Hypervalent iodine chemistry and light: photochemical reactions involving hypervalent iodine Chemistry

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Abstract

Chemistry of hypervalent iodine reagents have developed extensively after the discovery of IBX as a commercial reagent in organic synthesis. Their stability in air, environmentally nature and unique reactivity under mild reaction conditions makes them more suitable reagents for medicinal and natural product chemistry. Various synthetic transformations have been achieved by using hypervalent iodine reagents under mild reaction conditions. Hypervalent iodine catalysis is identified as an emerging research area in past couple of decades. In past few years, hypervalent iodine reagents have found their application in photoredox catalysis. In this review article, the progress of photoredox catalysis by involving hypervalent iodine reagents would be covered.

Keywords: Hypervalent iodine, photoredox, photocatalyst, LED, irradiation, photoexcited

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1. Introduction

In the past few decades, the chemistry of hypervalent iodine reagents has contributed significantly to organic synthesis and natural product chemistry. These reagents are known to achieve various oxidative transformations under mild and environment friendly reaction conditions. Several hypervalent iodine reagents have been identified as potential oxidants. Additionally, these reagents have been successfully applied to obtain several synthetic transformations including cyclizations, aminations, α-functionalizations of carbonyl compounds, arylation, atom-transfer reactions, and cycloaddition reactions. Moreover, these reagents have been used as catalyst to develop number of organic transformations. In recent years, hypervalent iodine reagents received a particular attention in visible-light photoredox catalysis. In this review article, the visible-light photoredox reactions are covered where the hypervalent iodine reagents are involved.
2. Photochemical Reactions with Photoredox Catalysis

2.1. Alkynylation

Alkynylation is an important reaction in synthetic organic chemistry and there are various routes available to achieve the alkynylation reactions in literature.\(^\text{56}\) In past decade, ethynylbenziodoxole (EBX) has been introduced successfully for the alkynylation of different organic species.\(^\text{57-59}\) Recently, alkynylation of different organic species has been successfully achieved by using the combination of hypervalent iodine reagents with various photoredox catalysts. Mainly, cyclic hypervalent iodine reagents have been used in photoredox catalysis and their role is to generate the radical species. In this section, various photo-catalyzed alkynylation of various organic compounds using hypervalent iodine reagents would be highlighted.

2.1.1. Deboronative alkynylation. In 2014, the deboronative alkynylation of potassium alkyl trifluoroborates was reported by using ruthenium complex 4 as photo-catalyst in the presence of blue light. This was the first photo-catalyzed radical alkynylation approach by using EBX (ethynylbenziodoxole) 2 as source of alkynic species. In all the reactions, blue light was used to driven the photoredox and 1,3-disubstituted alkynes 5 were isolated in good to high yields (Scheme 1).\(^\text{60}\) The combination of BI-OH (hydroxybenziodoxole) 3 (5.0 mol %) and photo-catalyst Ru(bpy)\(_3\)(PF\(_6\))\(_2\) 4 (2.0 mol %) was used as catalytic system. Interestingly, various functional groups were successfully tolerated under given reaction conditions and reaction products were obtained in good yields without detecting in side reactions.

\[
\begin{align*}
\text{R}^1\text{BF}_3\text{K} + \text{O} = \equiv \text{I} \rightarrow \text{O} = \equiv \text{R}^2 \\
\text{R}^1 = \text{1-Indeny1, Cy, Ph, Bn, 4-BrC}_4\text{H}_4 \text{ etc}; \text{R}^2 = \text{Ph, 4-CIC}_4\text{H}_4, 4-\text{PhC}_4\text{H}_4, 4-\text{MeC}_4\text{H}_4, 4-\text{CHOCC}_4\text{H}_4, 4-\text{MeCOC}_4\text{H}_4, 2-\text{CNC}_4\text{H}_4 \text{ etc}
\end{align*}
\]

Scheme 1. Photoredox-catalyzed deboronative alkynylation of potassium alkyl trifluoroborates 1 with alkynyl benziodoxole 2 to alkynes 5.

The possible mechanism for the deboronative alkynylation of potassium alkyl trifluoroborates 1 with EBX 2 in the presence of photoredox catalyst 4 is described in scheme 2. Initially, Ru(II)\(^{2+}\) absorbs the blue light and gets excited to Ru(II)\(^{2+*}\). The photo-excited ruthenium species is further oxidized to Ru(III)\(^{3+}\) probably either by benziodoxole radical or its precursor BI-OH 3. Furthermore, Ru(III)\(^{3+}\) oxidized organotrifluoroborate species 1 to corresponding alkyl R\(^1\) radical and regenerates Ru(II)\(^{2+}\). Finally, alkyl R\(^1\) radical provides desired alkynes 5 on α-addition to EBX. In this process, benziodoxole radical 6 eliminates which oxidize Ru(II)\(^{2+}\) to Ru(III)\(^{3+}\)and form ortho-iodobenzoic acid. Furthermore, the Ru(III)\(^{2+}\) enters into the next catalytic cycle.
Scheme 2. Mechanism for the photoredox-catalyzed deboronative alkynylation of potassium alkyl trifluoroborates 1 with alkynyl benziodoxole 2 to alkynes 5.

