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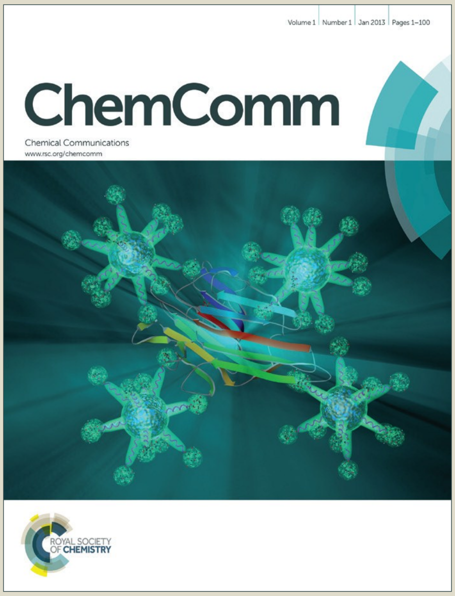

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Combining Visible Light Catalysis and Transfer Hydrogenation for *in situ* Efficient and Selective Semihydrogenation of Alkynes under Ambient Condition

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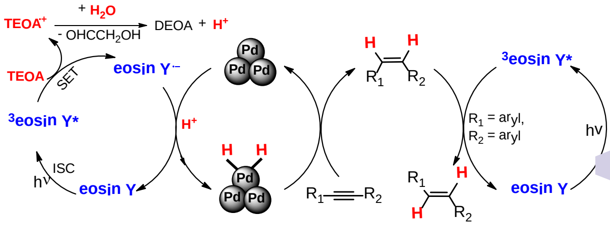
Jian-Ji Zhong[†,a] Qiang Liu[†,b] Cheng-Juan Wu,[a] Qing-Yuan Meng,[a] Xue-Wang Gao,[a] Zhi-Jun Li,[a] Bin Chen,[a] Chen-Ho Tung,[a] and Li-Zhu Wu*[a]

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] V[8] and Fe[9] have shown excellent performance for this transformation, the old-line Pd catalysis[10] 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 (H_2) is used as reducing agent[12] 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 hydrogenation[13] has been suggested, where organic molecules are employed as hydrogen donor, however, the air-sensitive 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 under ambient condition by visible light catalysis. Herein, an organic dye eosin Y is employed as a photosensitizer and colloidal Pd nanoparticle is selected as a catalyst to couple visible light catalysis and hydrogenation reaction for semihydrogenation (Scheme 1), in which triethanolamine (TEOA) and H_2O play important roles in catalytic transfer hydrogenation. As will be discussed later, this was found to be the case. Irradiation of the system consisting of eosin Y, colloidal Pd nanoparticle and alkyne in TEOA solution of H_2O/CH_3CN 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 mild character of light. However, the combination of visible light catalysis and transfer hydrogenation to form alkenes in one-pot is yet unknown. The present study demonstrates that such a coupling reaction is easily manipulated to produce alkenes efficiently and selectively from their corresponding alkynes. The cascade one-pot reaction is initiated by photoinduced electron transfer from TEOA to ^{3}[eosin Y]* to yield eosin Y radical anion [eosin Y]$^{\bullet-}$. The generated [eosin Y]$^{\bullet-}$ is able to deliver an electron to colloidal Pd nanoparticle, which then capture the protons from TEOA and H_2O to produce Pd-H speices. The *in situ* formed Pd-H speices undergoes suprafacial 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 isomerization of the generated alkene. As a result, *E*- or *Z*-alkenes are

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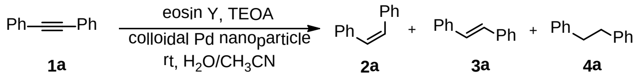
[a] *Key Laboratory of Photochemical Conversion and optoelectronic Materials, Technical Institute of Physics and Chemistry & University of the Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, P. R. China.*

[b] *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China.*

† The two authors contributed equally to this work.

