

Visible-Light Photoredox-Catalyzed Iminyl Radical Formation by N–H Cleavage with Hydrogen Release and Its Application in Synthesis of Isoquinolines

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Supporting Information



ABSTRACT: An unprecedented visible-light photoredox-catalyzed iminyl radical formation by N–H cleavage with H₂ release has been developed. Its application in the synthesis of various isoquinolines and related polyaromatics in high atom economy at ambient temperature by applying a photosensitizer, Acr^+ -Mes ClO_4^- , and a new cobalt catalyst, $Co(dmgH)_2(4-CONMe_2Py)Cl$ is reported. Mechanistic investigations indicated that the generated iminyl radical initiates the cascade C-N/C-C bonds formation and the catalytic cycle occurs by a simultaneous oxidative as well as reductive quenching pathway.

-Heterocycle motifs prevalently exist in bioactive compounds and organic functional materials.¹ Consequently, the development of atom-economical methods for their synthesis has been pursued for a long time.¹ Among these methods, cyclization of active nitrogen-centered radicals, such as amidyl, hydrazonyl, and iminyl radicals, is one of the important strategies.² In particular, generation of these radicals by N-H bond cleavage without the requirement of stoichiometric oxidants is highly desirable. In the case of amidyl radicals^{3a-d,f} and hydrazonyl radicals,^{3e,g} some examples have been developed. However, generation of iminyl radicals in this manner is rare. Until now, iminyl radicals were generated by the cleavage of N-Y (Y = OR, N_{2} , X, etc.) (Scheme 1a, condition A) via thermochemistry or photochemistry. Alternatively, they were formed by N-H cleavage in the presence of stoichiometric oxidants (Scheme 1a, condition B).⁵ Only recently, the Xu group demonstrated an elegant oxidantfree iminyl radical formation by electrochemical H₂ release through the cleavage of N-H bonds to directly undergo intramolecular cyclization for the synthesis of benzimidazoles and pyridoimidazoles (Scheme 1a, condition C).^o

 H_2 release coupling reactions demonstrate a nearly 100% atom-economic strategy for constructing various chemical bonds by thermochemistry,⁷ visible-light photoredox catalysis,⁸

Scheme 1. Strategies for the Iminyl Radicals' Formation and Their Application



and electrochemistry.^{3c,6,9} However, to the best of our knowledge, the cascade construction of more than one chemical bond is rare among these transformations.^{3c,8f,9c,e}

We developed a visible-light photoredox-catalyzed iminyl radical formation by N–H cleavage with H_2 release in the presence of a new cobalt catalyst. Its application in the synthesis of various isoquinolines and related polyaromatics in high atom-economy at ambient temperature by a cascade C–N/C–

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C bonds construction is accomplished (Scheme 1b, eq 2). In comparison with classic methods,¹⁰ the transition-metalcatalyzed oxidative-¹¹ and acceptorless-dehydrogenation annulation by thermochemistry,^{7a,c} a concise and high atomeconomic route, is developed at ambient temperature. The preactivation of N–H or stoichiometric oxidants is avoided. In addition, a new regioselectivity was observed.^{7c}

Continuing on our research around H_2 release and isoquinoline synthesis,^{7c,12} bis(4-methylphenyl)methanimine (1a) and 1,2-diphenylacetylene (2a) were selected as model substrates for synthesis of isoquinolines by photoredox catalysis with H_2 release (Scheme 2). By applying a photosensitizer (PS)



^{*a*1}H NMR yield of **3aa** was reported using $Cl_2CHCHCl_2$ as an internal standard. The yield of H_2 was detected by GC using CH_4 as an internal standard. ^{*b*}Isolated yield.