2.1.2. Decarboxylative alkynylation. Synthetic application of hypervalent iodine reagents in photoredox reactions were further explored in decarboxylative alkynylation reactions by different research groups. The same photoredox catalyst 4 was applied to develop decarboxylative ynonylation under mild reaction conditions. \(^{61}\) \(\alpha\)-Keto acids 10 were treated with alkynyl benziodoxoles 2 using BI-OAc (acetoxybenziodoxole) 11 as an additive and ruthenium species 4 as photoredox catalyst in the presence of blue light at 468 nm. The ynonylation reactions were proceeded well and functionalized ynones 12 were obtained in good to high yields (Scheme 3). Wide range of functional groups sensitive to the transitional metal catalysis were successfully tolerated under the conditions summarized in scheme 3. The decarboxylative alkynylation follow the free radical mechanism. Aromatic \(\alpha\)-keto acids showed better yields in the decarboxylative alkynylation reactions compare to the aliphatic keto acids. Interestingly, the dual decarboxylative-decarbonylative alkyne coupling product was observed in case of tert-alkyl keto acids.
Scheme 3. Photo-induced decarboxylative alkynylation of $\alpha$-ketoacids 10 with alkynyl benziodoxoles 2 to ynones 12.

$\alpha$-Ketoacids 10 were further employed in decarboxylative coupling with functionalized bromoacetylenes 13 using catalytic amount of BI-OH 3 in the presence of sunlight and functionalized ynones 12 were obtained in good yields (Scheme 4).52 Notably, these results were comparable with the results obtained by using blue light ($\lambda$=450–455 nm). Once again wide range of functional groups were studied during the progress of this reactions and bromoacetylenes functionalized with electron-donating groups showed poor yields compare to the electron-withdrawing groups. During the optimization studies, various organic and inorganic photoredox catalysts were also employed but showed poor yields.

Scheme 4. Sunlight-driven decarboxylative coupling of $\alpha$-ketoacids 10 with bromoacetylenes 13 to ynones 12.

The mechanism for sunlight-driven decarboxylative coupling is summarized in scheme 5. The reaction was initiated with reaction of BI-OH 3 with $\alpha$-keto acid 10 to form the intermediate 14. Iodine-oxygen bond of intermediate 14 cleaved in the presence of sunlight and generates the iodanyl radical 15 and acyl radical 17. Furthermore, the iodanyl radical 15 reacts with bromoacetylene 13 to give alkynyl benziodoxole intermediate 18 along with the formation of bromine radical. On addition of intermediate 18 with acyl radical 17, another intermediate 19 formed which releases the coupling product 12 along with the regeneration of intermediate 15. Finally, iodanyl radical 15 reacts with bromine radical to form BI-Br (bromobenziodoxole) 20 which undergoes hydrolysis to regenerate BI-OH 3. The regenerated species 3 enters into next the catalytic cycle.
Scheme 5. Mechanism for the sunlight-driven decarboxylative coupling of $\alpha$-ketoacids 10 with bromoacetylenes 13 to ynones 12.

In order to develop the decarboxylative alkynylation of carboxylic acids using photoredox catalysis, another report came in 2015 by Xiao and co-workers. In this report, iridium complex 21 was used as photocatalyst which was excited by blue light to generate the alkyl or cycloalkyl radical. Most of the coupling reactions proceeded well at room temperature in dichloromethane and 1,2-disubstituted acetylenes 5 were obtained in good to excellent yields (Scheme 6). Several carbocyclic carboxylic acids were successfully used as substrates during these coupling reactions but ynone based compounds were observed in case of benzoic and acetic acid. The course of the reaction was not much influenced by the presence of different aliphatic and aromatic groups in alkynyl benziodoxoles 2 and reaction products were isolated in excellent yields.
Scheme 6. Photo-catalytic decarboxylative alkynylation of carboxylic acids 20 with alkynyl benziodoxoles 2 to 1,2-disubstituted acetylenes 5.

Moreover, the same photocatalytic approach was used to develop decarboxylative carboxylative alkynylation of cyclic and acyclic carboxylic acids 20 with alkynyl benziodoxoles 2 in the presence of carbon monoxide (CO) under almost similar reaction conditions. Ynones 12 were afforded as reaction products in high yields (Scheme 7). Wide range of substrates scope and mild reaction conditions makes this approach for suitable for synthetic organic chemists. Like previous reports, the mechanism of the decarboxylative alkynylation and decarboxylative carboxylative alkynylation reactions followed the similar radical photoredox catalytic cycle.

Scheme 7. Photocatalytic decarboxylative carboxylative alkynylation of carboxylic acids 20 with alkynyl benziodoxoles 2 to ynones 12.

Furthermore, Waser and co-workers reported a more compact study on the decarboxylative alkynylation of carboxylic acids. In this study, various iridium and ruthenium based photo-catalysts were screened carefully and results obtained clearly the superiority of iridium catalyst over ruthenium in redox catalysis. This photoredox catalysis approach was advantageous over others due to low catalytic loading (up to 0.5 mol %) and its success in case of α-amino and α-oxo acids derived from biomass. Recently, alkynyl sulfones have been identified as potential alternative of alkynyl benziodoxoles 2 in photocatalytic decarboxylative alkynylation reactions.

In 2016, similar decarboxylative alkynylation of carboxylic acids were developed by replacing metal photoredox catalysts with organic photoredox catalyst. This approach was organophotocatalytic decarboxylative alkynylation of carboxylic acids with alkynyl benziodoxoles 2 and it was quite cost effective compare with other existing approaches. During these alkynylations, 5.0 mol % of 9,10-dicyanoanthracene...
(DCA) was used as photocatalyst in the presence of base in the presence of blue light. The reaction products 24 were obtained in good to excellent yields and scope of the substrates were widely studied (Scheme 8). 9,10-Dicyanoanthracene (DCA) 23 is having high singlet excited-state oxidation potential which makes it more suitable as photoredox catalyst.

![Cartoon](image)

**Scheme 8.** Organophotocatalytic decarboxylative carbonylative alkynylation of carboxylic acids 22 with alkynyl benziodoxoles 2 to 1,2-disubstituted acetylenes 24.

