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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Combining Visible Light Catalysis and Transfer Hydrogenation for *in situ* Efficient and Selective Semihydrogenation of Alkynes under Ambient Condition

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By combining visible light catalysis and transfer hydrogenation, we are able to convert a series of alkynes to their corresponding alkenes in high chemical yields. Then the visible light catalytic transfer hydrogenation reaction can couple photoisomerization to produce *E*-alkenes or *Z*-alkenes exclusively depending on the aryl or alkyl substituted alkynes.

Selective semihydrogenation of alkynes is one of the most direct and efficient transformation to afford alkenes in synthetic organic chemistry.¹ Because the defined alkenes are versatile building blocks for the synthesis of natural products, pharmaceuticals and agrochemical products, tremendous research effort has been devoted to such conversion by using transition-metal catalysis. Although Ru,² Rh,³ Ir,⁴ Au,⁵ Cu,⁶ Ni,⁷ V⁸ and Fe⁹ have shown excellent performance for this transformation, the old-line Pd catalysis¹⁰ is more attractive and popular so far. The famous Lindlar catalyst,¹¹ for example, is the most fundamental procedure to afford Z-alkenes, where hydrogen gas (H₂) is used as reducing agent¹² to suprafacially add two hydrogen atoms to the π system of alkynes. However, high pressure of H_2 suffers from the danger of explosion and elaborate experimental setup. Alternatively, a catalytic transfer hydrogenation¹³ has been suggested, where organic molecules are employed as hydrogen donor, however, the airsensitive or expensive ligands are often required and elevated temperatureis always needed to act as the driving force for transfer hydrogenation. For both hydrogenation and transfer hydrogenation, the difficulty to control the stereochemistry and minimize the formation of over-reduced products remains a challenging transformation. Developing simpler, safer, milder and ligand-free catalytic transfer hydrogenation approaches for selective semihydrogenation of alkynes is highly desired.

In this contribution, we wish to report a new way to realize the catalytic transfer hydrogenation reaction of alkynes urder ambient condition by visible light catalysis. Herein, an organic dye eosin Y is employed as a photosensitizer and colloida. . nanoparticle is selected as a catalyst to couple visible ligh catalysis and hydrogenation reaction for semihydrogenation (Scheme 1), in which triethanolamine (TEOA) and H₂O plaimportant roles in catalytic transfer hydrogenation. As will to discussed later, this was found to be the case. Irradiation of the system consisting of eosin Y, colloidal Pd nanoparticle ar. 1 alkyne in TEOA solution of H₂O/CH₃CN exclusively results in alkene formation.



Scheme 1. A proposed pathway for semihydrogenation of alkynes.

Visible light catalysis^{14,15} has recently spurred much interest from organic chemists owing to the inherent green and milu character of light. However, the combination of visible lig u catalysis and transfer hydrogenation to form alkenes in or . pot is yet unknown. The present study demonstrates that suc. a coupling reaction is easily manipulated to produce alkene efficiently and selectively from their corresponding alkyne. The cascade one-pot reaction is initiated by photoinduced electron transfer from TEOA to ³[eosin Y]* to yield eos Y radical anion [eosin Y]^{•-}. The generated [eosin Y]^{•-} is able ... deliver an electron to colloidal Pd nanoparticle, which the capture the protons from TEOA and H₂O to produce Pd-' speices. The in situ formed Pd-H speices undergoes suprafaci addition of two hydrogen atoms to the π system of the alkyne leading to the semihydrogenation of alkynes. Moreover, the rich spectroscopic property of eosin Y allows for isomerizatio of the generated alkene. As a result, E- or Z-alkenes ar

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Electronic Supplementary Information (ESI) available: for experimental procedures, methods, and product characterization. See DOI: 10.1039/x0xx00000x

exclusively achieved for diaryl alkynes or alkyl alkynes respectively at room temperature and pressure.