Acr⁺-Mes ClO₄⁻ (5 mol %) and a catalyst Co(dmgH)₂PyCl (5 mol %), **3aa** was obtained in 32% yield with 24% H_2 under blue LED irradiation at ambient temperature (Table S1, entry 1). Photosensitizers TPT and PDI resulted in lower yields (Table S1, entries 2-3, $\leq 14\%$). The influence of solvents was studied. Methanol totally inhibited the transformation (Table S1, entry 4). Dichloroethane (DCE) induced 3aa in 33% yield with 1% H_{2} , which should be explained by the DCE acting as an oxidant (Table S1, entry 5).¹³ When DCM was applied as the solvent, 3aa was obtained in 40% yield with 31% H₂ (Table S1, entry 6). Dilution of the substrate concentration (0.02 M based on 1a) and further improving the loadings of PS and catalyst to 10 mol % (Scheme 2, condition A) resulted in 3aa in 60% yield with 57% H₂. The substituent on the para position of the pyridine moiety of the cobalt catalyst should effect the reaction efficiency.

Thus, different cobalt catalysts bearing various substituents, such as dimethylaminyl ($-NMe_2$), methyl ester ($-CO_2Me$), N,N-dimethylamidyl ($-CONMe_2$), and N,N-dimethylamidyl ($-CONEt_2$), were investigated (Scheme 2, conditions B–E). To our delight, the catalyst Co(dmgH)₂(4-CONMe₂Py)Cl led to **3aa** in 92% yield with 89% H₂ (Scheme 2, condition D). Control experiments showed that blue LED irradiation, PS, and the cobalt catalyst are essential (Table S1, entries 10–12).

The substrate scope was investigated under optimized conditions (Schemes 3–5). The biaryl ketimines bearing electron-donating and weak electron-withdrawing groups on the para position of the phenyl rings, such as from methyl and methoxy to chloro, afforded products **3aa–da** in high yields (83–92%). Stronger electron-withdrawing groups, such as fluoro and trifluoromethyl, decreased the reaction efficiencies to some extent (**3ea**, 78%; **3fa**, 63%). The trifluoromethyl ether resulted in good reactivity (**3ga**, 60%). The methyl and chloro on the meta position led to good efficiency (**3ha** and **3ha**', 76%; **3ia** and **3ia**', 73%). In comparison with the steric effect,

Scheme 3. Substrate Scope of Various Ketimines⁴



^{*a*}Reaction conditions: 1 (0.1 mmol), 2a (0.2 mmol), optimized conditions, 12 h, isolated yields were reported; H_2 was detected by GC using CH₄ as an internal standard. ^{*b*}The structure of major regioisomer is shown. ^{*c*}The ratio of the isomers was determined by crude ¹H NMR spectrum.





"Reaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), optimized conditions, 12 h, isolated yields were reported; H_2 was detected by GC using CH₄ as an internal standard. *p*-Methylphenyl is abbreviated as PMeP. ^{b1}H NMR yield was reported. ^cThe ratio of the isomers was determined by the crude ¹H NMR spectrum.

the influence of the electronic effect on the *m*-methyl acted as a dominant role (**3ha:3ha'** = 2.0:1.0). The *m*-chloro of the biaryl ketamine displayed some steric effect (**3ia/3ia'** = 1.3:1.0). The methyl on the ortho position led to a decreased yield (**3ja**, 63%). When *n*-butyl and *tert*-butyl were investigated as the alkyl substituents of the alkyl aryl ketimines, the reaction showed moderate yields (**3ka**, 57%; **3ia**, 51%).

Next, various biaryl alkynes were studied. When the symmetric disubstituents on the para position of phenyl rings of the diarylacetylenes were varied from methyls to fluoros, obviously decreased reactivities were observed (3ab-ae, 85%-46%). 1,2-Bis(4-(trifluoromethyl)phenyl)ethyne totally inhibited the transformation. Interestingly, applying a methyl instead of one of the trifluoromethyls, the product was obtained in excellent yield (3af, 90%). The observation of one regioisomer should be explained by the distinctly biased electronic property on the triple bond of the alkyne. Similar results were observed for products 3ag and 3ag', 3ah and 3ah', and 3ai and 3ai'. The disubstituents on the phenyl rings of the diarylacetylenes were $-CF_3$ with -H, -F with $-CH_3$, and -Cl





