

Cross-Coupling Reactions

Photocatalytic Dehydrogenative Cross-Coupling of Alkenes with Alcohols or Azoles without External Oxidant

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Abstract: Direct cross-coupling between alkenes/R-H or alkenes/RXH is a dream reaction, especially without external oxidants. Inputting energy by photocatalysis and employing a cobalt catalyst as a two-electron acceptor, a direct C-H/X-Hcross-coupling with H_2 evolution has been achieved for C-Oand C-N bond formation. A new radical alkenylation using alkene as the redox compound is presented. A wide range of aliphatic alcohols—even long chain alcohols—are tolerated well in this system, providing a new route to multi-substituted enol ether derivatives using simple alkenes. Additionally, this protocol can also be used for N-vinylazole synthesis. Mechanistic insights reveal that the cobalt catalyst oxidizes the photocatalyst to revive the photocatalytic cycle.

Directly utilizing wide-ranging alkene feedstocks is a continuing challenge in chemical synthesis. A particularly active field of catalysis uses alkene reactants to realize alkenylation, thereby constructing substituted alkenes. A well-known process for alkenylation is the transition-metal-catalyzed Heck reaction, which has become a fundamental synthetic transformation in recent years.^[1] Key steps involved in the Heck reaction are alkene insertion and β -hydride elimination in the presence of a transition metal (Scheme 1 A part (a)). However, the Heck reaction mainly deals with the alkenylation of RX (aryl or vinyl electrophiles). The radical-mediated approach can be a complementary route to the functionalization of alkenes because radicals have high activity and react rapidly with olefinic acceptors.^[2] This strategy of alkenylation via a radical pathway has been widely researched over the vears, providing a novel choice of alkenvlation products.^[3] The addition of in situ generated radical to the alkenes is regarded as the key step (Scheme 1 A part (b)). By virtue of this radical alkenylation strategy, several inert C-H compounds,^[4] which are difficult to activate by the model Heck reaction, have been successfully transformed into the corresponding alkenes with high efficiency. Therefore, developing

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.

the author(s) of this article can be found under http://dx.doi.org/10. 1002/anie.201609274.

Angew. Chem. Int. Ed. 2016, 55, 1-6

Previous strategies

A. Heck reaction and radical alkenylation (a) $R^{1}-X/H \xrightarrow{[M]} R^{1}-M-X \xrightarrow{R^{2}} H \xrightarrow{R^{2}} R^{2} \xrightarrow{R^{1}} R^{2}$ (b) $R^{1}-X/H \xrightarrow{R^{1}} R^{1} \xrightarrow{R^{2}} R^{2} \xrightarrow{R^{1}} R^{2}$ *Our strategy*

B. New route for radical alkenylation using alkene cation as key intermediate

$$\begin{array}{c} \mathbb{R}^{3} \\ \mathbb{R}^{2} \end{array} \xrightarrow{\mathbb{R}^{3}} \mathbb{R}^{1} \xrightarrow{-e} \mathbb{R}^{3} \\ \mathbb{R}^{2} \xrightarrow{\mathbb{R}^{4}} \mathbb{R}^{1} \end{array} \xrightarrow{\mathbb{H}-\mathsf{Nu}} \mathbb{R}^{3} \xrightarrow{\mathbb{R}^{1}} \mathbb{R}^{1} \xrightarrow{-e} \mathbb{R}^{3} \xrightarrow{\mathbb{R}^{3}} \mathbb{R}^{1} \\ \mathbb{R}^{2} \xrightarrow{\mathbb{R}^{4}} \mathbb{N} u \end{array}$$

C. Oxidant-free radical alkenylation merging photoredox catalysis and cobalt catalysis



Scheme 1. Alkenylation using simple alkenes. A) Two alkenylation pathways: a) the Heck reaction and b) radical alkenylation. B) New route for radical alkenylation using an alkene cation as a key intermediate. C) Oxidant-free radical alkenylation merging photoredox catalysis and cobalt catalysis.

alkenylation by a radical pathway will have broad prospects in the synthesis of substituted alkenes.