The mechanism for the organophotocatalytic decarboxylative carbonylative alkynylation of carboxylic acids 22 is summarized in scheme 9. Initially, the organic photoredox catalyst 23 absorbs the blue light and get excited which oxidizes the deprotonated acid 22. As a result the exited catalytic species get reduced along with the formation of carboxyl radical 25. Furthermore, the addition of carboxyl radical 25 to alkynyl benziodoxoles 2 would lead another unstable radical adduct 26. Finally, radical intermediate 26 undergo a β-elimination to give the desired product 24 along with the formation of benziodoxolonyl radical 27. Benziodoxolonyl radical 27 could be reduced to 2-iodobenzoate 28 to complete the catalytic cycle. Additionally, the oxidation of deprotonated acid 22 to carboxyl radical 25 by 2-iodobenzoate 28 would be other possibility to propagate the reaction.
Scheme 9. Mechanism for organophotocatalytic decarboxylative carbonylative alkynylation of carboxylic acids 22 with alkynyl benziodoxoles 2 to 1,2-disubstituted acetylenes 24.

Recently, Waser and co-workers developed another photoorganocatalytic approach for the decarboxylative alkynylation of carboxylic acids. More importantly, the reported approach was successfully applied for the decarboxylative alkynylation of the C-terminus of peptides and hypervalent iodine species were used to introduce alkynyl functionality. Notably, the reaction showed a significant selectivity for the C-terminus despite in the presence of aspartic or glutamic acid residues.

2.1.3. Alkynylation of aldehydes. Furthermore, the photoredox catalysis was used for the alkynylation of aldehydes via hydrogen atom transfer process. In this approach, aldehydes 29 were treated with ethynylbenziodoxole (EBX) 2 by using catalytic combination sodium 2-iodobenzoate and BI-OAc 11 in the presence of iridium based photocatalyst 21 (Scheme 10). Blue LED (5 W) was used to activate the photocatalyst and yrones 12 were obtained in good yields. The scope of the substrates was widely explored and various sensitive functional groups were tolerated efficiently under given reaction conditions. Moreover, different amides and esters were also found the suitable substrates for these alkynylation reactions. In this reaction, the role of sodium 2-iodobenzoate is to quench the excited Ir$^{III*}$ to Ir$^{II}$ and generation of 2-iodobenzoioxyl radical which could undergo hydrogen-atom abstraction to form the carbonyl radical of substrates.
Scheme 10. Photoredox-catalyzed alkynylation of aldehydes 29 to ynones 12.

2.1.4. Alkynylation of alcohols with bond cleavage. In 2016, Chen and co-workers developed a visible-light induced C(sp^3)−C(sp^3) bond cleavage followed by alkynylation. During these alkynylation reactions, cyclopropanols 30 were oxidized to generate alkoxyl radicals by cyclic hypervalent iodine reagents and undergo C(sp^3)−C(sp^3) bond cleavage followed by alkynylations in one pot. This was the first report where alkoxyl radicals were successfully applied to achieve C(sp^3)−C(sp^3) bond cleavage with alkynylation under photoredox conditions. The reactions proceeded at room temperature and reaction products 31 were obtained in good yields (Scheme 11). Additionally, the reaction showed good potential for the other strained cycloalkanols such as cyclobutanols. Interestingly, the scope of this approach was not limited to the strained cycloalkanols but also applicable for the linear alcohols as well.

Scheme 11. Photoredox-catalyzed alkynylation of cyclopropanols 30 to alkynylation adduct 31.

Furthermore, the photoredox catalysis was applied to develop another carbon–carbon bond cleavage/alkynylation approach by same research group using almost similar catalytic system. In this approach, selective carbonyl C(sp^3) bond cleavage/alkynylation of β-carbonyl alcohols 31 was developed under mild reaction conditions and afforded ynones 12 in good yields (Scheme 12). Once again reaction was progressed with the formation of alkoxyl radicals but BI-OH 3 was not found successful to generate there radicals. Highly fluorinated BI-OH 32 showed great potential to generate alkoxyl radical of β-carbonyl alcohols 31 with high redox potential. The scope of this reaction was expanded to other β-carbonyl alcohols such as β-amide and β-ester alcohols to produce ynamides and ynoates respectively, in good yields.

Moreover, the same research group reported a phosphorus-C(sp³) bond cleavage/alkynylation approach by using photoredox catalysis.⁷¹ In this report, α-diarylphosphinoyl alcohols 33 were treated with alkynyl benziodoxoles 2 and BI-OAc 11 in the presence of photocatalyst 4 and phosphonoalkynes 34 were isolated in good to excellent yields (Scheme 13). The scope of substrates was studied extensively and substrates in which aryl groups attached with the phosphorus atom showed better reactivity compared to alkyl groups. The phosphorus-C(sp³) bond cleavage/alkynylation reactions proceeded via radical α-addition of phosphorus radical to alkynyl benziodoxole 2. Actually, the phosphorus radical generates from alkoxyl radical which was formed by the reaction of α-diarylphosphinoyl alcohol with BI-OAc 11. Interestingly, the protected α-diarylphosphinoyl alcohols could not find the suitable substrates for these reactions. This is supporting evidence for the generation of alkoxyl radical.

Scheme 13. Photoredox-catalyzed phosphorus-C(sp³) bond cleavage/alkynylation of α-diarylphosphinoyl alcohols 33 to phosphonoalkynes 34.