Table	1.	Optimization	of reaction	conditions

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Ph PhPhPhPhPh Ph							
1a		rt, H ₂ O/CH ₃	CN 2a	3a		4a	
ontru	TEOA (eq.)	eosin Y (%)	Con. (%) ^b	yield (%) ^c			
entry				alkene	E/Z	alkane	
1	1.0 eq.	3%	55	50	>95:5	5	
2	2.0 eq.	3%	90	82	>95:5	8	
3	3.0 eq.	3%	100	85	>95:5	15	
4	5.0 eq.	3%	100	84	>95:5	16	
5	3.0 eq.	1%	48	38	>95:5	10	
6	3.0 eq.	5%	100	85	>95:5	15	
7 ^d	3.0 eq.	3%	60	60	2:1		
8 ^e	3.0 eq.	3%	100	99	>95:5	1	

^a Reaction conditions: 0.1 mmol 1,2-diphenylacetylene **1a** in 1.0 mL CH₃CN, 4.0 mL colloidal Pd nanoparticle aqueous solution (5.0×10^{-4} M), 525 nm green LEDs, 2 h irradiation at room temperature and pressure; ^b Conversion yield is isolated yields; ^cThe yield and ratio are based on ¹H NMR; ^dH₂O/CH₃CN 4:2; ^e H₂O/CH₃CN 8:3.

Our study was initiated from the hydrogenation of 1,2diphenylacetylene 1a. According to the procedure in the literature,¹⁶ colloidal Pd nanoparticle was conveniently prepared in aqueous solution (Figure S1). With the addition of one equivalent of triethanolamine (TEOA) and 3 mol% of eosin Y into a mixture of CH₃CN and colloidal Pd nanoparticles aqueous solution $(5.0 \times 10^{-4} \text{ M})$ containing 1,2diphenylacetylene 1a, the reaction solution was degassed and then irradiated by green LEDs (λ = 525 ± 10 nm) at room temperature and pressure. To our delight, 55 mol% of starting material **1a** was consumed to yield semihydrogenation product with high stereoselectivity (3a/2a E/Z > 95:5) in 2 h (Table 1, entry 1). The increase in the amount of TEOA resulted in a large improvement of conversion and yield without loss of stere oselectivity (E/Z > 95:5) (Table 1, entries 1-4). Subsequently, 3 mol% of eosin Y was proved to be the most effective (Table 1, entries 3, 5, 6), and a ratio of H₂O/CH₃CN 8:3 was the best for the reaction (Table 1, entries 3, 7, 8). Control experiments suggested that the conversion of 1a was negligible if eosin Y, colloidal Pd nanoparticles or TEOA was absent from the reaction mixture, and no any product could be obtained if the reaction was conducted in darkness (Table S1). A simple and easily manipulated approach as 3 mol% of eosin Y, 5.0×10^{-4} M colloidal Pd nanoparticles, 3.0 equiv. TEOA in a mixture with a ratio of H₂O/CH₃CN 8:3 under irradiation by green LEDs for 2h, is established.

With the optimal conditions in hand, various diaryl alkynes were studied to examine the scope of the approach. Both symmetric and unsymmetrical diaryl alkynes showed excellent performance with yield up to 99 mol% and stereoselectivity (E/Z) up to >95:5 (Table 2). Importantly, this protocol is suitable for selective reduction of carbon-carbon triple bond of

alkynes under mild conditions. In addition to carbon cather triple bond existing in the substrates, reducible function affor involving halogen, carbon-nitrogen triple bond and carbon group remained intact (Table 2, entries 2-7). Irrespective of the electron-withdrawing or -donating substituent on the aromat rings of diaryl alkynes, the reaction underwent smoothly to afford the corresponding *E*-alkenes exclusively in high chemic I yields, which is inherently difficult to achieve by general approaches.¹⁷

Table 2. Scope of diaryl alkynes.^a

entrv	substrates	Con.	,		
citery		(%) ^ь	alkenes	E/Z	alkar
1	$\bigcirc = \bigcirc$	100	99	>95:5	1
2		95	93	>95:5	2
3		100	99	>95:5	1
4	⟨Br	97	95	>95:5	2
5		99	95	>95:5	4
6	CN	98	97	>95:5	1
7		100	99	>95:5	1
8	CH3	100	97	>95:5	3
9	н ₃ со-	100	94	>95:5	6
10		100	95	>95:5	5

^a Reaction conditions: 0.1 mmol corresponding diaryl alkynes **1** in 1. mL CH₃CN, 3.0 eq. TEOA, 3 % eosin Y, 4 mL colloidal Pd nanopartic aqueous solution (5.0×10^{-4} M), 525 nm green LEDs, 2 h irradiation room temperature and pressure; ^b Conversion yield is isolated yields; The yield and ratio are based on ¹H NMR.

