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Letter

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Photocatalysis Enabling Acceptorless Dehydrogenation of Diaryl hydrazines at Room Temperature

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KEYWORDS: Azo benzene, acceptorless dehydrogenation, hydrogen, photoredox catalysis, dual catalysis.

ABSTRACT: Aromatic azo compounds are privileged structural motifs, and they show myriad pharmaceutical as well as industrial applications. Here, we report an unprecedented catalytic acceptorless dehydrogenation of diarylhydrazine derivatives to access wide verity of aryl-azo compounds with the removal of molecular hydrogen as the sole byproduct. This distinctive reactivity has been achieved under dual catalytic conditions by merging the visible-light active $[Ru(bpy)_3]^{2+}$ as the photoredox catalyst and $Co(dmgH)_2(py)Cl$ as the proton-reduction catalyst. The reaction proceeds smoothly under very mild and benign conditions and operates at room temperature. This dual catalytic approach is highly compatible with many different functional groups and has a broad substrate scope. We have also demonstrated the reversible hydrogen storage and release phenomenon on hydrazobenzene/azobenzene couple to show the utility of these compounds as hydrogen storage materials. Further diversification of azobenzene was shown by a transition-metal catalyzed azo group directed *ortho* C-H bond functionalization.

Aromatic compounds with the N=N motif are highly valuable products as they show profound applications[1-6] in dyes and pigment industry,[1] therapeutic agents,[2] photo-responsive switches and chemosensors, polymers, soft materials, radical initiators, bioactive ligands, and food additives.[3-6] In recent times, several methods have been reported for the synthesis of aromatic azo derivatives (Figure 1).[7-11] These methods include oxidative dehydrogenative couplings of anilines,[7] reductive coupling of aromatic nitro compounds,[8] the coupling of aromatic compounds with aryl diazonium salts,[9] and Mills reaction.[10] There are few reports on direct oxidative dehydrogenation (ODH) of hydrazobenzene derivatives to azobenzenes.[11-12] These synthetic methods suffer from harsh reaction conditions such as high catalyst loading, need of stoichiometric reagents or strong oxidants and thus, generate an equivalent amount of waste.

Jiao and co-workers reported a Cu-catalyzed oxidative dehydrogenation of anilines[7d] to azobenzenes using air as the oxidant. Notably, due to the competing self-coupling of anilines, the unsymmetrical azo compounds were obtained in poor yields. Of late, Suib and his group reported the synthesis of symmetrical azobenzene derivatives by oxidative dehydrogenation of anilines using *meso*-Mn_2O_3.[7e] The reaction operates at elevated temperature with very high catalyst loading. Very recently, Lin and co-workers reported a method to prepare azo compounds by oxidative dehydrogenation of anilines using a stoichiometric amount of NBS and DBU under cryogenic conditions.[7a] Ma and co-workers described the synthesis of diaryl hydrazines using heterogeneous graphene oxide system with high catalyst loading (10 weight%) under oxidative conditions.[11c] Gozin and co-workers reported oxidative dehydrogenation of hydrazobenzene using the toxic $TiCl_3/HBr$ system.[11e] Recently, Hashimoto and co-workers reported oxidative dehydrogenation of hydrazobenzene using a catalytic amount of strong KO^tBu.[11a] Although this method has a broad substrate scope, the use of liquid NH_3 as solvent medium and strong base limited the practical applicability of the reaction.

In recent times, catalytic dehydrogenation of organic molecules with the liberation of molecular hydrogen is one of the most important key reactions in contemporary science.[13] The catalytic acceptorless dehydrogenation reactions (ADH) obviate the requirement of external oxidants and produce less toxic waste. The ADH method with the liberation of hydrogen gas is much superior over the classical oxidative dehydrogenation methods in view of atom-economy, and environmental sustainability.[14] Removal of hydrogen atoms from adjacent atomic centers of an organic molecule is a thermodynamically uphill process; however, recent experimental and computational studies showed that the presence of nitrogen atom makes the removal of hydrogen atom more easier.[15] Herein, we report ADH of hydrazobenzene derivatives using a dual catalytic system comprising photoredox catalysis coupled with proton reduction catalysis. This unprecedented reaction operates under very mild, benign conditions. A consequence of this finding with only molecular hydrogen as the by-product makes this process more eco-benign and sustainable for the effective synthesis of a wide range of aromatic azo compounds for various applications. Interestingly, the reversible hydrogen storage/release phenomenon on hydrazobenzene /azobenzene system is also demonstrated.

