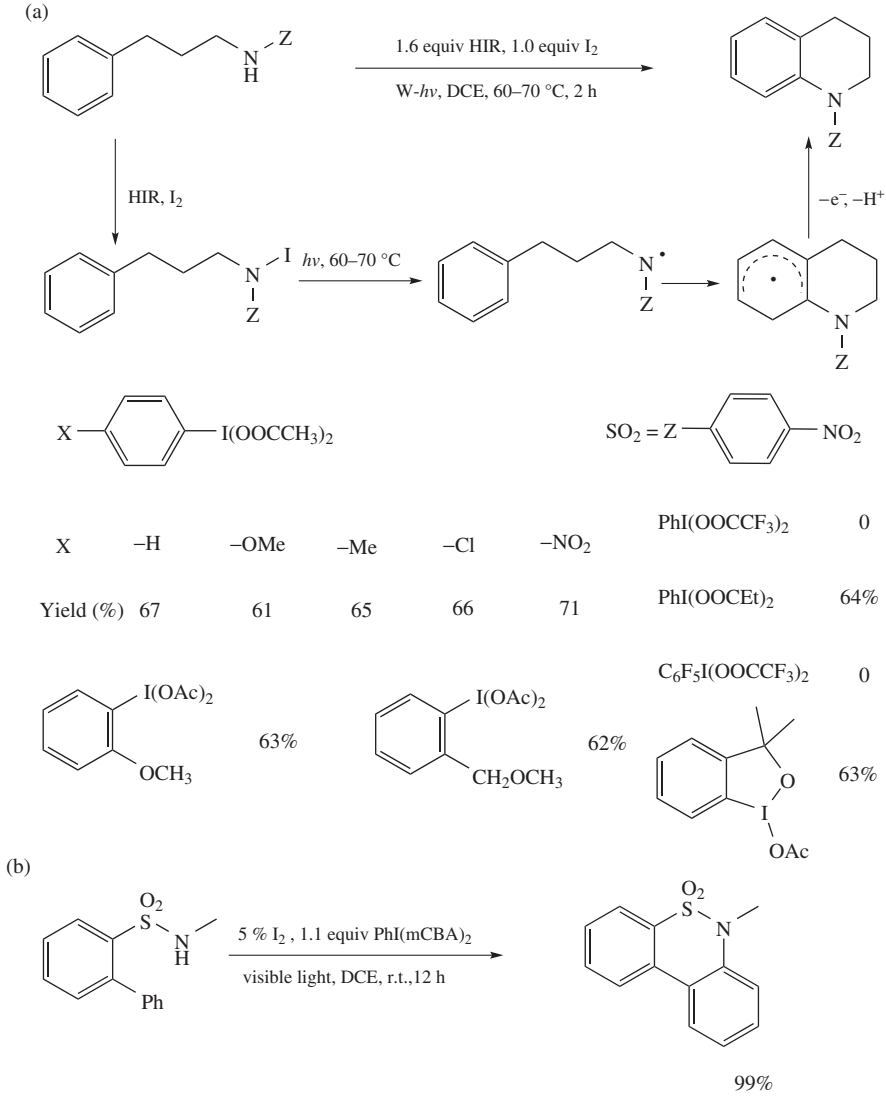

FIGURE 22. The cyclic amine formation with amines by arene additions.

Electron-rich or electron-deficient substituents on diacyloxyiodo-arenes did not significantly affect the reaction. Muñiz and coworkers reported in 2016 the synthesis of cyclic aniline with PhI(*m*CBA)$_2$ and catalytic amount of iodine[43].

In summary, in the presence of PhI(OAc)$_2$ and iodine, the protected amine generates the iodine(I)-bound amines *in situ*, which undergoes homolytic bond cleavage reaction to yield the nitrogen radical with direct light irradiation. The nitrogen radical undergoes hydrogen abstraction on the intramolecular alkyl group for alkyl radical generation or on the intramolecular aryl

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group for cyclization reaction. The amine-coordinated hypervalent iodine compound in photoredox catalysis for single-electron oxidation reaction of the nitrogen–iodine bond remains to be explored.

III. HYPERVALENT IODINE COMPOUNDS AS REAGENTS IN PHOTOCHEMISTRY

Hypervalent iodine(III) compound reagents demonstrate different roles under photoredox catalysis conditions (Figure 23). The diaryl iodonium salts, trifluoromethyl benziodoxoles, and azido benziodoxoles are aryl radical, trifluoromethyl radical, and azido radical precursors. The hydroxyl/acetoxyl/alkoxyl benziodoxoles can oxidatively quench photoexcited photocatalysts in photoredox catalysis. The alkynyl benziodoxoles and cyano benziodoxoles can facilitate the photocatalytic turnover and undergo radical alkynylation or cyanation.

A. Diaryl Iodonium Salts

Greaney and Fumagalli reported in 2013 the difunctionalization of styrenes using diaryl iodonium salts and methanol by iridium photoredox catalysis (Figure 24a)[44]. The reaction mechanism involves the reduction of the diaryl iodonium salt by photoexcited Ir^{III}* to generate the aryl radical after nitrogen extrusion, which is then trapped by styrene to yield the benzyl radical. The benzyl radical is oxidized by Ir^{IV} to the carbocation and attacked by the methanol to obtain the difunctionalization product. Akita and coworkers later reported in 2016 the similar difunctionalization of styrenes using diaryl iodonium salts and water by ruthenium photoredox catalysis (Figure 24b)[45]. Fensterbank, Ollivier, and coworkers reported in 2013 the allylation reaction using diaryl iodonium salts and allyl sulfones by copper photoredox catalysis with green light irradiation (Figure 24c)[46].

Wang and coworkers reported in 2013 the arylation of pyrrole derivatives using diaryl iodonium salts by ruthenium photoredox catalysis (Figure 25a)[47]. The reaction mechanism involves the reduction of the diaryl iodonium salt by photoexcited Ru^{II}* to generate the aryl radical after nitrogen extrusion, which is then trapped by pyrrole derivatives to yield the dearomatized radical. The radical is oxidized by Ru^{III} to the carbocation and eliminates the proton to obtain the pyrrole arylation product. Chatani and coworkers later reported the similar arylation

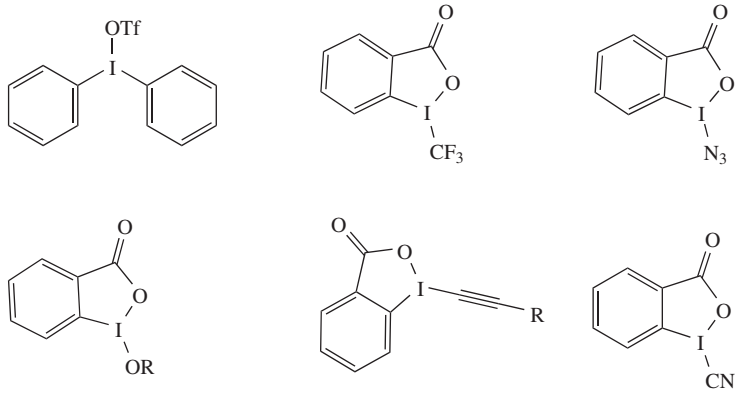

FIGURE 23. Structures of hypervalent iodine reagents in photochemistry.

