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Photo-Oxidation Induced Selective Oxidative [4+2] Imine/Alkene Annulation with H_2 Liberation

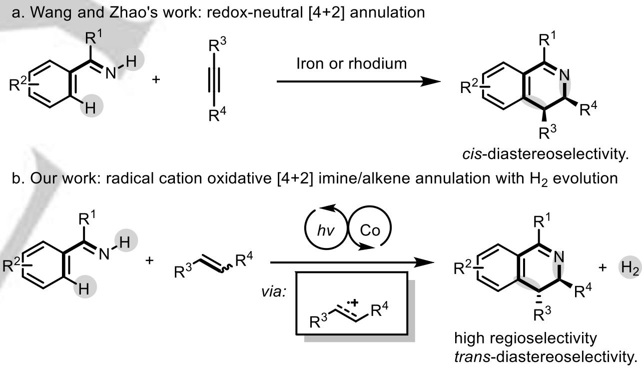
Xia Hu,[1] † Guoting Zhang,[1] † Faxiang Bu[1] and Aiwen Lei[1],[2]*

Abstract: The oxidative [4+2] annulation reaction represents an elegant and versatile synthetic protocol for the construction of six-membered heterocyclic compounds. Herein, a photo-induced oxidative [4+2] annulation of N-H imines and alkenes was developed by utilizing a dual photoredox/cobaloxime catalytic system. Various multi-substituted 3,4-dihydroisoquinolines can be obtained in good yields. This method not only obviated the need of stiochiometric oxidants but also exhibited excellent atom economy by generating H_2 as the only byproduct. Remarkably, high regioselectivity and *trans*-diastereoselectivity can be achieved in this transformation even if the Z/E mixture of alkenes were employed.

The single-electron oxidation of alkenes would lead the formation of the corresponding open-shell reactive cationic radical species, which has been increasing utilized as the key intermediates in the sythesis, such as pericyclic reactions,[1] rearrangement reactions[2] and coupling reactions.[3] Among the manners of single-electron oxidation, photo-redox catalysis provides a convenient tool to access such highly reactive odd-electron species under mild conditions.[4] A number of photo-induced Diels-Alder cycloaddition and hydrofunctionalization reactions of alkenes have been well studied.[5] Recently, the directly photo-redox/cobaloxime catalyzed oxidative C-H functionalization of alkenes with H_2 evolution has been achieved by our group.[6] These achievements call us to question whether this reactive intermediate can be utilized into the oxidative aza-Diels-Alder reaction of alkenes with the nitrogen-containing 4π-compounds.

The [4+2] annulation reaction represents a versatile synthetic protocol for the construction of valuable six-membered heterocyclic compounds, which are commonly exited in natural products, pharmaceuticals, and bioactive molecules.[7] In particular, the [4+2] annulation of N-H imine with two-carbon compounds provided a straightforward strategy for the access to isoquinoline derivatives.[8] Recently, the 3,4-dihydroisoquinolines synthesis from transition-metal catalyzed redox-neutral N-H imines/alkynes [4+2] annulations has been reported independently by Wang[8c] and Zhao[8d]. Compared with this protocol, we believed that the oxidative N-H imine/alkene [4+2] annulation protocol might provide more opportunity to form the multi-substituted 3,4-dihydroisoquinolines by a single-step procedure, since alkenes allow more substituents to be introduced into the carbon-carbon unsaturated bond. In contrast to oxidative N-H imine/alkyne [4+2] annulation reactions, very limited success has been achieved toward oxidative [4+2] annulation reactions of N-H imine and alkene.

In addition, it is appealing to develop the oxidative [4+2] annulation reaction with H_2 evolution, which obviates the requirement of stoichiometric oxidants.[9] Wang's group has successfully developed a dehydrogenative Mn-catalyzed [4+2] annulation of N-H ketimines and alkynes without using any oxidants,[8b] while the dehydrogenative [4+2] imine/alkene annulation process remains elusive. Recently, the dual catalytic system containing a photoredox catalyst and a cobloxime catalyst has be widely utilized in the oxidative cross-coupling reaction with the H_2 evolution.[10] Herein, we described a dehydrogenative [4+2] annulation reaction between aromatic N-H ketimines and alkenes to form 3,4-dihydroisoquinoline derivatives in high regioselectivity and trans-diastereoselectivity by using the dual catalytic system.


a. Wang and Zhao's work: redox-neutral [4+2] annulation

b. Our work: radical cation oxidative [4+2] imine/alkene annulation with H_2 evolution

Scheme 1. [4+2] annulation for the synthesis of dihydroisoquinolines.