Table 3. Scope of non-diaryl internal alkynes

entry	substrates	Con.	yield (%) ^c				
		(%) ^b	alkenes	E/Z	alkane		
1 ^d	⊘он	100	99	<5:95	1		
2	CO2Me	100	98	<5:95	2		
3	CO2Et	95	94	<5:95	1		
4	C4H9	92	87	<5:95	5		
5		96	89	7:93	7		
6	HO5	91	85	8:92	6		
7	γ_{0}^{0}	90	86	6:94	4		

^a Reaction conditions: 0.1 mmol corresponding alkynes **1** in 1.5 n l. CH₃CN, 3.0 eq. TEOA, 3 % eosin Y, 4 mL colloidal Pd nanopartic a aqueous solution (5.0×10^{-4} M), 525 nm green LEDs, 2 h irradiation room temperature and pressure; ^b Conversion yield is isolated yields; ^c The yield and ratio are based on ¹H NMR; ^d reaction was complete 1 within 20 min.

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Unlike the diaryl alkynes, non-diaryl internal alkynes *i.e.* arylalkyl alkynes and dialkyl alkynes gave rise to 95 mol% of *Z*alkene rather than *E*-alkene under the optimized conditions. 3-Phenylprop-2-yn-1-ol was completely consumed within 20 min (Table 3, entry 1). Similar results were also obtained for other non-diaryl internal alkynes (Table 3, entries 2-7). And the performance of the internal alkynes containing one aryl group is better than the dialkyl alkynes. Of particular significance, a gram-scale reaction could proceed smoothly with a 95% yield at room temperature and pressure under green LEDs irradiation (Scheme S1).

Scheme 2. Photoinduced Z- to E- isomerization.

The inverse E/Z selectivity¹⁸ prompted us to carefully design a series of experiments for understanding the reaction. As shown in Scheme 2, when Z-1,2-diphenylethylene 2a was used as the substrate instead of 1,2-diphenylacetylene 1a in the system, the reaction was completed to form E-1,2diphenylethylene 3a exclusively within 2 min. The same result was obtained in the absence of colloidal Pd nanoparticle and TEOA, where only were eosin Y and Z-1,2-diphenylethylene 2a presented in the reaction (Scheme 2). However, non-diaryl internal alkenes could not isomerize under the same condition. Only could diaryl alkenes undergo such a photoinduced Z- to Eisomerization. This could be interpreted by the fact that the triplet energy of non-diaryl internal alkenes is much higher than that of eosin Y,¹⁹ thus leading to the triplet energy transfer from excited ³[eosin Y]* to alkenes thermodynamically unfavorable for photoisomerization.²⁰ For diaryl alkenes, the rate of energy transfer from triplet state ³[eosin Y]* (E_T = 179.9 $kJ \cdot mol^{-1}$) to *E*-alkenes is much slower than to *Z*-alkenes so that the E-alkenes dominates in the final product.²⁰ Overall, the combination of visible light catalysis and semihydrogenation of alkynes to Z-alkenes, and then a fast photoinduced Z- to Eisomerization for diaryl alkenes is responsible for the Eselectivity of diaryl alkynes. Herein visible light catalysis not only initiates the reaction, but also plays a crucial role in the selectivity.