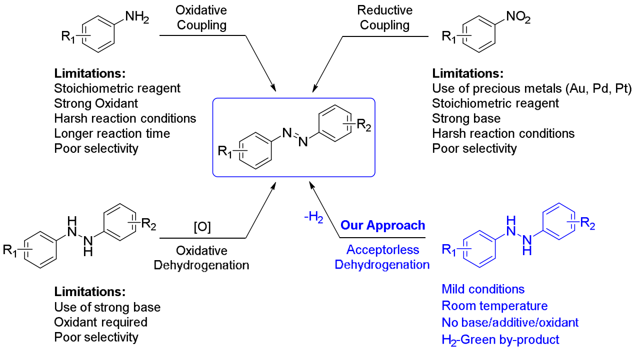
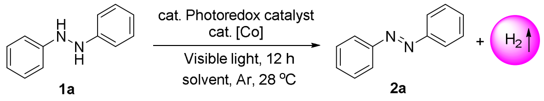


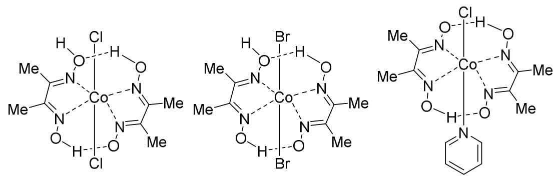
Figure 1. Previous reports on catalytic approches to synthesis of azobenzene derivatives.

We began optimization of the ADH reaction using diphenyl hydrazine **1a** as a model substrate. We screened a number of photoredox catalysts merged with different proton reduction catalysts (**I-III**) in various solvent systems (Table-1). We found that 1 mol% of photoredox catalyst, 2 mol % of Co-based proton reduction catalyst, in 0.1 M ethanol gave the desired dehydrogenated azobenzene **2a** in 93% isolated yield (Table 1, entry 1). Among the various photoredox catalysts, $[Ru(bpy)_3]^{2+}$ catalyst was found to be optimal for this reaction (Table 1, entries 1-4). Simillary, $Co(dmgH)_2(py)Cl$ (**III**) proton reduction catalyst was found to give superior activity, and gave the maximum yield of **2a** (Table 1, entries 1, 5-6). The liberated hydrogen gas was qualitatively analyzed on gas chromatography (GC-TCD).[16] Among a number of solvents screened, EtOH was found to be the most suitable solvent for this ADH reaction (Table 1, entries 1, 7-8). A series of control experiments were carried out to show the necessity of each of the reaction components such as photoredox catalyst, proton reduction catalyst, and light source (Table 1, entries 9-11). The product **2a** formation was not observed in the absence of either photoredox or proton reduction catalyst (Table 1, entries 9-10). Similarly, in the absence of the light source, no formation of **2a** was observed (Table 1, entry 11). Notably, reducing the photoredox catalyst loading to 0.5 mol% gave the desired product **2a** in moderate yield (Table 1, entry 12). Gratifyingly, this unprecedented catalytic ADH reaction proceeds very smoothly at ambient temperature under neutral conditions in presence of visible-light source with no generation of waste except hydrogen gas.

Table 1. Optimization of the reaction conditions.[a]



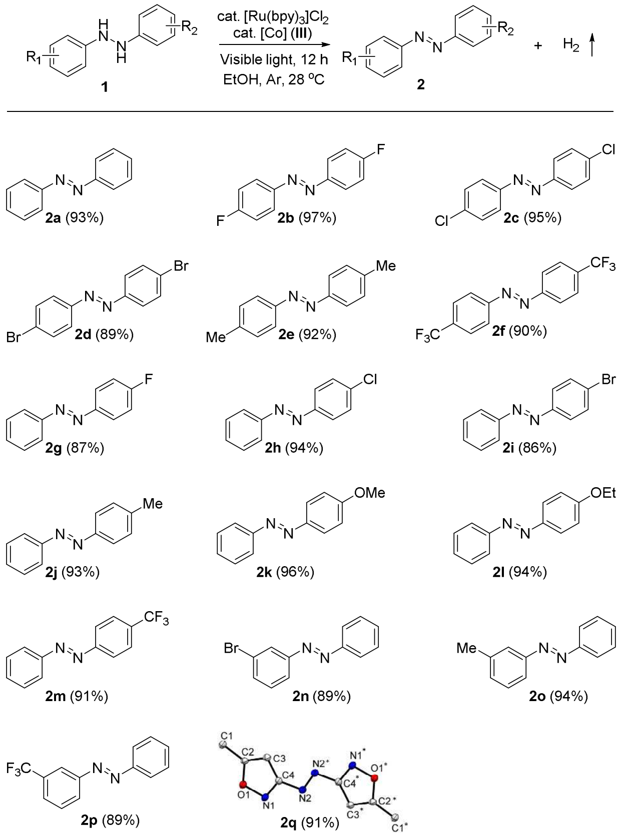
Entry	[Co] source	Photoredox catalyst	Solvent	Yield (%)[b]
1	III	$[Ru(bpy)_3]Cl_2$	EtOH	93[c]
2	III	$[Ru(bpy)_3][PF_6]_2$	EtOH	95[c]
3	III	Eosin Y	EtOH	trace
4	III	Rose bengal	EtOH	trace
5	I	$[Ru(bpy)_3]Cl_2$	EtOH	36
6	II	$[Ru(bpy)_3]Cl_2$	EtOH	42
7	III	$[Ru(bpy)_3]Cl_2$	MeOH	89[c]
8	III	$[Ru(bpy)_3]Cl_2$	MeCN	0
9	---	$[Ru(bpy)_3]Cl_2$	EtOH	0
10	III	---	EtOH	0
11	III	$[Ru(bpy)_3]Cl_2$	EtOH	0[d]
12	III	$[Ru(bpy)_3]Cl_2$	EtOH	69[e]