In traditional radical alkenylation, alkenes are always used as radical acceptors and react with various radicals to form addition products.^[5] Alkenes can also serve as redox compounds, and the resulting radical cations can be generated by removal of a single electron from a neutral parent compound.^[6] Visible-light-mediated photoredox catalysis has captured extensive attention recently^[7] and offers an intriguing opportunity to explore synthetic chemistry. Alkenes can be transformed into their corresponding radical cations using a recently developed photocatalysis strategy, which can be used in cyclizations or alkene hydrofunctionalization reactions.^[8] We hypothesize that an alkene radical cation can be obtained by a single electron transfer (SET) and that this radical cation can then be trapped by a nucleophile because of the electrophilic reactivity of this type of species (such as an alcohol or amine), giving a radical intermediate (Scheme 1B). The formed radical intermediate may be further oxidized to a cation intermediate, which then loses one proton to afford the desired allkenylation product. This new strategy employs alkene as the redox compound and the

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generated alkene radical cation is considered the key intermediate.

The above hypothesis in Scheme 1 involves loss of two electrons and two protons; therefore, extra stoichiometric oxidants and proton acceptors have to be applied as the sacrificial reagents in cross-coupling reactions.^[9] Using an oxidant-free strategy to realize radical alkenylation is very appealing. Inputting energy by photocatalysis and employing a cobalt catalyst as an acceptor of two electrons,^[10] we attempted to apply the oxidant-free system to radical alkenylation. Herein, we describe our efforts to develop a new model of radical alkenylation under oxidant-free conditions (Scheme 1 C). Merging photocatalysis and cobalt catalysis achieved direct C–H/X–H cross-coupling and C–O and C–N bond formation with H₂ evolution, affording enol ether derivatives and *N*-vinylazoles.

Initially, 1,1-diphenylethylene (1a) and methanol (2a) were chosen as the standard substrates for the desired coupling reaction. The acridinium moiety has a strong absorption band in the visible region ($\lambda = 430$ nm) and high excited state oxidizing power,^[7a,11] which has already been employed photocatalytically and has been successful in the transformation of a diverse range of alkenes into cation radicals. Thus, we consider $Acr^+-Mes ClO_4^-$ to be an ideal photocatalyst for alkenylation. As shown in Table 1, Acr⁺-Mes ClO_4^- (3 mol%) and Co(dmgH)₂PyCl (3 mol%) were added to a solution of 1a and 2a in an organic solvent under an ambient nitrogen atmosphere. After 12 h of irradiation with blue light-emitting diodes (LEDs), 79% yield of the desired cross-coupling product 3a was obtained (Table 1, entry 1). Other screening photocatalysts, such as Eosin Y or $Ru(bpy)_3(PF_6)_2$, did not promote this reaction and did not afford the desired product (Table 1, entries 2 and 3).

Table 1:	Optimization	of the	reaction	conditions.	a]
IUDIE I.	Optimization	UI LIIC	reaction	conunions.	

Ph Ph	+ MeOH 2a	3 mol% Photocatalyst 3 mol% Co catalyst CH ₃ CN, blue LEDs	OMe Ph + H−H ↑ 3a
Entry	Photocataly	st Co catalyst	Yield [%] ^[b]
1	Acr ⁺ -Mes Cl	D_4^- Co(dmgH) ₂ PyCl	79
2	EUSITI T Ru(boy) (PE) Co(dmgH) PyCl	ri.d. n.d
4	Acr ⁺ -Mes Cl	D_{1}^{-} Co(dmgH) ₂ ()	51
5	Acr ⁺ -Mes Cl	$D_4^- = -$	n.d.
6	-	Co(dmgH) ₂ PyCl	n.d.
7 ^[c]	Acr ⁺ -Mes ClO	D₄ [−] Co(dmgH)₂PyCl	n.d.
	Me	$\begin{array}{c c} Me & CI \\ Me & N^{O^{-}H} \\ N & N^{O^{-}H} \\ \hline \\ N & N^{O^{-}N} \\ H^{-}O^{-}N \\ \hline \\ M & Me \\ \hline \\ N & Me \\ \hline \\ \end{array}$	
[Acr ⁺ -Mes	CIO₄⁻]	[Co(dmgH) ₂ PyCl]	[Co(dmgH) ₂ Cl ₂]

[a] Conditions: **1a** (0.2 mmol), photocatalyst (3 mol%), Co catalyst (3 mol%) in solvent (CH₃CN/MeOH = 1.5 mL/0.5 mL) under a nitrogen atmosphere, irradiation with 3 W blue LEDs, at room temperature for 12 h; [b] yields of isolated products; [c] without light.