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.[a]



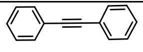
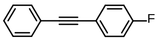
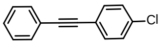
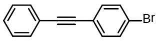
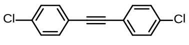
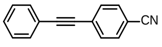
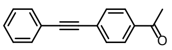
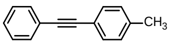
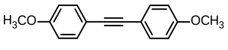
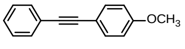
entry	TEOA (eq.)	eosin Y (%)	Con. (%)[b]	yield (%)[c]		
				alkene	*E/Z*	alkane
1	1.0 eq.	3%	55	50	>95:5	5
2	2.0 eq.	3%	90	82	>95:5	8
3	3.0 eq.	3%	100	85	>95:5	15
4	5.0 eq.	3%	100	84	>95:5	16
5	3.0 eq.	1%	48	38	>95:5	10
6	3.0 eq.	5%	100	85	>95:5	15
7[d]	3.0 eq.	3%	60	60	2:1	--
8[e]	3.0 eq.	3%	100	99	>95:5	1

[a] Reaction conditions: 0.1 mmol 1,2-diphenylacetylene **1a** in 1.0 mL CH_3CN, 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; [c] The yield and ratio are based on ^1H NMR; [d] H_2O/CH_3CN 4:2; [e] H_2O/CH_3CN 8:3.

Our study was initiated from the hydrogenation of 1,2-diphenylacetylene **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 CH_3CN and colloidal Pd nanoparticles aqueous solution (5.0 × 10^{-4} M) containing 1,2-diphenylacetylene **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 stereoselectivity (*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 H_2O/CH_3CN 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 H_2O/CH_3CN 8:3 under irradiation by green LEDs for 2h, is established.

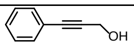
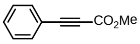
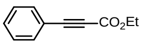
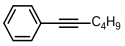
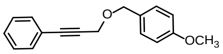
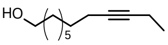
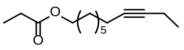
With the optimal conditions in hand, various diaryl alkynes were studied to examine the scope of the approach. Both symmetric and unsymmetrical diaryl alkynes showed excellent performance with yield up to 99 mol% and stereoselectivity (*E/Z*) up to >95:5 (Table 2). Importantly, this protocol is suitable for selective reduction of carbon-carbon triple bond of alkynes under mild conditions. In addition to carbon-carbon triple bond existing in the substrates, reducible functionalities involving halogen, carbon-nitrogen triple bond and carbonyl group remained intact (Table 2, entries 2-7). Irrespective of the electron-withdrawing or -donating substituent on the aromatic rings of diaryl alkynes, the reaction underwent smoothly to afford the corresponding *E*-alkenes exclusively in high chemical yields, which is inherently difficult to achieve by general approaches.[17]

Table 2. Scope of diaryl alkynes.[a]

entry	substrates	Con. (%)[b]	yield (%)[c]		
			alkenes	*E/Z*	alkane
1		100	99	>95:5	1
2		95	93	>95:5	2
3		100	99	>95:5	1
4		97	95	>95:5	2
5		99	95	>95:5	4
6		98	97	>95:5	1
7		100	99	>95:5	1
8		100	97	>95:5	3
9		100	94	>95:5	6
10		100	95	>95:5	5

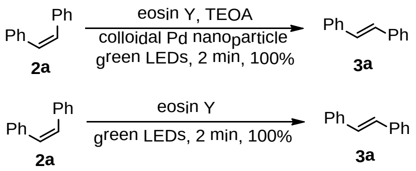
[a] Reaction conditions: 0.1 mmol corresponding diaryl alkynes **1** in 1.5 mL CH_3CN, 3.0 eq. TEOA, 3 % eosin Y, 4 mL colloidal Pd nanoparticle aqueous solution (5.0 × 10^{-4} M), 525 nm green LEDs, 2 h irradiation at room temperature and pressure; [b] Conversion yield is isolated yields; [c] The yield and ratio are based on ^1H NMR.