2.1.5. Alkynylation of cyclic oxime ethers. Recently, photoredox catalysis has been used successfully used to achieve alkynylation cascade of cyclic oxime ethers.⁷² In this report, fragmentation/alkynylation reaction of cyclic oxime ethers 35 was developed with ethynylbenziodoxolone (EBX) reagents 2 by using high reduction potential organic dye 36 as photocatalyst under mild reaction conditions. The reaction products 37 having
nitrile and alkyne functionalities were isolated in good yields (Scheme 14). Organic dye 36 showed better photocatalytic potential in photoredox catalysis over the traditional iridium and ruthenium photo-catalysts due to its high reduction potential. During these transformations, alkyl nitrile radicals were generated via oxidative ring opening of cyclic alkyl ketone oxime ethers 35. Moreover, the redox properties of the dye were determined by cyclic voltammetry and computational studies.

Scheme 14. Alkynylation cascade of cyclic oxime ethers 35 to reaction products 37 with EBX 2 by using organic dye 36 as photocatalyst.

2.1.6. Amidoalkynylation of unactivated alkenes. Jiang and Studer employed the photoredox catalysis for the 1,2-amidoalkynylation of unactivated alkenes 39 by using similar organic photo-catalyst 40. During these transformations, unactivated olefins 39 were treated with ethynylbenziodoxolone (EBX) reagents 2 and α-amido-oxo acids 38 in the presence of organic photocatalyst 40 and reaction mixture was irradiated with blue light from blue LED. Reaction showed good functional group tolerance and 1,2-amidoalkynylation products 41 were obtained in good yields (Scheme 15). Amidoalkynylation was proceeded via amidyl radical formation which adds to the olefinic double bond to form adduct radicals. Eventually, adduct radicals trapped by EBX 2 to yield desired product 41. Moreover, photoredox catalysis showed a significant potential for the alkynylation of C(sp³)-H bonds.
Scheme 15. 1,2-Amidoalkynylation of unactivated alkenes 39 to products 41 with EBX 2 by using organic photoredox catalyst 40.

2.2. Alkenylation

In 2015, Chen and co-workers reported the application of photoredox catalysis for alkenylation reactions by using hypervalent iodine reagents.\textsuperscript{75} In this report, potassium aryl/alkyl trifluoroborates 1 were treated with olefinic acids 42 and cyclic hypervalent iodine reagent 11 in the presence of photocatalyst 4 to afford the aryl- and acyl-substituted alkenes 43 in good yields (Scheme 16). During these transformations, a photoredox induced C(sp\textsuperscript{3})–C(sp\textsuperscript{2}) coupling reaction occurred via deboronation/decarboxylation sequence under aqueous reaction conditions. Actually, this was the beginning of radical decarboxylative alkenylation reaction using redox catalysis by involving hypervalent iodine reagents. Additionally, various sensitive functional groups were successfully tolerated during these transformations under mild reaction conditions.

Scheme 16. Photoredox induced C(sp\textsuperscript{3})–C(sp\textsuperscript{2}) coupling reaction of potassium trifluoroborates 1 with olefinic acids 42 via deboronation/decarboxylation sequence by involving BI-OAc 11.

The next report on the photoredox based alkenylation was came by same research group in 2016.\textsuperscript{69} In this approach, linear alcohol 44 was treated with olefinic carboxylic acids 42 by using ruthenium complex 4 as photoredox catalyst 4 and BI-OAc 11 as oxidant to undergo decarboxylative alkenylation in good yields.
(Scheme 17). During these alkenylations, BI-OAc 11 was used to achieve alkoxy radicals by the oxidation of linear alcohol 44 which leads the cleavage of C(sp³)–C(sp³) and alkenylation sequence. This was the first alkenylation approach following alkoxy radical-induced C−C bond cleavage using photoredox catalysis by involving cyclic hypervalent iodine reagents.

\[
\begin{align*}
\text{MeO} & \quad \text{Ru(bpy)}_3(\text{PF}_6)_2 \quad 4 \quad (2.0 \text{ mol\%}) \\
\text{BI-OAc 11, blue LED, DCE/H}_2\text{O} \:(1:1), \text{rt, 15 h} \\
& \quad 3 \text{ examples}
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{R}^1 & \quad \text{OH} \\
\text{Me} & \quad \text{R}^2 \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{45a: 72\%} \\
\text{45b: 44\%} \\
\text{45c: 54\%}
\end{align*}
\]

**Scheme 17.** Photoredox induced decarboxylative alkenylation of linear alcohol 44 with olefinic acids 42 via alkoxy radical-induced C−C bond cleavage/decarboxylation sequence by involving BI-OAc 11.

### 2.3. Cyanation reactions

Cyanation is another reaction which has been achieved successfully by photoredox catalysis involving hypervalent iodine reagents. Xu and co-workers developed a direct method for deboronative cyanation of potassium alkyltrifluoroborate salts by using photoredox catalysis.⁷⁶ In this reaction, potassium alkyltrifluoroborate salts 45 were treated with p-toluenesulfonyl cyanide 46 in the presence of photoredox catalyst 4 to achieve deboronative cyanation in good yields (Scheme 18). The cyanation reaction was proceeded by radical pathway and BI-OAc 11 was used to generate the alkyl radicals. TFA was used as an additive which was probably required to protonate the carboxylate ion formed during the reaction from an oxidant BI-OAc 11. Various primary alkyl trifluoroborates were successfully converted to corresponding alkyl cyanides in good yields.