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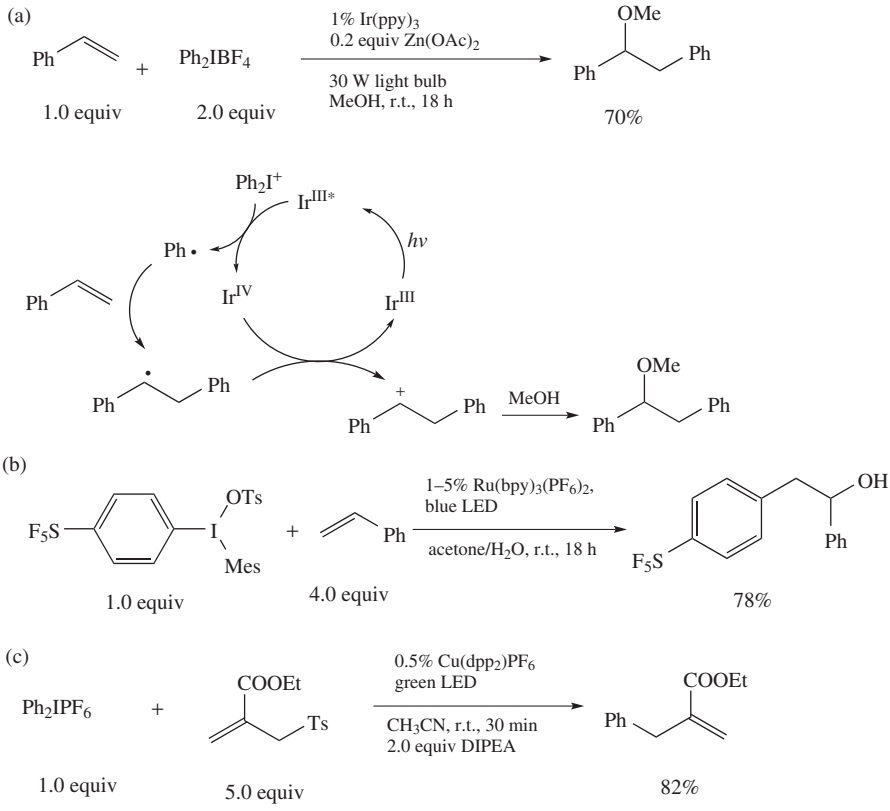

FIGURE 24. The alkene addition with diaryl iodonium salts.

of pyrroles and arenes using diaryl iodonium salts by iridium photoredox catalysis, and the reaction of pyrroles could be run in the absence of photocatalysts (Figure 25b)[48]. Denton and coworkers reported in 2016 the construction of quaternary aryl phosphonium salts using diaryl iodonium salts and triaryl phosphine by ruthenium photoredox catalysis (Figure 25c)[49].

Sanford and Neufeldt reported in 2012 the arylation of electron-rich arenes using diaryl iodonium salts by dual palladium/iridium photoredox catalysis for the first time (Figure 26a)[50]. The reaction mechanism is proposed to involve the reduction of the diaryl iodonium salt by photoexcited $Ir^{III}*$ to generate the aryl radical after nitrogen extrusion, which then attacks the cyclopalladated complex Pd^{II} to yield the Pd^{III}. The Pd^{III} is oxidized by Ir^{IV} to the Pd^{IV} and undergoes reductive elimination to yield the arylation product. Alternatively, Pd^{III} directly undergoes reductive elimination to release Pd^{I} and the arylation product. Glorius and coworkers reported in 2014 the difunctionalization of terminal alkenes using diaryl iodonium salts and methanol by dual gold/iridium photoredox catalysis (Figure 26b)[51]. The reaction mechanism involves the coordination of Au^{I} to the alkene followed by methanol attack to yield the alkyl Au^{I} complex. The photoredox cycle involves the reduction of the diaryl iodonium salt by photoexcited $Ir^{III}*$ to generate the aryl radical after nitrogen extrusion, which is then trapped by alkyl Au^{I} intermediate to yield the Au^{II}. The Au^{II} is oxidized by Ir^{IV} to Au^{III} and undergoes reductive elimination to release Au^{I} and the difunctionalization product.

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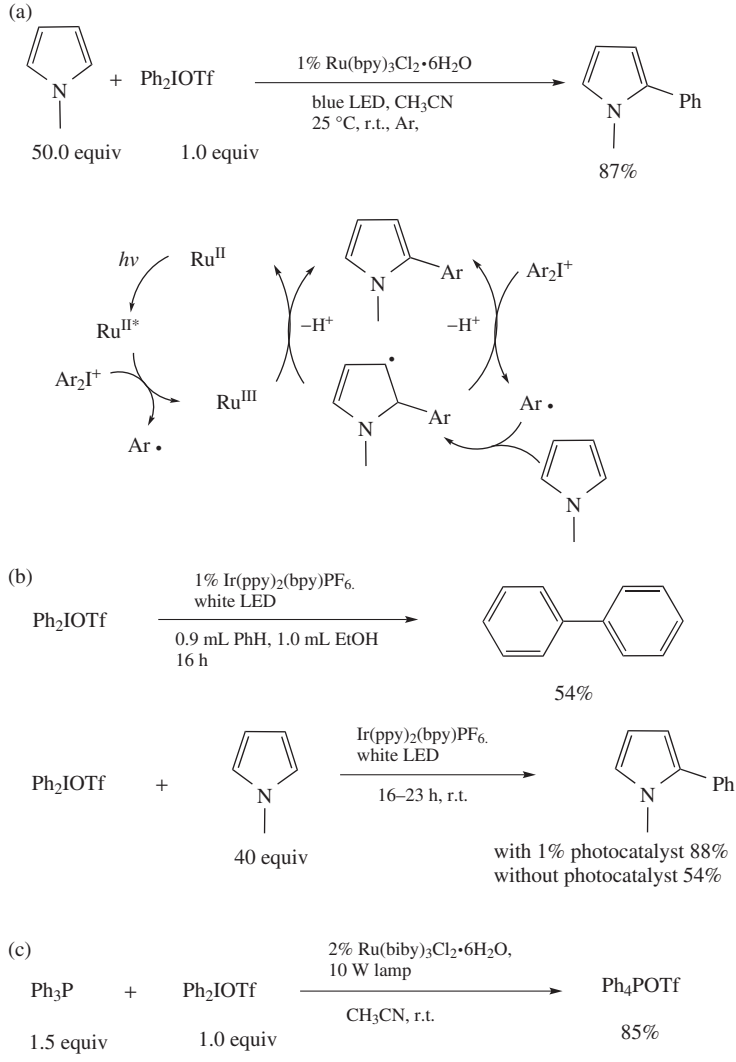

FIGURE 25. The alkene and arene addition with diaryl iodonium salts by dual metal/photoredox catalysis.