To begin the study, the reaction between benzophenone imine (**1a**) and β-methyl-styrene (**2a**, Z/E mixture) was performed in acetonitrile by employing the Fukuzumi's acridinium as the photosensitizer and a cobaloxime $Co(dmgH)_2py_2PF_6$ (dmgH = dimethylglyoximate, py = pyridine)[11] as co-catalyst (Table 1, entry 1). 4 Å molecular sieve was added to inhibit the hydrolysis of aromatic imine. To our delight, 3-methyl-1,4-diphenyl-3,4-dihydroisoquinoline (**3a**) can be detected in 9% yield with high regioselectivity and diastereoselectivity after the irradiation of blue LED. It is worth noting that [4+2] annulation reactions of imines through metal-catalyzed C-H activation process usually suffer from the uncontrolled regioselectivity when the unsymmetrical two-carbon compounds were employed. Further investigation of solvent revealed that DCE gave the best result (entry 3). Subsequently, it was found that the yield was increased by the addition of fluorine-containing co-solvents, such as TFE and HFIP. When the reaction was conducted in a mix-solvent system

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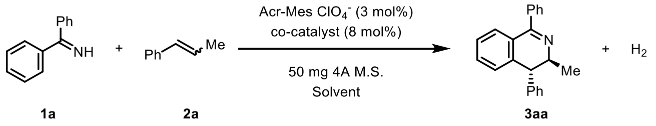
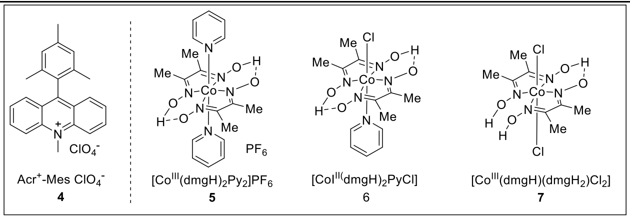
DCE/HFIP (60:1), the yield would increase to 71% (Table 1, entry 5). Changing the cobaloxime catalyst into others would decrease the reactivity (entry 6-7). Control experiments indicated the essential roles of each compenent in this transformation (Table S1).

Table 1. Optimization Studies.[a]



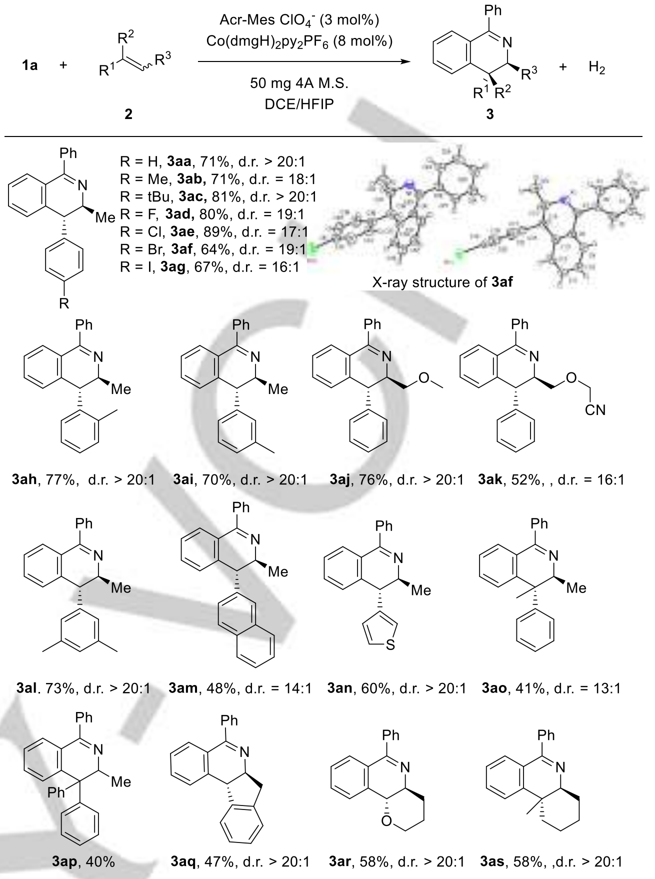
Entry	Co-Catalyst	Solvent	Yield (%)[b]
1	$Co(dmgH)py_2PF_6$	CH_3CN	9
2	$Co(dmgH)py_2PF_6$	$CHCl_3$	26
3	$Co(dmgH)py_2PF_6$	DCE	45
4	$Co(dmgH)py_2PF_6$	DCE/TFE	56
5	$Co(dmgH)py_2PF_6$	DCE/HFIP	73(71[c])
6	Co(dmgH)pyCl	DCE/HFIP	59
7[c]	$Co(dmgH)(dmgH_2)Cl_2$	DCE/HFIP	43