\[
\begin{align*}
\text{R}^1 & \quad \text{BF}_3\text{K} + \quad \text{Me} & \quad \text{S} & \quad \text{N} \\
\text{45} & \quad \text{46} \\
\text{BIOAc 11 (3.0 equiv)} & \quad \text{Ru(bpy)}_3(\text{PF}_6)_2 \quad 4 \quad (2.0 \text{ mol\%}) \\
& \quad \text{TFA (3.0 equiv), blue LED, CH}_2\text{Cl}_2/\text{H}_2\text{O} \:(1:1), \text{rt, 24 h} \\
& \quad 17 \text{ examples}
\end{align*}
\]

\[
\begin{align*}
\text{R} \quad = \quad \text{Bn, 4-MeC}_6\text{H}_4\text{CH}_2, 4-\text{ClC}_6\text{H}_4\text{CH}_2, \\
\quad \text{Phth(C}_2\text{H}_2\text{)}_2\text{CH}_2, \quad \text{PhOCH}_2\text{CH}_2, 4-\text{CNC}_6\text{H}_4\text{OCH}_2\text{CH}_2, \\
\quad 4-\text{BrC}_6\text{H}_4\text{OCH}_2\text{CH}_2, \quad \text{Me(CH}_2)_7\text{CH}_2, \quad \text{EtOOC(CH}_2)_3 \text{etc.}
\end{align*}
\]

**Scheme 18.** Photoredox-catalyzed deboronative cyanation of primary alkyltrifluoroborate salts 45 to corresponding alkyl cyanides using BI-OAc 11 as an oxidant.
Furthermore, the same reaction conditions could not provide the effective results for the deboronative cyanation of secondary and tertiary alkyl trifluoroborate salts 48. Interestingly, excess of p-toluenesulfonyl cyanide 46 was needed without using TFA to achieve the deboronative cyanation of both secondary and tertiary alkyl trifluoroborates in good yields (Scheme 19). Sensitive functional groups such as ether, cyano, ketone and ester showed good tolerance under given reaction conditions. Additionally, the deboronative cyanation of the alkyl trifluoroborates showed the complete dominance over aryl trifluoroborates when a competitive reaction was performed under same reaction conditions.

Scheme 19. Photoredox-catalyzed deboronative cyanation of secondary and tertiary alkyltrifluoroborate salts 48 to corresponding alkyl cyanides 49 using excess of p-toluenesulfonyl cyanide 46.

In 2018, Waser and his co-workers developed the cyanation of aliphatic carboxylic acids by using photoredox catalysis.77 Decarboxylative cyanation of various synthetic and natural amino acids 50 was achieved in good yields by using cyanobenziodoxolones (CBX) 51 as an oxidant and source of cyanide species in the presence of iridium-based photoredox catalyst 21 and base. Various sensitive groups in amino acids were successfully tolerated under given reaction conditions and corresponding cyanides were obtained in good yields (Scheme 20). Moreover, the reaction showed good potential for the cyanation of dipeptides and some drug precursors. As like photoredox alkynylation reactions, the reaction followed the radical pathway. Recently, cyanobenziodoxolones (CBX) 51 has been used for the cyanation of amines by using electrophilic nitrogen radical under photoredox reaction conditions.74
**Scheme 20.** Photoredox-catalyzed decarboxylative cyanation of amino acids 50 to corresponding alkyl cyanides 49 using cyanobenziodoxolones (CBX) 51 as source of cyanide species.

### 2.4. C–H Alkylation reactions

Photoredox catalysis has been shown a significant potential for the C–H alkylation reactions. Photoredox-catalyzed Minisci C–H alkylation of N-heteroarenes 53 was developed with alkyl boronic acids 54 in the presence of visible light in HFIP by using BI-OAc 11 as an oxidant and ruthenium complex 55 as photoredox catalyst (Scheme 21). Various primary and secondary alkyl groups were successfully incorporated in different N-heterocycles under mild reaction conditions and alkylated N-heterocycles 56 were isolated in high yields except the alkylation of quinolines. Moreover, this approach was efficiently used for the alkylation of complex natural products and drug molecules.78 Probably, the reaction was working by forming an intramolecularly stabilized ortho-iodobenzoyloxy radical intermediate.

**Scheme 21.** Photoredox-catalyzed Minisci C–H alkylation of N-heteroarenes 53 with alkyl boronic acids 54 to alkylated N-heterocycles 51.

Furthermore, the photoredox catalysis was used for the alkylation of pyridine N-oxides 57 at C2 position.79 Once again the ruthenium complex 4 was used as photoredox catalyst while potassium alkyl trifluoroborates salts 1 were used as source of alkyl species. The alkylated pyridine N-oxides 58 were isolated in good yields (Scheme 22). Cyclic hypervalent iodine reagent (BI-OAc) 11 was used to generate the ortho-iodobenzoyloxy radical which found as the reaction intermediate for these transformations. Notably, the reaction showed significant substrates tolerance under given reaction conditions.
Scheme 22. Photo-catalyzed alkylation of pyridine N-oxides 57 at C2 position with potassium alkyl trifluoroborates salts 1.

2.5. Arylation reactions

In past few years, the attention of few hypervalent iodine chemists has been shifted towards the development of arylation reactions by using photoredox catalysis. In 2016, Denton and co-workers reported the arylation of trisubstituted phosphines 59 with diaryliodonium triflates 60 in the presence of visible light by using ruthenium based photoredox catalyst 61 (Scheme 23). The reactions were completed in short reaction time and aryl phoshonium salts 62 were isolated in good yields. This reaction involves the coupling of phosphines with aryl radical and provides quaternary aryl phoshonium salts which are quite unique in organic synthesis.

Scheme 23. Arylation of phosphines 59 with diaryliodonium triflates 60 by ruthenium based photoredox catalysis.