B. Trifluoromethyl Benziodoxoles (Togni Reagent)

Akita, Koike, and coworkers reported in 2013 the trifluoromethylation of vinylborates using the trifluoromethyl benziodoxoles (Togni reagent) by ruthenium photoredox catalysis (Figure 27)[52]. The reaction mechanism involves the reduction of the trifluoromethyl benziodoxoles by the photoexcited Ru^{II}* to generate the trifluoromethyl radical, which does radical addition to vinyl boronates to yield the alkyl radical. The alkyl radical is oxidized to carbocation by Ru^{III} and eliminates boron-containing species to obtain the *trans*-trifluoromethylated

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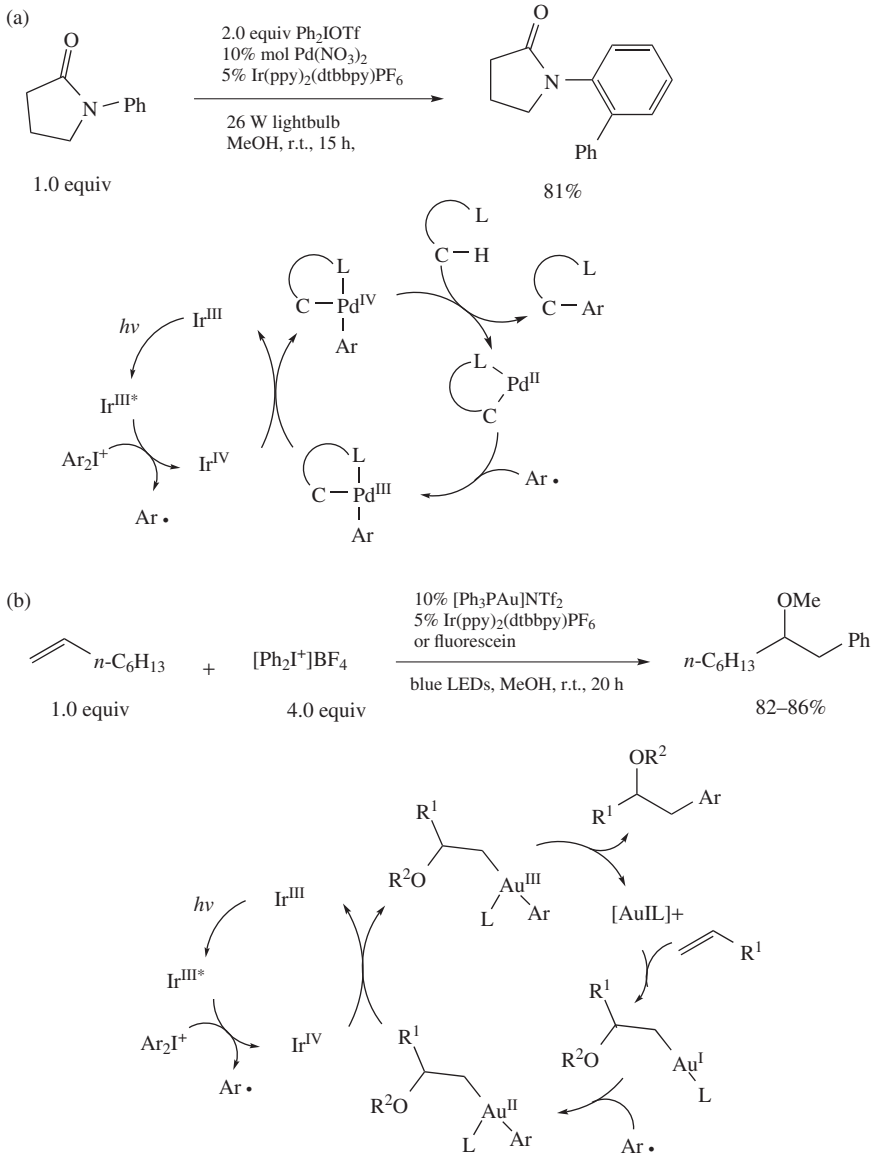

FIGURE 26. The alkene and arene addition with diaryl iodonium salts by dual metal/photoredox catalysis.

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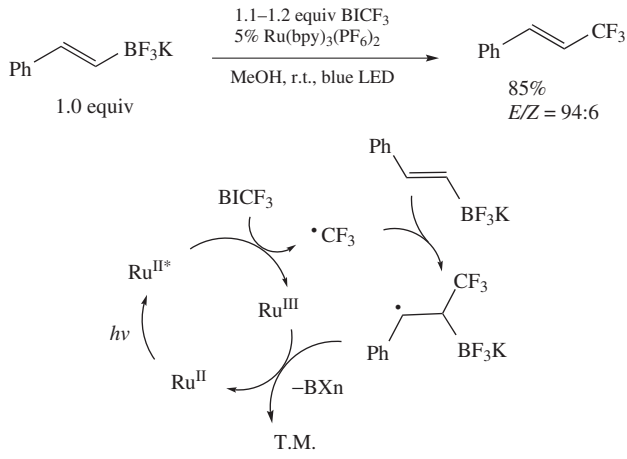

FIGURE 27. The alkene addition with trifluoromethyl benziodoxoles.

alkene. Alternatively, the oxidation of the radical intermediate may proceed in radical chain mechanism.