To ensure the typical characteristic hydrogenation, H_2 was directly used for the reaction. When TEOA and eosin Y was replaced by 1 atm H_2 to conduct the same reaction at 40 $^{\circ}$ C for 2 h in darkness, 70 mol% of 1,2-diphenylacetylene **1a** was consumed to yield overreduction product 1,2-diphenylethane (Scheme 3, eq 1). Significantly, only *Z*-1,2-diphenylethylene **2a** was reduced by H_2 to form 1,2-diphenylethane, while *E*-1,2-diphenylethylene was silent (Scheme 3, eq 2, eq 3). For the non-diaryl internal *Z*-alkene, *Z*-3-phenylprop-2-en-1-ol remained intact in the H_2 direct hydrogenation reaction (Scheme 3, eq 4). That is to say, only *Z*-alkenes could produce overreduction alkanes product when H_2 was directly used for

hydrogenation of diaryl alkynes. However, in vith A_{rtic} with A_{rtic} system, diaryl alkenes could undergo a fast photomole as 297, *E*-isomerization so that the overreduction is avoided ensuring the reaction at the stage of *E*-alkenes.



Scheme 3. Reactions using H₂ as reducing agent.



Scheme 4. Reactions with and without TEMPO (5); Deuterium incorporation experiments (6).

It should be pointed out that 1) in the absence of 1a, 1 2 could evolve from the reaction system containing eosin Y TEOA and colloidal Pd nanoparticle; but 2) in the absence r colloidal Pd nanoparticle, no H₂ was detected at all. Addition on 1a into the H₂ evolution system resulted in semihydrogenatic 1 instead of H₂ evolution (Figure S2). These results suggested that the colloidal Pd nanoparticle is a catalytic center for semihydrogenation. Known in traditional Pd catalysis 🦳 hydrogenation, H₂ is commonly homolytic cleavage to generate Pd-H species.²¹ When TEMPO was added into the solution, the efficiency of semihydrogenation sharp. decreased from 95 mol% to 19 mol% (Scheme 4, eq 5, suggesting the visible light induced in situ generated active Pu-H species is responsible for the semihydrogenation of alkyne. In an effort to determine the H_2 source, the reaction w() conducted in D2O. E-1,2-deuteriodiphenylethylene 3a-D2 wa exclusively obtained in a yield of 90 mol% (Scheme 4, eq 6) Because TEOA would be deprotonated and exchanged proto with H₂O and the amount of H₂O is essential to the result of reaction, the cheap and commercial available TEOA seems not only to act as electron donor but also to combine H₂O as hydrogen donor for catalytic transfer hydrogenation.

Flash photolysis investigation was further performed t shed light on the reaction intermediate (Figure S3). Excitation of eosin Y by 532 nm light led to the characteristic absorption of the triplet ³[eosin Y]* at 560 nm.²² When TEOA was introduced into the solution, the eosin Y radical anion [eosin Y]^{•-} at 410 nm²² was observed at the expense of the ³[eosin

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Y]* absorption at 560 nm. The result suggested that the electron transfer from TEOA to ³[eosin Y]* occurred. According to the lifetime change as a function of the concentration of TEOA, the rate constant of the electron transfer was estimated to be $6.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S3, d, e). Further addition of colloidal Pd nanoparticle aqueous solution into the solution of TEOA and eosin Y resulted in a distinct quenching of [eosin Y]* (Figure S3). The electrons from [eosin Y]* to colloidal Pd nanoparticle, and the protons releasing from TEOA and H₂O captured by the colloidal Pd nanoparticle could generate Pd-H species *in situ* for semihydrogenation.

In summary, we have successfully combined visible light catalysis with transfer hydrogenation to realize efficient and selective semihydrogenation of alkynes at room temperature and pressure. Under visible light irradiation for 2 h, good to excellent yields of alkenes have been achieved. More interestingly, the visible light induced catalytic transfer hydrogenation enables coupling photoisomerization of the generated alkenes, depending on the substituted aryl or alkyl groups, to produce *E*-alkenes and *Z*-alkenes exclusively. The interesting protocol can accomplish the semihydrogenation in a cleaner, safer, more efficient and selective manner.

Financial support from the Ministry of Science and Technology of China (2013CB834804, 2014CB239402 and 2013CB834505), the National Natural Science Foundation of China (21390404, 91427303 and 21402217), the Key Research Programme of the Chinese Academy of Sciences (KGZD-EW-T05), and the Chinese Academy of Sciences.

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