Furthermore, different photoredox catalysts were designed and used in photoredox-catalyzed arylation of amines. Photoredox-catalyzed three component reaction afforded functionalized N-aminosulfonamides 65 in good yields by the reaction of diaryliodonium salts 60, hydrazines 63 and SO2 in the presence of perylenediimide (PDI) 64 photoredox catalyst (Scheme 24). Actually, sulfur dioxide was generated in situ either by the acid-mediated decomposition of potassium bisulfite or added as the sulfur dioxide surrogate DABCO·(SO2)2. The scope of substrates was studied in detail and different aryl groups in salts and hydrazines were successfully tolerated under mild reaction conditions.
Scheme 24. Photoredox-catalyzed synthesis of functionalized N-aminosulfonamides 65 by three component reaction of diaryliodonium salts 60, hydrazines 63 and SO₂ by using photoredox catalyst 64.

The catalytic cycle for the photoredox-catalyzed arylation of hydrazines 63 is depicted in scheme 25. The catalytic cycle was initiated by the reaction of hydrazine 63 with sulfur dioxide to form a stable hydrazine-sulfur dioxide adduct 68. On the other hand, the photoredox catalytic species PDI 64 absorb the light and gets excited to form photoexcited PDI* 66. The excited photoexcited PDI* 66 further undergo reductive quenching on reaction with adduct 68 to form radical cation 70 along with the formation of reduced catalytic species 69. The radical cation 70 gave radical adduct 71 on deprotonation. Furthermore, the diaryliodonium salt 60 gets reduced into intermediate 72 via electron-transfer process from reduced catalytic species 69 and generates PDI 64 in its ground state. The reduced species 72 further fragments into aryl radical 74 along with the formation of aryl iodide 73. Finally, the free-radical addition (FRA) of aryl radical 74 with the radical adducts 71 yields the final product 65. The other possibility for the proceeding of this reaction is the formation of charge-transfer complex 75 which playing as a key role to absorb visible light directly.
Scheme 25. Catalytic cycle for the photoredox-catalyzed synthesis of functionalized N-aminosulfonamides 65 via three component reaction of diaryliodonium salts 60, hydrazines 63 and SO₂ BY using photo-catalyst 64.

Recently, photoredox catalysis has been used for the arylation of quinoline N-oxides 76 at C2 position by using diaryliodonium tetrafluoroborates 77 as arylation reagent in the presence of eosin Y 78 photoredox catalyst. Most of the reaction were required three days to complete and variety of N-heterobiaryls 79 were isolated in good to excellent yields (Scheme 26). Interestingly, arylation reaction was not found quite effective in case of ruthenium and iridium based photoredox catalysts while organic dye eosin Y 78 showed great potential as photoredox catalyst during these transformations. Moreover, this approach was applicable for the arylation of pyridine N-oxides under similar reaction and conditions.
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Scheme 26. Photoredox-catalyzed arylation of quinoline \( N \)-oxides 76 at C2 position by using diaryliodonium tetrafluoroborates 77 as arylation reagent and eosin Y 78 as photoredox catalyst.

2.6. \( C-H \) Diazomethylation of arenes

Photoredox catalysis involving hypervalent iodine reagents has been used to achieve \( C-H \) diazomethylation of arenes. In 2018, Suero and co-workers reported the synthesis of novel hypervalent iodine reagent 80 and used successfully for \( C-H \) diazomethylation of arenes 81 under mild reaction conditions. During these diazomethylation reactions, the newly synthesized hypervalent iodine compound 80 was reacted with different functionalized arenes 81 in the presence of base by using 1.0 mol % of ruthenium based photocatalytic species 4. The reaction mixture was irradiated with while LED and diazomethylated arenes 82 were isolated in good to excellent yields (Scheme 27). In case of disubstituted arenes, the generated radicals reacts preferentially at electron rich site and corresponding functionally arenes were obtained in excellent yields. Notably, the reaction occurred at the ortho-position in case of mono-substituted alkenes. Additionally, unsubstituted arenes were efficiently diazomethylated under same reaction conditions. Different cyclic and pseudocyclic hypervalent reagents cored with diazo group were used in this reaction but diazo was transferred more efficiently in case of pseudocyclic hypervalent reagents.

Scheme 27. \( C-H \) Diazomethylation of substituted and unsubstituted arenes 81 using iodine(III) reagent 80 as diazo group transfer reagent using photoredox catalysis.
Moreover, this reaction was used efficiently for diazomethylation of various complex naturally occurring compounds and drug molecules. Interestingly, the expected product was not obtained when isobutylbenzene 83 was used as a substrate under same reaction condition and racemic indane derivative 84 was isolated in 32% yields (Scheme 28). Probably, the cyclization reaction was proceeded via double site-selective C–H functionalization reaction. Moreover, the valuable chiral building blocks were synthesized under same reaction conditions.

Scheme 28. Photoredox-catalyzed cyclization of isobutylbenzene 83 to indane derivative 84 with iodine(III) reagent 80 in the presence of ruthenium-based photoredox catalyst 4.

2.7. Azidation reactions

In 2015, Waser and co-workers developed ring expansions by photoredox catalysis using copper based new photoredox catalyst 83. Cyclic hypervalent iodine reagent 83 (azidobenziodazolone) were synthesized and used for the photoredox-catalyzed azidation reactions of olefins 82 cored with spirocyclic ring in the presence of copper-based photoredox catalyst 84. The reaction mixture was irradiated with green light and new azides 85 were obtained in high yields (Scheme 29). The azidation reactions were irradiated with green LED and ring expansion was observed along with azidation.

Scheme 29. Photoredox-catalyzed azidation of olefins 85 to azides 88 with ABZ (azidobenziodazolone) 86 in the presence of copper-based photoredox catalyst 87.