(I) (II) (III)

[a] General reaction conditions: Substrate **1a** (0.25 mmol), photoredox catalyst (1.0 mol%), proton-reduction (**I-III**) catalyst (2.0 mol%), solvent 2.5 mL, 28 °C, visible-light, 12 h. [b] Based on ^1H NMR yield. [c] Isolated yield. [d] Dark conditions. [e] 0.5 mol% of photoredox catalyst.

With an optimal reaction conditions in hand, several hydrazobenzene derivatives **1** were subjected to the ADH reaction in presence of $[Ru(bpy)_3]Cl_2$ (1 mol%), proton-reduction cobalt catalyst (**III**) (2 mol%) under visible-light irradiation in EtOH at room temperature. As shown in Table 2, the present ADH strategy shows a wide substrate scope and high functional-group tolerance and gives dehydrogenated azobenzene derivatives in good to excellent yields (up to 97%). Electron-donating as well as electron-withdrawing groups at different position in the phenyl ring of the hydrazobenzene derivatives did not affect the reactivity and yielded the corresponding dehydrogenated products (Table-2). Among symmetrical hydrazobenzene derivatives, substrates bearing electron-withdrawing group at the *para* position of the phenyl ring, such as fluoro, chloro, bromo and trifluoromethyl proceeded smoothly to give the corresponding azobenzenes in 89%-97% isolated yields (products **2b-2d**, and **2f**) under the optimized conditions. Also substrates with electron-donating groups such as *p*-methyl gave **2e** in 92% isolated yield. Like symmetrical hydrazobenzenes, unsymmetrically substituted hydrazobenzenes showed a similar trend in their reactivity. Thus, substrates with electron-withdrawing groups such as 4-F, 4-Cl, 4-Br, 4-CF_3, 3-Br, and 3-CF_3 were well tolerated and afforded the corresponding azobenzenes in good to excellent yields of 86% to 94% (Table 1, products **2g-2i**, **2m-2n**, and **2p**). The diaryl hydrazines with electron-donating groups such as 4-Me, 4-MeO, 4-EtO, and 3-Me were well tolerated and offered the corresponding dehydrogenated products in excellent yields (Table 2, products **2j-2l**, and **2o**). Similarly, a heterocyclic azo derivative was obtained with 91% isolated yield under the optimized condition (Table 2, product **2q**).

Table 2. Substrate scope for room temperature dual catalyzed ADH of hydrazobenzene.[a-b]



2a (93%) **2b** (97%) **2c** (95%)
2d (89%) **2e** (92%) **2f** (90%)
2g (87%) **2h** (94%) **2i** (86%)
2j (93%) **2k** (96%) **2l** (94%)
2m (91%) **2n** (89%) **2o** (94%)
2p (89%) **2q** (91%)

[a] Reaction conditions: **1** (0.25 mmol), $[Ru(bpy)_3]Cl_2$ (1 mol%), Co-catalyst (**III**) (2 mol%), EtOH (2.5 mL), Ar atm, 36W blue LED, 28 °C, 12 h. [b] Isolated yields.