C. Azido Benziodoxoles

Greaney and coworkers reported in 2016 the azidation of benzylic C−H bond using azido benziodoxoles by copper photoredox catalysis (Figure 28a)[53]. The reaction mechanism involves the reduction of the azido benziodoxoles by photoexcited Cu^{I}* to generate the azido radical after o-iodobenzoic acid extrusion, which then undergoes hydrogen abstraction to yield the benzyl radical. The benzyl radical further reacts with azido benziodoxoles to obtain the benzyl azide and the benziodoxole radical, which initiates the radical chain reaction. Chen and coworkers reported independently in 2016 the azidation or halogenation of tertiary aliphatic C−H bonds using azido benziodoxoles by ruthenium photoredox catalysis (Figure 28b)[54].

Greaney and coworkers reported in 2015 the difunctionalization of styrene using azido benziodoxoles by copper photoredox catalysis (Figure 29)[55]. The reaction mechanism involves the reduction of the azido benziodoxoles by photoexcited Cu^{I}* to generate the azido radical after *o*-iodobenzoic acid extrusion, which is then trapped by styrene to yield the benzyl radical. The benzyl radical is oxidized by Cu^{II} to the carbocation and attacked by methanol or bromide nucleophile to obtain the difunctionalization product. In the absence of light, the double azidation product was obtained instead.

D. Hydroxyl/acetoxyl/alkoxyl Benziodoxoles

The cyclic iodine(III) reagents are unreactive under most reaction conditions and do not demonstrate strong oxidative reactivity as noncyclic iodine(III) reagents such as $PhI(OAc)_2$. However, it demonstrates facile oxidative quenching reactivity of photoexcited ruthenium complexes in photoredox catalysis. Since the discovery of this unique reactivity in 2014, it has found many synthetic applications for the facile generation of oxidized photocatalyst intermediate under photoredox catalysis conditions.

Chen reported in 2014 the first use of hydroxyl benziodoxoles (BIOH) as the oxidative quencher in ruthenium photoredox catalysis for deboronative alkynylation (Figure 30)[56]. The

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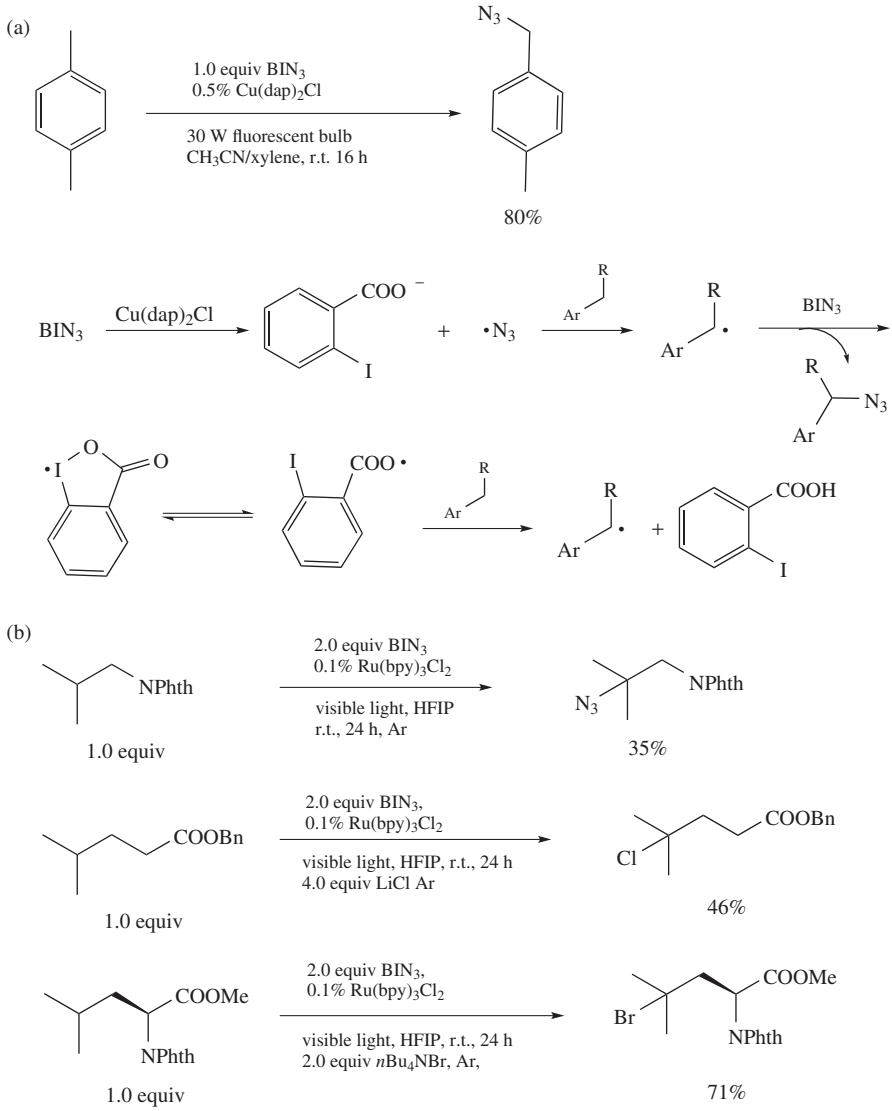

FIGURE 28. The C−H functionalization with azido benziodoxoles.

hydroxyl/acetoxyl/alkoxyl benziodoxoles effectively enable the photocatalytic reaction and show superior reactivity compared to the persulfates. The reaction mechanism involves the key oxidation of photoexcited Ru^{II}* by the hydroxyl benziodoxole or its resulting benziodoxole radical to Ru^{III}. The Ru^{III} oxidizes alkyl trifluoroborate to alkyl radical, whose α-addition to BI-alkynes eliminates benziodoxole radical for photocatalytic turnover.

Chen and coworkers later reported in 2015 a deboronative/decarboxylative alkenylation reaction with acetoxyl benziodoxoles (BIOAc) by ruthenium photoredox catalysis (Figure 31a)[20].

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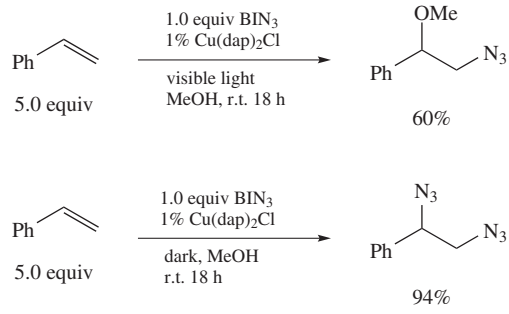

FIGURE 29. The alkene addition with azido benziodoxoles.