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Moreover, a screened hydrogen evolving catalyst, Co- $(dmgH)_2Cl_2$, was less efficient than Co $(dmgH)_2PyCl$. In the control experiments, no desired product was observed without photoredox catalyst, cobalt catalyst, or visible light, indicating that the photoredox and cobalt catalysts are essential in this transformation (Table 1, entries 5, 6, and 7).

With the optimal conditions established, we firstly examined the scope of different alkenes in this oxidant-free alkenylation protocol (Table 2). The 1,1-disubstituted alkenes with phenyl groups were well-tolerated under standard conditions reacted with methanol (3a-3f). Meanwhile, the

Table 2: Substrate scope for the oxidant-free coupling of alkenes 1 with MeOH $\mathbf{2a}^{\scriptscriptstyle[a]}$



[a] Conditions: 1 (0.2 mmol), Acr⁺-Mes ClO₄⁻ (3 mol%), Co-(dmgH)₂PyCl (3 mol%) in solvent (CH₃CN/MeOH (**2**a) = 1.5 mL/ 0.5 mL) under a nitrogen atmosphere, irradiation using 3 W blue LEDs, at room temperature for 12 h; yields of isolated products. The ratio of isomers was determined by NMR spectroscopy. [b] 0.3 mmol scale. [c] 0.5 mmol scale.

alkene substituted with a Cl group was also smoothly converted into ester product in high yield, which has the potential for further transformation. Notably, cyclic alkenes such as indene and 1,2-dihydronaphthalene derivatives could also be employed to reach the target enol ether scaffolds without any difficulty (3g-3i). α -methylstyrene was, likewise, well-tolerated and afforded the product in 69% yield (3j). Furthermore, internal olefin such as (E)-1-bromo-4-(prop-1en-1-yl)benzene furnished the enol ether product in moderate yield as well (3k). This method provides an easy route to multi-substituted enol ether derivatives, which are widely used synthetic intermediates in organic synthesis.^[12]

Subsequently, we turned our attention to defining the capacity of different alkyl alcohols using 1,1-diphenylethylene (1a) as the model substrate under oxidant-free conditions. Primary alcohols such as MeOH, EtOH, nPrOH, nBuOH, and iBuOH (Table 3, entries 1–4 and 8) afforded the desired

Table 3: Substrate scope for the oxidant-free coupling of 1,1-diphenylethylene **1a** with alcohols **2**.^[a]

	+ 804	3 mol% Acr-Mes ⁺ ClO ₄ ⁻ 3 mol% Co(dmgH) ₂ PyCl	OR
Ph Ph	NOT 1	CH ₃ CN, 3 W blue LEDs	Ph Ph
1a	2		3
Entry	ROH	3	Yield [%] ^{[b}
1	MeOH	3a	79
2	EtOH	31	80
3	∕Oŀ	[⊣] 3m	89
4	$\sim \sim c$	0H 3n	81
5	<i>n</i> -C ₆ H ₁₃ OI	⊣ 3o	72
6	n-C ₇ H ₁₅ OI	⊣ 3p	85
7	n-C ₁₁ H ₂₃ O	Н 3q	70
8	, ol	⊣ 3r	85
9	Ph	OH 3s	65
10	∕−он	3t	81
11	→-0	H 3u	68
12	—— он	3v	76
13	∕}он	⊣ 3w	71

[a] Conditions: **1a** (0.2 mmol), Acr⁺-Mes ClO₄⁻ (3 mol%), Co-

enol ether products in moderate to high yields. Long chain primary alcohols such as $n-C_6H_{13}OH$, $n-C_7H_{15}OH$, and $n-C_{11}H_{23}OH$ were suitable for this reaction and yielded the corresponding products with good efficiency (Table 3, entries 5-7; **30–3q**). Phenylethyl alcohol could be transformed into the desired product with up to 65% yield (Table 3, entry 9; **3s**). Additionally, secondary alcohols were also tested for this procedure under standard conditions. The alcohols *i*PrOH and heptan-2-ol were appropriate substrates (Table 3, entries 10 and 11). To our surprise, sterically hindered tertiary alcohols were smoothly and effectively accommodated into this process (Table 3, entries 12 and 13). In general, primary, secondary, and tertiary alcohols are all efficient coupling partners in this oxidant-free alkenylation method.