[a] Conditions: 1a (0.20 mmol), 2a (0.4 mmol), Acr+-Mes ClO4− (3 mol %) and co-catalyst (10 mol %) were added in solvent (2 mL) under an N_2 and irradiation of blue LEDs for 24 h. [b] Yields were determined by GC using naphthalene as the internal standard. [c] Isolated yield.

With the optimized reaction conditions in hand, the scope and generality of this catalytic oxidative imine/alkene [4+2] annulation reaction with respect to the alkenes was examined by using diphenylmethanimine (**1a**) as the coupling partner. A range of alkenes bearing various substitution patterns were tolerated in this transformation, thus giving the corresponding substituted 3,4-dihydroisoquinolines in moderate to good yields (Scheme 2). The β-methyl-styrene derivative bearing the electron-donating *para*-substituents, such as methyl and *tert*-butyl provided the corresponding products in moderate to good yields (**3ab**, **3ac**). This transformation is tolerant of the styrenes with halogen functional groups (Scheme 2, **3ae**–**3ag**), which can be applied in the subsequent functionalization. Both o*rtho*- (**3bh**) and *meta*- (**3bi**) substituted aromatic alkynes provided good yields of the desired products. When 2-(prop-1-en-1-yl)naphthalene was employed to couple with benzophenone imine, the reaction proceeded with good reactivity (**3am**, 48%). This method could be extended to the heteroaromatic alkene (**3bn**, 60%). Furthermore, the procedure was applicable for trisubstituted aryl alkenes to formed corresponding multi-substituted 3,4-dihydroisoquinoline (**3ao**, **3ap**), which is hardly obtained from the imine/alkyne [4+2] annulation. Indene can be adapted to this dual catalytic system, resulting in the 3,4-dihydroisoquinoline product being isolated at moderate yield in moderate yield (**3aq**, 47%). Aliphatic alkene 1-methylcyclohexene and 3,4-dihydro-2H-pyran could be also compatible to produce the corresponding products in moderate yields under the standard conditions (Scheme 2, **3ar**, **3as**).

Scheme 2. Substrates scope of alkenes.[a]



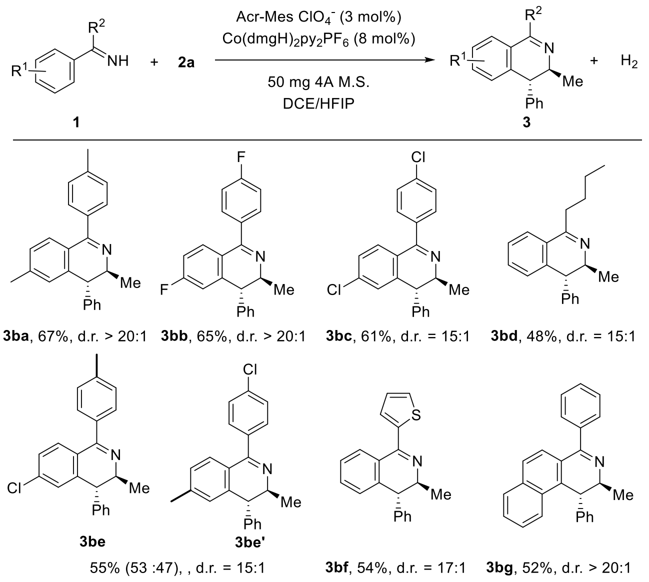
[a] Conditions: **1a** (0.20 mmol), **2a** (0.4 mmol), Acr^+-Mes ClO_4^- (3 mol %) and co-catalyst (10 mol %) were added in solvent (2 mL) under an N_2 and irradiation of blue LEDs for 24 h, isolated yields were shown.

Interesting, even if the Z/E mixture of alkenes were used as the 2π-compounds, excellent diastereoselectivity can be observed in all of these cases. The structure of **3af** was unambiguously confirmed by single-crystal XRD analysis.[12] It was found that the reaction provided a racemic 3,4-dihydroisoquinoline isomer with single trans-configuration. By sharp contrast, the reported metal-catalyzed redox-neutral N-H imines/alkynes [4+2] annulations displayed the opposite cis-diastereoselectivity. This result indicated that a benzylic radical intermediate might be involved in the transformation.