^{*a*}Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol), optimized conditions, 12 h, isolated yields were reported; H_2 was detected by GC using CH₄ as an internal standard; the ratios of isomers were determined by the isolated yields. ^{*b*}Thermal ellipsoids are drawn at 30% probability with H atoms omitted for clarity.

with -Me, respectively. Regioselectivity was also observed on products 3aj and 3aj' (4.9:1.0) with the disubstituents of -H and $-CH_3$. The *m*-methyls on the phenyl rings of the diarylacetylene resulted 3ak in excellent yield. However, the *o*-methyls inhibited the reactivity by steric effect. The trimethylsilane-substituted arylacetylene led to moderate yield (3al, 48%).

Thus, naphthaleneyl- and phenanthryl-substituted ketimines were further explored. The phenylnaphthalenyl ketimines resulted in cyclization exclusively on the phenyl ring (3ma, 87%; 3na, 82%). When phenylphenanthryl-substituted ketimines were studied, besides the products of the cyclization on the phenyl ring (30a-oe), new regioselective products of the cyclization on the phenanthryl rings (30a'-oe') were also obtained in considerable amounts.^{7c} The structure of 3oa'was further confirmed by X-ray crystallography. Electron-donating and weak electron-withdrawing groups on the phenyl rings of the ketimines, as well as methyl and fluoro on the phenylrings of 1,2-diphenylacetylenes, resulted in good reaction efficiency (30a, 30a'-oe, 30e', 64-85%). A rough tendency was observed that the ratio of the cyclized products on the phenanthryl rings was increased (30a'-ua') when the substituents on the phenyl rings varied from methyl and methoxy to trifluoromethyl. This method affords a concise route for synthesis of polycyclic aromatic compounds under mild conditions.¹⁴

To demonstrate the potential synthetic application, a gramscale reaction of **1a** with **2a** was performed with a lower concentration (0.01 M based on **1a**). Compound **3aa** (1.65 g) was achieved in 85% yield with 83% H₂ using 5 mol % of Acr⁺-Mes ClO_4^- and $Co(dmgH)_2(4$ -CONMe₂Py)Cl (Scheme 6).

Subsequently, a series of experiments were conducted to give insight into the reaction mechanism. First, the detection of the UV-vis absorption spectrum of each component and the

Scheme 6. Gram-Scale Synthesis of 3aa



reaction mixture confirmed that only Acr⁺-Mes ClO₄⁻ acts as a visible-light photosensitizer (Figure S1). Then, radical-trap experiments were conducted by introducing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical capture reagent (eq S2). Compound 3aa was obtained in 70% yield without observation of radical capture and H₂ release. This should be attributed that the generated radicals are too active. TEMPO is acted as the terminal oxidant in this transformation. To our delight, when 1,2-diphenylethene was used instead, the desired TEMPO captured compound 5, N-(1,2-diphenyl-2-((2,2,6,6tetramethylpiperidin-1-yl)oxy)ethyl)-1,1-di-p-tolylmethanimine, was obtained in 60% yield with a trace amount of H_2 (eq S3). Its formation should originate from the capture of the benzyl radical, possiblely generated by the iminyl radical addition to the double bond of 1,2-diphenylethene, by TEMPO. This result indicates the possibility of iminyl radical generation by N–H cleavage in the demonstrated conversion. In addition, the quantum yield, Φ ,¹⁵ was calculated to be 0.19. At this stage, the data are inconclusive on whether the reaction proceeded via a photoredox-catalytic pathway or a radical-chain pathway.