With this dual-catalytic system, we further explored another application; namely, the synthesis of *N*-vinylazoles, which are an important class of building blocks in organic synthesis and are also key structural motifs in many medicaments. It has been shown in the literature that palladium, mercury, or copper complexes are often used to catalyze vinylation of azoles with vinyl bromides.^[13] To our delight, this dual-catalytic system could also achieve the oxidant-free alkene C–H amination process when pyrazole was selected as an N–H nucleophile to couple with indene derivatives in dichloroethane (Table 4; **5a–5c**). The conditions were successfully extended to the coupling of pyrazole with a variety of substituted alkenes described above, including 1,2-dihydronaphthalene, 1,1-diphenylethene, and β -methyl-

Table 4: Substrate scope for the oxidant-free coupling of alkenes 1 with azoles $\mathbf{4}^{[a]}$

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[a] Conditions: 1 (0.2 mmol), 4 (0.4 mmol), Acr⁺-Mes ClO₄⁻ (3 mol%), Co(dmgH)₂PyCl (3 mol%) in dichloroethane under an argon atmosphere, irradiation with 3 W blue LEDs, at room temperature for 24 h; yields of isolated products. The ratio of isomers was determined by NMR spectroscopy.

styrene derivatives (Table 4; **5d–5k**). Other *N*-heterocyclic nucleophiles, such as pyrrole **51**, substituted pyrazoles **5m–5p**, benzotriazole **5q**, and indazole **5r**, also produced the corresponding amination products in good yields under the same conditions. However, some other amines, such as aniline, diphenylamine, and dibenzylamine did not afford the desired products under this catalytic system.

Mechanistic studies were conducted to gain insights into the aforementioned transformation. We initially detected the H₂ in the reaction system by GC-TCD. Under standard conditions, 79% and 60% yield of the desired cross-coupling product 3a and H_2 were obtained, respectively (Scheme 2 A). Hydrogenation of 1,1-diphenylene was the main side-reaction detected by GC-MS, which explains why the yield of H₂ is lower than our enol ether product. When using (2-methoxyethane-1,1-diyl)dibenzene 6a as the starting material under oxidant-free conditions, no desired product or H₂ was detected (Scheme 2B). It is implied that (2-methoxyethane-1,1-diyl)dibenzene 6a is not the intermediate in the reaction. Moreover, the time profile of the photocatalytic reaction revealed that the reaction was totally inhibited in the absence of light (Supporting Information, Figure S1), which suggests that continuous visible-light irradiation is essential to this photocatalytic transformation. As shown in Figure S2 (Supporting Information), 1,1-diphenylethylene displayed luminescence quenching of activated acridinium salt. Furthermore, we found that Co(dmgH)₂PyCl could quench the photocatalyst (Supporting Information, Figure S3). That is, the electron transfer of $[Acr^+-Mes ClO_4^-]^*$ proceeds with 1,1-diphenylethylene as well as Co(dmgH)₂PyCl. We pre-

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 $⁽dmgH)_2$ PyCl (3 mol%) in solvent (CH₃CN/ROH (**2**) = 1.5 mL/0.5 mL) under a nitrogen atmosphere, irradiation using 3 W blue LEDs, at room temperature for 12 h; [b] yields of isolated products.