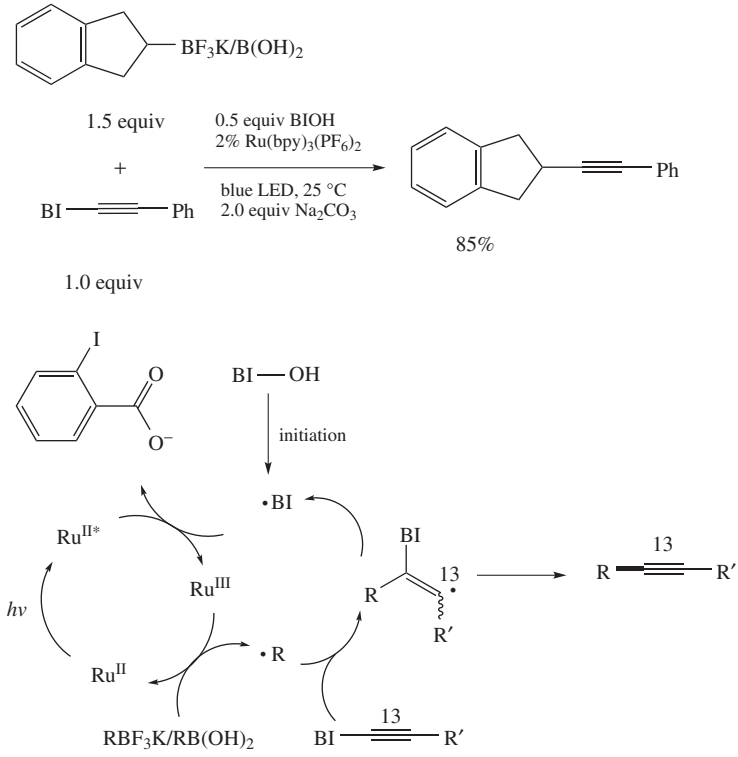

FIGURE 30. The oxidative quench of excited photocatalysts with hydroxyl/acetoxyl/alkoxyl benziodoxoles.

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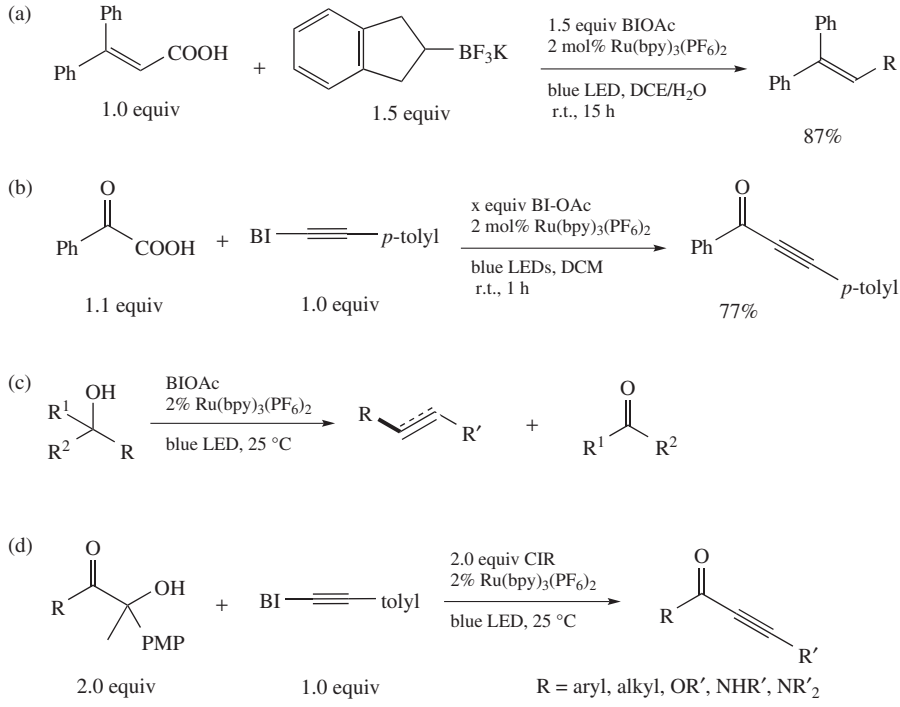

FIGURE 31. The applications of hydroxyl/acetoxyl benziodoxoles as oxidative quenchers.

The same group reported in 2015 a decarboxylative ynonylation reaction with acetoxyl benziodoxoles by ruthenium photoredox catalysis (Figure 31b)[17]. In both reactions, the acetoxyl benziodoxoles oxidatively quench the photoexcited Ru^{II}* for reaction initiation. In addition, the acetoxyl benziodoxoles activate the vinyl carboxylic acids for alkyl radical addition and the keto acids for acyl radical formation (see Section II.A for details). Chen and coworkers reported in 2016 that the alkoxyl radical enabled $C(sp^3)$–$C(sp^3)$ bond cleavage and alkynylation reaction with acetoxyl benziodoxoles by ruthenium photoredox catalysis (Figure 31c)[24a]. Later in 2017, the same group reported that the alkoxyl radical enabled carbonyl–$C(sp^3)$ bond cleavage and alkynylation reaction with acetoxyl benziodoxole derivatives by ruthenium photoredox catalysis (Figure 31d)[24b]. In both reactions, the acetoxyl benziodoxoles oxidatively quench the photoexcited Ru^{II}* for reaction initiation. In addition, the acetoxyl benziodoxoles activate the tertiary alcohols and the β-carbonyl tertiary alcohols for alkoxyl radical generation (see Section II.B for details).

Xu and coworkers reported in 2016 a deboronative cyanation with acetoxyl benziodoxoles by ruthenium photoredox catalysis (Figure 32a)[57]. The tosyl cyanide was used as the radical cyanation reagent, and the use of trifluoroacetic acid was necessary for the reaction. Chen and coworkers reported in 2016 a deboronative arylation of *N*-heteroarenes with acetoxyl benziodoxoles by ruthenium photoredox catalysis (Figure 32b)[58]. The reaction mechanism involves the initial oxidation of photoexcited Ru^{II}* by the acetoxyl benziodoxole to Ru^{III}. The resulting Ru^{III} oxidizes alkyl boronic acids to alkyl radicals, whose Minisci-type addition to *N*-heteroarenes eliminates benziodoxole radical for photocatalytic turnover. Xu and coworkers later reported in 2017 a deboronative pyridination with acetoxyl benziodoxoles by ruthenium