The emission-quenching experiments showed that Co-(dmgH)₂(4-CONMe₂Py)Cl, 1a, and 2a could quench the excited photosensitizer Acr[•]-Mes^{•+} ClO₄⁻ (Figure S7). Meanwhile, no reactivity of 1,2-bis(4-methoxyphenyl)acetylene (6) under optimized conditions as well as a larger quenching rate than that of 1a and 2a were observed (Figure S7). These phenomena suggest that generation of the corresponding diarylacetylene radical cation inhibits iminyl radical formation, while the diarylacetylene radical cation does not initiate the catalytic cycle. This deduction is also supported by the oxidation potentials of 1a, 2a, and 6 ($E^{1a \bullet + / 1a} = +1.62$ V vs SCE, $E^{2a \bullet \frac{1}{2a}} = +1.86$ V vs SCE, $E^{6 \bullet +/6} = +1.28$ V vs SCE, see the SI) and the reported reduction potential of $E^{\text{Acre-Mese+ClO4}-/\text{Acre-MesClO4}-}$ as +2.06 V vs SCE.¹⁶ Obviously, 1a could undergo singe-electron transfer (SET) to the excited photosensitizer Acr[•]-Mes^{•+} ClO₄⁻. The oxidation potential of $E^{\text{Acr}\bullet-\text{MesClO4}-/\text{Acr}+-\text{MesClO4}-}$ was detected as -0.55 V vs SCE.¹⁶ The reduction potentials $E^{\text{III/II}}$ and $E^{\text{II/I}}$ of the cobalt catalyst were determined as -0.77 V vs SCE and -1.04 V vs SCE, respectively. Thus, the SET between Acr[•]-Mes ClO₄⁻ and Co^{III} or Co^{II} is not favorable. On the other hand, based on the reduction of O_2 to $O_2^{\bullet-}$ by the excite state of Acr[•]-Mes^{•+} ClO₄⁻ ($E^{O2\bullet-/O2} = -0.87$ V vs SCE),¹⁷ and the high quenching rate of Acr[•]-Mes^{•+} ClO₄⁻ by Co(dmgH)₂(4-CONMe₂Py)Cl, the SET from Acr[•]-Mes^{•+} ClO_4^- to the Co(III) is possible.

On the basis of the above results, a plausible reaction mechanism is proposed in Scheme 7. Under blue LED irradiation, Acr^+ -Mes ClO_4^- is excited to the state Acr^{\bullet} -Mes^{$\bullet+$} ClO_4^- . The Mes^{$\bullet+$} moiety is reductively quenched by **1a**, and the acridinyl radical moiety is oxidatively quenched by the Co^{III}

Scheme 7. Proposed Mechanism



simultaneously by two SETs to regenerate the ground-state Acr⁺-Mes ClO_4^- . Meanwhile, the iminyl radical 7, H⁺, and the Co^{II} are generated. 7 reacts with **2a** to construct the C–N bond to afford intermediate **8**. **8** undergoes radical cyclization to construct the C–C bond to give **3aa** by intermediate **9** with the release of an electron (e⁻) and the second H⁺. The Co^{II} is reduced to Co^I by the released e⁻. The reaction of Co^I with H⁺ gives Co^{III} –H, which further reacts with the second H⁺ to release H₂ to close the cobalt catalyst cycle. The reduction of Co^{III} –H to Co^{II} –H followed by protonation to release H₂ and produce Co^{II} or the homolytic cleavage involving two Co^{III} –H to evolve H₂ can not be ruled out.¹⁸

In summary, we have developed the first visible-light photoredox-catalyzed iminyl radical formation by N–H bond cleavage with H₂ release and its application in the synthesis of isoquinolines and related polyaromatics in high atom economy under ambient temperature. During the transformation, the generated iminyl radical initiates cascade C–N/C–C bond construction. The new cobalt catalyst Co(dmgH)₂(4-CON-Me₂Py)Cl plays an important role in achieving the high reaction efficiency and wide substrate scope. The advantages of the established method will inspire the utilization of the iminyl radical by visible light irradiation with H₂ release for various N-heterocycle synthesis.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b00193.

Experimental procedure, product characterization, and spectral data (PDF)

Accession Codes

CCDC 1576204 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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