(A) The detection of H_2 in the reaction system

(B) The intermediate experiment



(C) Visible-light-induced C-H/O-H coupling to enol ethers using TEMPO as terminal oxidant^{[a]}



Scheme 2. Mechanistic insights. [a] Conditions: **1a** (0.2 mmol), $Acr^+Mes ClO_4^-$ (3 mol%), TEMPO (0.4 mmol) in solvent (CH₃CN/ROH = 1.5 mL/0.5 mL) under a nitrogen atmosphere, irradiation with 3 W blue LEDs, at room temperature for 12 h. Yields of isolated products.

ferred a single-electron transfer between $[Acr^+-Mes ClO_4^-]^*$ and alkene as the key initial step.^[14]

In this oxidant-free system, a cobalt catalyst serves solely as an oxidant of the photocatalyst, thereby reviving the catalytic cycle. A variety of oxidants were examined to probe the role of the cobalt catalyst. We were pleased to find that radical alkenylation could also be achieved utilizing Acr⁺⁻ Mes ClO₄⁻⁻ as the catalyst and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the terminal oxidant, which is also used as an oxidant in several photocatalytic reactions.^[15] As shown in Scheme 2C, primary alcohols (especially long chain aliphatic alcohols), secondary alcohols, or tertiary alcohols could all be transformed into the desired products in high yields using a photocatalyst/TEMPO system.

A detailed description of our proposed mechanistic cycle for the photoredox/cobalt-catalyzed radical alkenylation is outlined in Scheme 3. After irradiating with low-energy visible light (3 W blue LEDs), the photocatalyst Acr⁺-Mes ClO_4^- 7 was converted into the excited species [Acr⁺-Mes $ClO_4^{-}]^*$ 8 $(E_{1/2red}[Acr - Mes^{+}/Acr - Mes] = +2.06 V$ VS. SCE),^[16] which underwent a SET process with an alkene to generate alkene radical cation 10 and Acr⁺-Mes ClO_4^{-} radical anion 9. Subsequently, the alkene radical cation 10 reacted with alcohol nucleophile to generate the radical intermediate 11. The carbon-centered radical was further oxidized by Co^{III} $(E_{1/2\text{red}}[\text{Co}^{\text{III}}/\text{Co}^{\text{II}}] = -0.67 \text{ V} \text{ vs. SCE})^{[17]}$ to generate Co^{II} species and a cation intermediate 12, which loses a proton to produce ether enol product **3**. This Acr^+ -Mes ClO_4^- radical anion 9 may be oxidized by CoII to reinitiate the photocatalytic reaction and generate a Co^I species. Protonation of the formed Co^I species provides a Co^{III}-H hydride,^[18] which can react with a proton to release H₂ eventually.



Scheme 3. Proposed mechanism for oxidant-free C-H/ O-H cross-coupling.

Overall, a conceptually new and synthetically valuable oxidant-free C–H/O–H and C–H/N–H cross-coupling reaction achieved C–O or C–N bond formation with H₂ evolution, using a photoredox catalytic system promoted by visible light. A new radical alkenylation pathway using alkene as the redox compound was presented and the alkene radical cation was the key intermediate in this oxidant-free system. This method provides a mild and robust synthesis of multisubstituted enol ethers and *N*-vinylazoles from simple and easily available alkenes, alcohols, and azoles. This oxidant-free system, using a photocatalyst and cobalt catalyst, offers a new strategy beyond traditional photoredox catalysis using a stoichiometric oxidant. A detailed mechanistic investigation of this reaction is under way in our laboratory.

Acknowledgements

This work was supported by the 973 Program (2011CB808600, 2012CB725302, 2013CB834804), the National Natural Science Foundation of China (21390400, 21272180, 21302148, 2109343, and 21402217), the Research Fund for the Doctoral Program of Higher Education of China (20120141130002), the Ministry of Science and Technology of China (2012YQ120060), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1030). The Program of Introducing Talents of Discipline to Universities of China (111 Program) is also appreciated.

Keywords: C–N bond formation · C–O bond formation · oxidant-free · photocatalysis · radical alkenylation

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Manuscript received: September 21, 2016 Revised: November 6, 2016 Final Article published:

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OR² **Cross-Coupling Reactions** H-OR² Со PC H. Yi, L. Niu, C. Song, Y. Li, B. Dou, or or н–н ⋪ A. K. Singh, A. Lei* _____ R^3 Н Photocatalytic Dehydrogenative Cross-Coupling of Alkenes with Alcohols or Azoles without External Oxidant Footloose and oxidant-free: A photodirect C–H/X–H cross-coupling and H_2 catalytic process that employs a cobalt evolution, achieving C–O and C–N bond catalyst as an electron acceptor mediates formation.

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Angew. Chem. Int. Ed. 2016, 55, 1-6

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