Similar reagents were further explored in other azidation reactions such as azidation of olefinic acids and different arenes. Azidation/lactonization was observed when the same reagent 86 was treated with olefinic acid 89 under same reaction conditions. The reaction proceeded well and azide-cored lactone 90 was isolated in 81% yield (Scheme 30).
Scheme 30. Photoredox-catalyzed azidation/lactonization of olefinic acid 89 to azide-cored lactone 90 with ABZ (azidobenziodazolone) 83 in the presence of photoredox catalyst 87.

2.8. Trifluoromethylation reactions

Trifluoromethylation reactions are the key functionalizations in organic synthesis and achieved by using different electrophilic trifluoromethylating agents.\textsuperscript{85,86} In the past two decades, Togni reagents have been successfully used as source of trifluoromethyl electrophile to achieve different trifluoromethylation reactions.\textsuperscript{87} Few photoredox reactions have been successfully developed to achieve different trifluoromethylation reactions using Togni reagents.\textsuperscript{88,89} In 2012, Togni’s reagents was used to generate trifluoromethyl (CF\textsubscript{3}) radical in the presence of photoredox catalyst.\textsuperscript{90} Furthermore, Zhu and coworkers developed the trifluoromethylation of N-acrylamides using photoredox catalysis by involving Togni’s reagent.\textsuperscript{91} In 2013, Akita and co-workers developed the trifluoromethylation of vinyltrifluoroborates 91 in the presence of ruthenium complex 4 as photoredox catalyst by using Togni’s reagent 92 as a CF\textsubscript{3} radical. All the reactions were irradiated with blue LED and trifluoromethylated olefins 93 were obtained in good yields with high selectivity (Scheme 31).\textsuperscript{92}

Scheme 31. Photoredox-catalyzed trifluoromethylation of vinyltrifluoroborates 91 in the presence of ruthenium complex 4 as photoredox catalyst by serving Togni’s reagent 92 as a source of CF\textsubscript{3} radical.

Gouverneur and co-workers reported the trifluoromethylation of allylsilanes 94 under similar photoredox catalytic system by using Togni’s reagent 92 as source of trifluoromethyl group. The trifluoromethylation reactions were working smoothly and reaction products 95 were obtained in good yields except few reactions (Scheme 32).\textsuperscript{93}
Scheme 32. Photoredox-catalyzed trifluoromethylation of allylsilanes 94 in the presence of ruthenium complex 4 as photoredox catalyst by serving Togni’s reagent 92 as a source of CF$_3$ radical.

Furthermore, the Togni’s reagent 92 was used to achieve the decarboxylative trifluoromethylation of $\alpha,\beta$-unsaturated carboxylic acids 96 using Ir(ppy)$_3$ 97 as photoredox catalyst under alkaline reaction conditions. Wide range of substrates were successfully tolerated and trifluoromethylated alkenes 98 were obtained in good yields with excellent stereoselectivity (Scheme 33).

Scheme 33. Photoredox-catalyzed trifluoromethylation of $\alpha,\beta$-unsaturated acids 96 in the presence of iridium complex 97 as photoredox catalyst using same CF$_3$ radical 92.

The same iridium based photoredox catalyst Ir(ppy)$_3$ 97 was used for the trifluoromethylation of unprotected anilines 99 using Togni’s reagent 92 as trifluoromethyl radical source and trifluoromethylated anilines 100 were obtained in moderate to good yields (Scheme 34). Various electron withdrawing and donating groups were successfully tolerated and yields of the products were not much influenced by the electronic effect. Interestingly, trifluoromethylated products were obtained as single regioisomers in case of $p$-substituted anilines while mixture of regioisomers was observed in case of $o$- or $m$-substituted anilines. Additionally, Togni reagent 92 was used to develop photoredox catalyzed oxy-, amino-, and carbotrifluoromethylation reactions with good success.
Scheme 34. Photoredox-catalyzed trifluoromethylation of unprotected anilines 99 in the presence of iridium complex 97 as photoredox catalyst using same CF₃ radical 92.

2.10. Conversion of arylboronic acids to phenols

In 2015, Yadav and co-workers reported the conversion of arylboronic acids 101 to corresponding phenols 103 by using organic photoredox catalysis under mild reaction conditions. During these transformations, the organic dye eosin Y 78 was used as photoredox catalyst and PhI(OAc)₂ 102 was used to generate the radical species. All the reactions were performed in the presence of visible light and functionalized phenols 103 were isolated in excellent yields (Scheme 35). Organic photoredox catalytic species could be excited in the presence of light and reacts with PhI(OAc)₂ 102 to form the methyl radical which plays a vital role for conversion of arylboronic acids to phenols.

Scheme 35. Photoredox-catalyzed conversions of arylboronic acids 101 to phenols 103 by using photoredox catalysis.
3. Photochemical Reactions without Photoredox Catalysis

There are few photochemical reactions developed by involving hypervalent iodine reagents without using any photoredox catalyst. In this section, non-photoredox photochemical reactions achieved in past few years using hypervalent iodine reagents have been would be covered.

3.1. Aminocyclization reactions

In 2015, iodine-catalyzed aminocyclizations of substituted butyl amines 104 was developed by using Phl(mCBA)_2 105 as an oxidant and molecular iodine as catalyst in the presence of visible light. The cyclization reactions were working smoothly and substituted pyrrolidines 106 were obtained in good to excellent yields (Scheme 36). This approach was found quite useful to construct the fused pyrrolidine scaffolds in good yields. Various sensitive functional groups were successfully tolerated under given reaction conditions.