Table 3. Scope of non-diaryl internal alkynes.[a]

entry	substrates	Con. (%)[b]	yield (%)[c]		
			alkenes	*E/Z*	alkane
1[d]		100	99	<5:95	1
2		100	98	<5:95	2
3		95	94	<5:95	1
4		92	87	<5:95	5
5		96	89	7:93	7
6		91	85	8:92	6
7		90	86	6:94	4

[a] Reaction conditions: 0.1 mmol corresponding alkynes **1** in 1.5 mL CH_3CN, 3.0 eq. TEOA, 3 % eosin Y, 4 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; [c] The yield and ratio are based on ^1H NMR; [d] reaction was completed within 20 min.

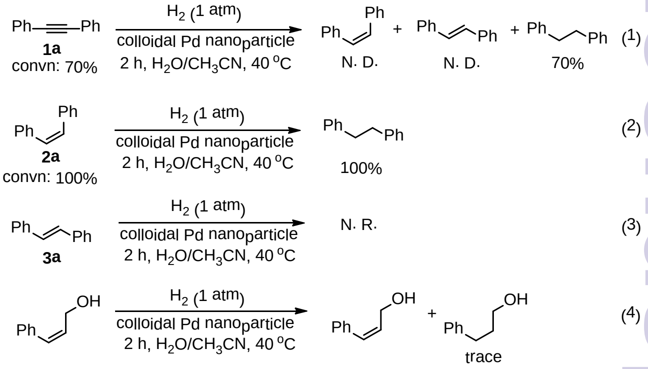
Unlike the diaryl alkynes, non-diaryl internal alkynes *i.e.* aryl-alkyl alkynes and dialkyl alkynes gave rise to 95 mol% of *Z*-alkene rather than *E*-alkene under the optimized conditions. 3-Phenylprop-2-yn-1-ol was completely consumed within 20 min (Table 3, entry 1). Similar results were also obtained 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).



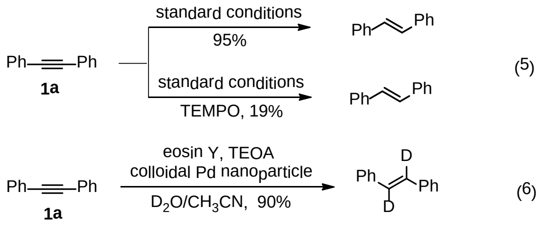
Scheme 2. Photoinduced *Z*- to *E*- isomerization.

The inverse *E/Z* selectivity[18] 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*-1,2-diphenylethylene **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 *E*-isomerization. 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·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 *E*-isomerization for diaryl alkenes is responsible for the *E*-selectivity 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 ℃ 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 the current system, diaryl alkenes could undergo a fast photoinduced *Z*- to *E*-isomerization so that the overreduction is avoided ensuring the reaction at the stage of *E*-alkenes.



Scheme 3. Reactions using H_2 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**, H_2 could evolve from the reaction system containing eosin Y, TEOA and colloidal Pd nanoparticle; but 2) in the absence of colloidal Pd nanoparticle, no H_2 was detected at all. Addition of **1a** into the H_2 evolution system resulted in semihydrogenation instead of H_2 evolution (Figure S2). These results suggested that the colloidal Pd nanoparticle is a catalytic center for semihydrogenation. Known in traditional Pd catalysis for hydrogenation, H_2 is commonly homolytic cleavage to generate Pd-H species.[21] When TEMPO was added into the solution, the efficiency of semihydrogenation sharply decreased from 95 mol% to 19 mol% (Scheme 4, eq 5), suggesting the visible light induced *in situ* generated active Pd-H species is responsible for the semihydrogenation of alkynes. In an effort to determine the H_2 source, the reaction was conducted in D_2O. *E*-1,2-deuteriodiphenylethylene **3a-D2** was exclusively obtained in a yield of 90 mol% (Scheme 4, eq 6). Because TEOA would be deprotonated and exchanged proton with H_2O and the amount of H_2O 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 H_2O as hydrogen donor for catalytic transfer hydrogenation.

Flash photolysis investigation was further performed to 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]$^{\bullet-}$ at 410 nm[22] was observed at the expense of the ^{3}[eosin

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 6.7×10^8 M^{-1} 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]$^{\bullet-}$ (Figure S3). The electrons from [eosin Y]$^{\bullet-}$ to colloidal Pd nanoparticle, and the protons releasing from TEOA and H_2O 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.

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