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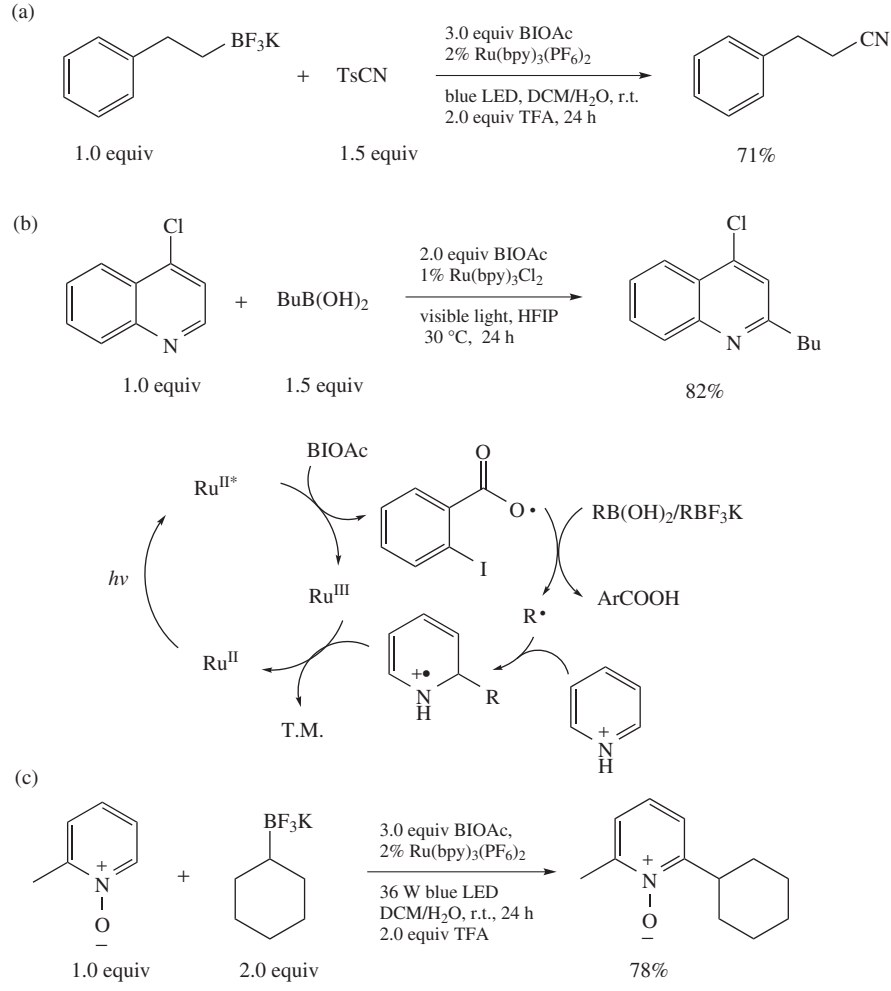

FIGURE 32. The applications of acetoxyl benziodoxoles as oxidative quenchers.

photoredox catalysis (Figure 32c). The radical Minisci-type reaction mechanism was proposed for the alkyl radical addition to pyridine *N*-oxides[59].

Itami and coworkers reported in 2017 the dehydrogenative coupling between sulfonimides and arenes with butoxyl benziodoxoles by ruthenium photoredox catalysis (Figure 33)[60]. The butoxyl benziodoxoles facilitate the photocatalytic reaction more effectively compared to other oxidants. The reaction mechanism involves the initial oxidation of photoexcited $Ru^{II}*$ by the butoxyl benziodoxole to Ru^{III}. The resulting Ru^{III} oxidizes sulfonimides to sulfonimidyl radical, which does Minisci-type addition to arenes to afford the arene imidation product.

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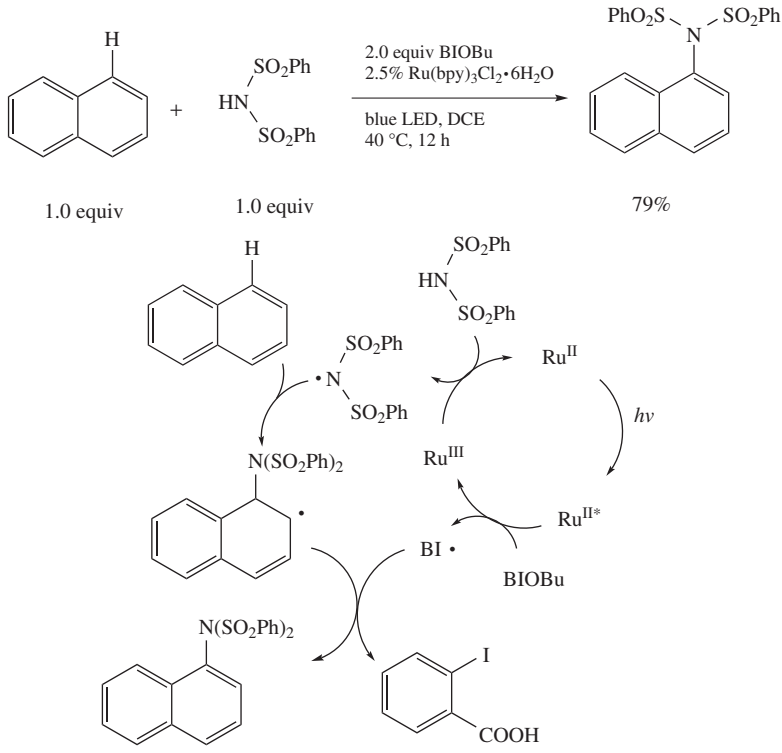

FIGURE 33. The applications of alkoxyl benziodoxoles as oxidative quenchers.

E. Alkynyl Benziodoxoles

Chen and coworkers first used alkynyl benziodoxoles (BI-alkyne) in ruthenium photoredox catalysis for deboronative alkynylation in 2014 (Figure 34a)[56]. The reaction mechanism involves the oxidation of photoexcited Ru^{II}* by the benziodoxole radical (or its precursor hydroxyl benziodoxole) to Ru^{III}. The resulting Ru^{III} oxidizes alkyl trifluoroborate to alkyl radical and regenerates Ru^{II}. The alkyl radical does α-addition to BI-alkyne and yields the alkyne. The eliminated benziodoxole radical oxidizes Ru^{II}* to generate the *o*-iodobenzoic acid, which is removed by the addition of bases (see Figure 30 for details). The same group reported later the decarboxylative ynonylation reaction using BI-alkyne and ketoacids by ruthenium photoredox catalysis (Figure 34b)[17].

Waser, Xiao, and coworkers independently reported in 2015 the decarboxylative alkynylation using aliphatic carboxylic acids and BI-alkyne by iridium photoredox catalysis (Figure 35a)[61]. The reaction mechanism involves the oxidation of aliphatic carboxylates by photoexcited Ir^{III}* to aliphatic carboxyl radical, followed by decarboxylation to yield the alkyl radical for α-addition to BI-alkyne. Xiao and coworkers also found the alkyl radical could incorporate carbon monoxide to yield the acyl radical for ynonylation reaction (Figure 35b).