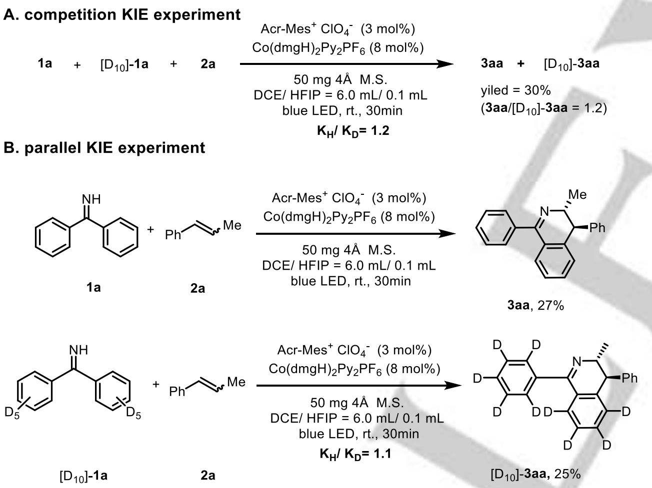
Next, the scope of the reaction with respect to N-H imines was investigated by using Z/E mixture of β-methyl-styrene as the coupling-partner (Scheme 3). Variation functional groups on the phenyl rings of symmetrical diaryl ketimines were tolerated (**3ba−3bc**). Notably, 1-phenylpentan-1-imine gave moderate yield under the standard conditions (**3bd**, 48%). A unsymmetrical diaryl ketamine, (4-chlorophenyl)(p-tolyl)methanimine would produce corresponding products in a mixture of **3be** and **3be'**. When phenyl(thiophen-2-yl)methanimine was employed in the reaction, the product that selective addition onto phenyl was observed (**3bf**). However, when naphthalen-2-yl(phenyl)methanimine was used, the regioselective cyclization onto the napthyl over phenyl to produce 3-methyl-1,4-diphenyl-3,4-dihydrobenzo[g]isoquinoline (**3bg**) can be observed with only trace amount of isomer (the ratio of regioisomer was determined by GC-MS as 92:8).

Intermolecular competitive reaction and parallel-reaction kinetic isotope effect (KIE) experiments were performed, thus giving KIE values of 1.2 and 1.1 respectively (Scheme 4). These results indicate that the C-H bond cleavage might not be involved in the rate-determining step.

Scheme 3. Substrates scope of N-H imines.[a]

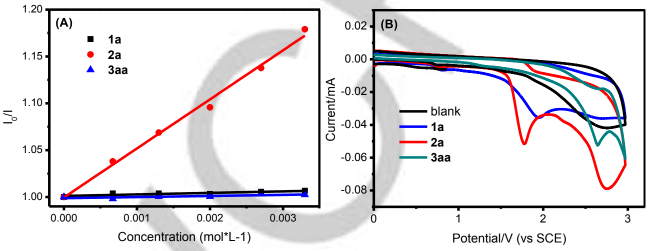


[a]Conditions: **1a** (0.20 mmol), **2a** (0.4 mmol), Acr$^+$-Mes ClO_4^- (3 mol %) and co-catalyst (10 mol %) were added in solvent (2 mL) under an N_2 and irradiation of blue LEDs for 24 h, isolated yields were shown.



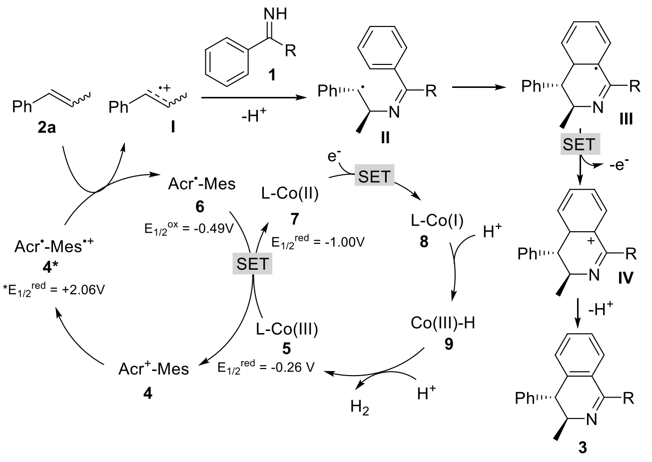
Scheme 4. Kinetic isotope effect experiments by competition reaction and parallel reaction.