Scheme 36. Visible light-mediated iodine-catalyzed aminocyclizations of aliphatic amines 104 to pyrrolidines 106 by using Phl(mCBA)_2 105 as an oxidant.

The catalytic cycle for the visible light-mediated iodine-catalyzed aminocyclizations of aliphatic amines 104 to pyrrolidines 106 is discussed in scheme 37. The catalytic cycle was initiated with formation of in situ generated catalytic species I(mCBA) 108 which further reacts with the amine 104 to form crucial intermediate 109. The N-I bond of the intermediate 109 cleaved homolytically in the presence of visible light and form radical 110. The nitrogen-centered radical undergo 1,5-hydrogen atom abstraction to generate carbon-centered radical 111. Radical intermediate 111 reacts with iodine radical and forms iodinated intermediate 112. Furthermore, the iodine atom of intermediate 112 was oxidized by Phl(mCBA)_2 105 to iodine(III)-intermediate 113. Finally, intermediate 113 cyclizes to final product 106 by involving N-H and carbon attached to iodine(III) species and generates I(mCBA) 108 to enter into the next catalytic cycle. Notably, the free acid 107 stabilizes the active catalytic species 108 and regenerated upon dissociation.
Scheme 37. Catalytic cycle for visible light-mediated iodine-catalyzed aminocyclizations of aliphatic amines 104 to pyrrolidines 106 by using PhI(mCBA)₂ 105 as an oxidant.

Nagib and co-workers reported triiodide-mediated aminocyclization of unactivated amines 114 to functionalized pyrrolidines 115 in the presence of visible light without using any photo-catalyst.⁹⁹ Triiodide species was generated in situ by the oxidation of iodide species using PhI(OAc)₂ 102 as an oxidant and functionalized pyrrolidines 115 were obtained in good to excellent yields (Scheme 38). Different functional groups showed good tolerance during these aminocyclizations.

Scheme 38. Triiodide-mediated aminocyclization of unactivated amines 114 to pyrrolidines 115.

3.2. Decarboxylative acylarylation
In 2015, Wang and co-workers reported an iodine(III)-catalyzed decarboxylative acylarylation of acrylamides 116 with ketoacids 10 in the presence of visible-light without using photoredox catalyst to afford functionalized 2-oxindoles 117 in good yields (Scheme 39).¹⁰⁰ BI-OAc 11 was used to generate the radical
species by cleavage of oxygen-iodine bond in the presence of blue LED (450–455 nm). Various electron donating and withdrawing groups in benzene ring of substrates 116 were used but the course of reaction was quite similar and produced 2-oxindoles in almost similar yields. Notably, the yields were slightly enhanced when electron donating substituents were installed in the aryl ring of ketoacids 10.

\[
\begin{align*}
\text{R}^1 & \quad \text{R}^2
\end{align*}
\]

**Scheme 39.** Iodine(III)-catalyzed decarboxylative acylarylation of acrylamides 116 with ketoacids 10 to 2-oxindoles 117 driven by visible light.

A plausible mechanism for iodine(III)-catalyzed decarboxylative acylarylation of acrylamides 114 to 2-oxindoles 117 driven by visible light is depicted in scheme 40. The catalytic cycle was initiated with transesterification of BI-OAc 11 with ketoacid 10 to intermediate 118. Intermediate 118 undergo homolytic cleavage in the presence of visible light and forms benzoyl radical 119 and iodanyl radical 120 followed by the release of CO\(_2\). Furthermore, the formation of another intermediate 121 occurred by the free radical addition of radical 119 to olefinic double bond of substrate 116. Finally, the intermediate 121 yields the cyclized product 117 on hydrogen atom abstraction and form another intermediate 122. Intermediate 122 further releases hydrogen gas and afford the intermediate 118 to enter in the next catalytic cycle.
3.3. Cyclopropanation reaction

Recently, a photochemical cyclopropanation of olefins was developed by the reaction with iodonium ylides without using any photoredox catalyst. During these transformations, the reaction mixture of olefins 117 and β-dicarbonyl-derived iodonium ylides 124-126 was irradiated with blue light obtained from blue LED and doubly activated cyclopropanes 128 were obtained in good to excellent yields (Scheme 41). The cyclopropanation reaction proceeded well with cyclic and acyclic iodonium ylides and showed versatility with different electronically diverse olefins.
Scheme 37. Cyclopropanation of olefins 127 with iodonium ylides 124-127 in the presence of blue light without using any photoredox catalyst.

4. Conclusions

In this review article, we have summarized various photochemical reactions by involving hypervalent iodine reagents. The combination of cyclic hypervalent iodine reagents with photoredox catalysts has contributed successfully in organic synthesis. Photoredox catalysis enables various synthetic transformations such as alkynylation, alkenylation, cyanation, amination, cyclization ring expansion reactions under mild reaction conditions. Photoredox catalysis is not limited to inorganic photoredox catalysts but several organic dyes have been used potential as photoredox catalysts. There are few photochemical reactions involving hypervalent iodine reagents have been developed with using photoredox catalysis. This review highlights various photoredox-catalyzed reactions by using hypervalent iodine reagents. Moreover, the photochemical reactions involving hypervalent iodine reagents without using photoredox catalyst are also covered.

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Thomas Wirth is professor of organic chemistry at Cardiff University. After receiving his PhD from TU Berlin, he stayed at Kyoto University as a JSPS fellow. Then he worked independently at the University of Basel before taking up his current position at Cardiff University in 2000. He was awarded the Werner-Prize from the New Swiss Chemical Society, the Wolfson Research Merit Award from the Royal Society and the Bader-Award from the Royal Society of Chemistry. In 2016 he was elected as a fellow of The Learned Society of Wales. His main
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