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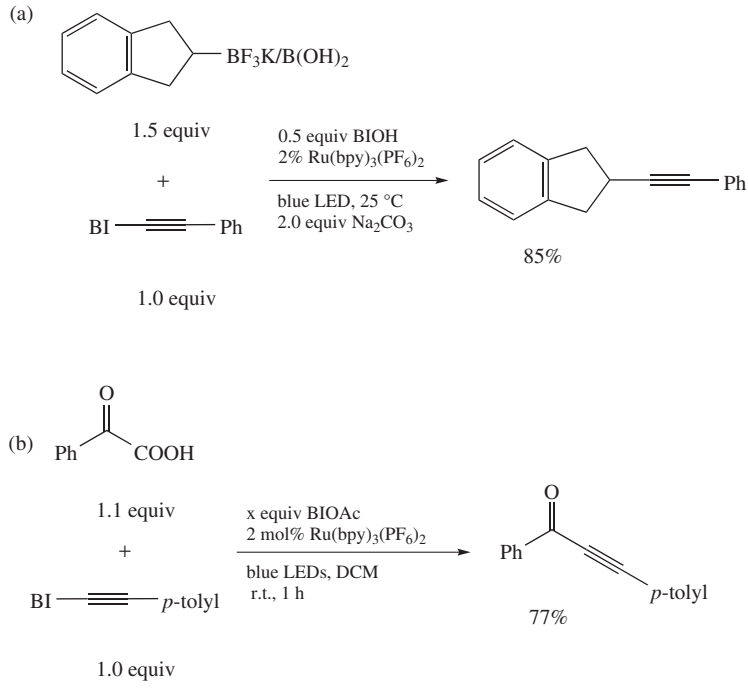

FIGURE 34. The alkyl or acyl radical addition to alkynyl benziodoxoles.

Chen and coworkers reported in 2016 the alkoxyl radical enabled C(sp^3)–C(sp^3) bond cleavage and alkynylation reaction using BI-alkyne and tertiary alcohols by ruthenium photoredox catalysis (Figure 36a)[24a]. The same group later reported in 2017 the alkoxyl radical enabled carbonyl–C(sp^3) bond cleavage and alkynylation reaction using BI-alkyne and β-carbonyl tertiary alcohols by ruthenium photoredox catalysis (Figure 36b)[24b].

F. Cyano Benziodoxoles

Xiao and coworkers reported in 2017 the α-cyanation reaction of tertiary amines using cyano benziodoxole by iridium photoredox catalysis (Figure 37)[62]. The proposed reaction mechanism involves an initial single-electron oxidation of tertiary amines by Ir^{III}*, which delivers the alkyl radical and Ir^{II}. The addition of the alkyl radical to cyanobenziodoxole generates the cyanation product and benziodoxole radical, which oxidizes Ir^{II} to Ir^{III}. Isolated examples of aliphatic carboxylic acids decarboxylated to afford the corresponding nitriles were also reported.

Waser and coworkers reported independently in 2017 the decarboxylative cyanation of aliphatic carboxylic acids to the corresponding nitriles by iridium photoredox catalysis (Figure 38)[63]. The experimental and computational studies were carried out to explore the reaction mechanism. The proposed mechanism involves the initial single-electron oxidation of carboxylic acid by the Ir^{III}* to deliver the alkyl radical and Ir^{II}. Subsequently, direct radical reaction of the alkyl radical to cyanobenziodoxole was higher in energy. In contrast, the single-electron oxidation of alkyl radicals by cyanobenziodoxole is proposed by computational studies to form an iminium intermediate, which undergoes nucleophilic cyanide addition to afford the nitriles.

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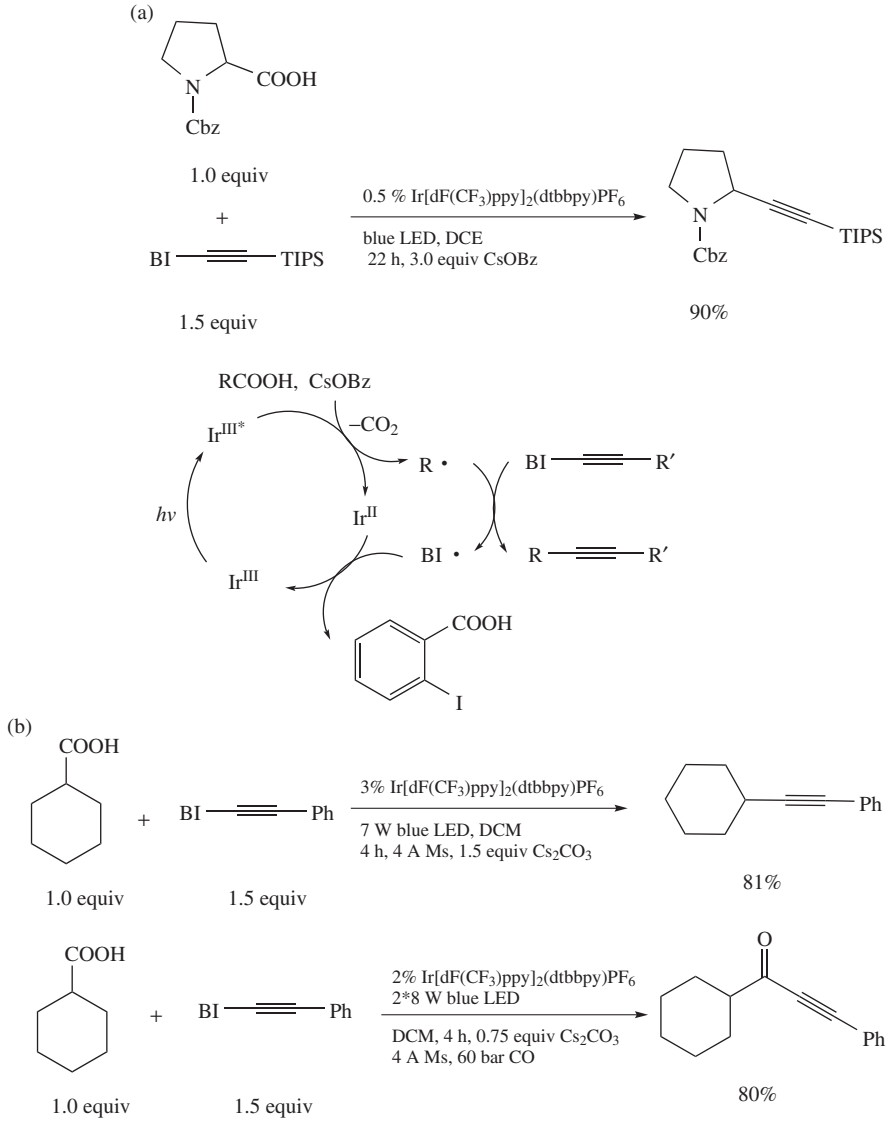

FIGURE 35. The alkyl or acyl radical addition to alkynyl benziodoxoles.