To acquire further insight of the photo-redox catalytic cycle, the Stern-Volmer studies were performed (Scheme 5A), the emission intensity of the excited state of the photosensitizer **4** was weakened in the presence of β-methylstyrene (**2a**) following linear Stern-Volmer behavior. In contrast, the emission quenching of photosensitizer by benzophenonimine (**1a**) could not be observed. These results indicated that alkene might be oxidized by the excited state of photosensitizer to form the alkene radical cation intermediate. The cyclic voltammetry (CV) experiments were also carried out to study the redox potential of the substrates (Scheme 5B). An oxidation peak of **2a** in acetonitrile was observed at 1.77 V (vs SCE in acetonitrile). At the same time, oxidation peaks of **1a** could also be observed at 1.96 V (vs SCE in acetonitrile). Therefore the **2a** is more easily oxidized than imine **1a** under the standard condition. For the product **3aa**, an 2.63 V oxidation peak can be observed, and the half-peak potential was measured as 2.40 V (vs SCE), which indicated that the 3,4-dihydroisoquinolines is hardly oxidized by exited state of Acr$^+$-Mes ClO_4^- (*$E_{1/2}^{red}$ = +2.06 V vs SCE). And the emission quenching of photosensitizer by dihydroisoquinoline (**3aa**) could not be observed. Therefore, the 3,4-dihydroisoquinolines can be obtained under the standard conditions without further oxidative aromatization.



Scheme 5. Mechanistic studies. (A) Stern−Volmer emission quenching studies; (B) Cyclic voltammetry of **1a**, **2a** and **3aa** in CH_3CN.

Based on above results, a proposed mechanism was shown in Scheme 6. Firstly, single-electron oxidation of β-methyl-styrene (**2a**) by the excited-state of photosensitizer (**4***, $E_{1/2}^{red}$ = +2.06 V vs SCE) would lead the generation of the alkene radical cation intermediate **I** and the reduced photosensitizer (**6**). Subsequently, the nucleophilic attack of ketamine **2** to the radical cation **I** would furnish a radical **II** after deprotonation. The addition process would show a β-regioselectivity due to the stability of the generated benzyl radical. We proposed that the rotation of carbon-carbon single bond in the benzyl radical intermediate would form a more stable *trans*-configuration. Next, the radical cyclization of **II** would give the intermediate **III**, which is further oxidized to furnish **IV**. The elimination of a proton from **IV** would produce the desired 3,4-dihydroisoquinoline product. In other hand, the reduced photosensitizer (**6**, $E_{1/2}^{ox}$ = -0.49 V vs SCE) was oxidized by Co(III) species ($E_{1/2}^{red}$ $_{Co(III)/Co(II)}$ = -0.26 V vs SCE) to complete the photoredox catalytic cycle. In the cobalt side, Co(II) species was reduced to form a Co(I) intermediate, which can be protonated to produce Co(III)-hydride (**9**). The Co(III)-hydride species would release H_2 by the interaction with proton.[11]



Scheme 6. Proposed Mechanism.

In conclusion, the dual catalytic system containing a photosensitizer and a cobaloxime enables the acceptorless dehydrogenative [4+2] annulation of aromatic ketimine derivatives with styrenes. This methodology provided an powerful synthetic tool for the formation of multi-substituted 3,4-dihydroisoquinoline derivatives form commercially available materials. The photo-oxidation of alkene lead the formation of alkene radical cation, which would achieve the well control of the regioselectivity. And the excellent *trans*-diastereoselectivity could be observed in this radical reaction. The mildness and high atomic economy of this approach would make it appealing for the further application into synthesis of important natural products, pharmaceuticals, and functional materials.

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Keywords: alkenes · radical cation · annulation · heterocyles · synthetic method

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[12] CCDC 1561984 (**3af**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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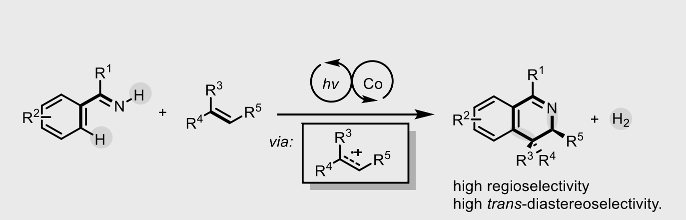

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