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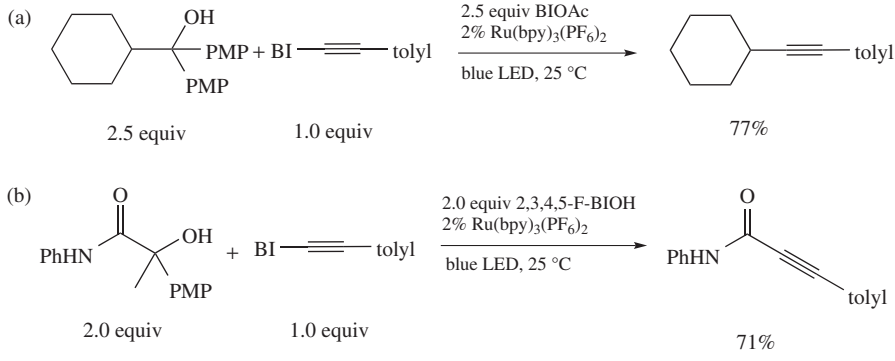

FIGURE 36. The alkyl or acyl radical addition to alkynyl benziodoxoles.

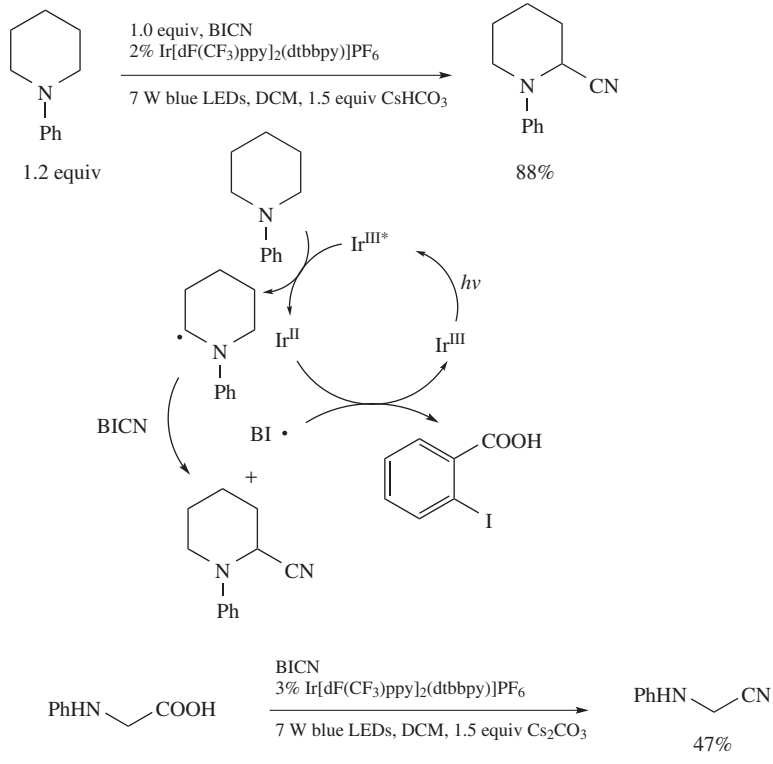

FIGURE 37. The alkyl radical addition to cyano benziodoxoles.

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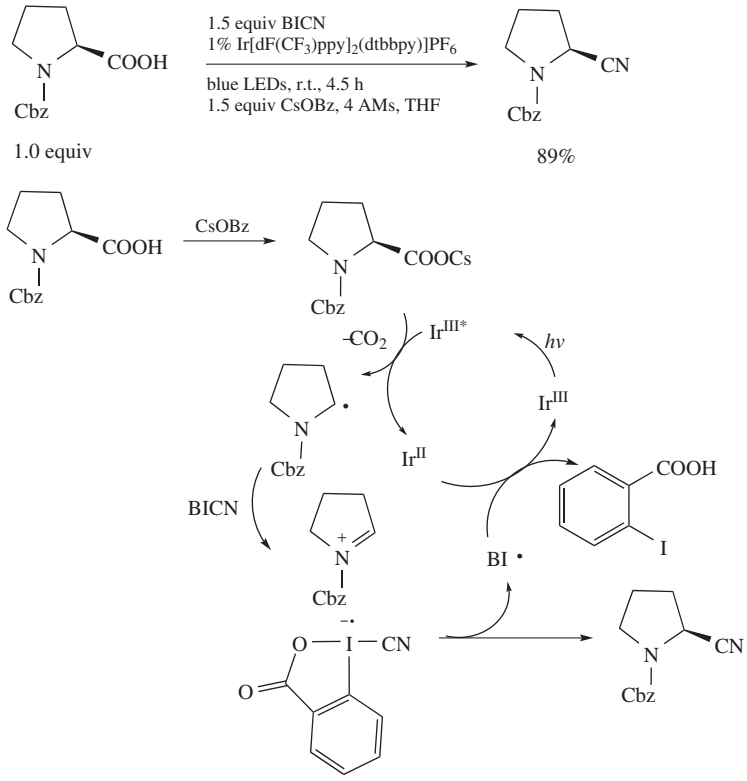

FIGURE 38. The decarboxylative addition to cyano benziodoxoles.

IV. CONCLUSION AND OUTLOOK

In conclusion, hypervalent iodine compounds have demonstrated unique substrate activation reactivity for carboxylic acids, alcohols, and amines for generation of oxygen radicals and nitrogen radials in photochemistry. In addition, the hypervalent iodine-coordinated carbon and azide species readily participated in photoredox catalysis reactions as radical precursors, oxidative quenchers, or radical acceptors. Traditionally, the photochemical reactivity is demonstrated with direct photoexcitation using noncyclic iodine(III) reagents or in combination with iodine. Recently, the use of cyclic iodine(III) reagents in photoredox catalysis has demonstrated unprecedented reactivity with better chemoselectivity under mild reaction conditions. It is expected that hypervalent iodine compounds will find further photochemical reactivity especially under photoredox catalysis conditions.

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