The progress of the present ADH reaction was monitored by UV-Visible absorption spectroscopy (Figure 2). From UV-Visible absorption spectroscopic analysis, it is observed that the rate of the reaction decreases as the concentration of product (**2a**) increases. This is because azo products are typically absorbing in a visible range, and as more and more azo product is generated in the reaction mixture, it obscures the activity of the photocatalyst. The reaction kinetics was measured by applying the Beer Lambert's law the concentration of azobenzene was determined at a different time interval of the reaction, and a plot was drawn between azobenzene yield *vs* time.[16]

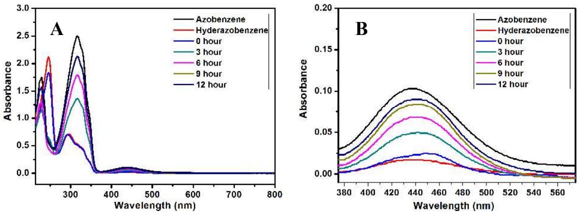
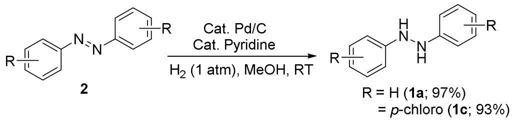


Figure 2. UV-Visible spectra of reaction mixture at different time intervals.

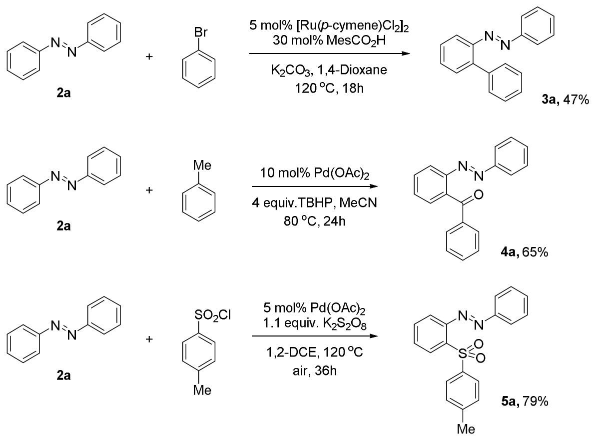
In recent times, liquid organic hydrogen carriers (LOHCs) as efficient hydrogen storage have been paid much attention in contemporary science.[15a-c,17-18] However, the viability of azobenzene as hydrogen storage system is only possible when both the dehydrogenation of hydrazobenzenes and hydrogenation of azobenzenes become feasible under mild reaction conditions. Gratifyingly, the reversible hydrogen storage/release phenomenon on hydrazobenzene/azobenzene couple is successfully demonstrated. In this context, we have developed an efficient method for hydrogenation of azobenzene to hydrazobenzene under very mild conditions using a commercially available heterogeneous catalyst. The hydrogenation reaction was carried out using catalytic amount of Pd/C (5 weight% of Pd) and catalytic amount of pyridine as additive under 1 atm pressure of hydrogen at ambient temperature (Scheme 1).[16]



Reaction conditions: **2a** (0.25 mmol), Pd/C (1.0 mg), pyridine (10 mol%), methanol (5.0 mL), H_2 (1 atm), rt, 15 min.

Scheme 1. Catalytic hyderogenation of azobenzenes to hydrazobenzenes.

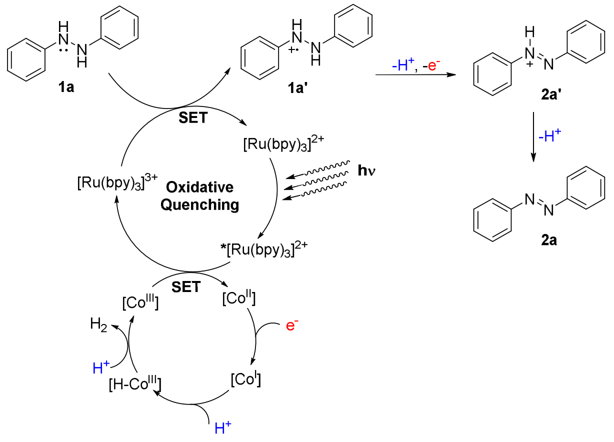
Next, we have shown the diversification of azobenzene (acts as a good directing group[19] in the C-H bond activation chemistry) and illustrated in Scheme 2. The Ru-catalyzed *ortho* C-H bond arylation of azobenzene gave **3a** in 47% isolated yield.[19a] Similarly, Pd-catalyzed *ortho*-C-H bond acylation was achieved using toluene as the acyl equivalent and TBHP as the oxidant gave **4a** in 65% isolated yield.[19b] The Pd-catalyzed *ortho*-C-H bond sulfonylation of azobenzene (**2a**) proceeded smoothly in the presence of catalytic amount of $Pd(OAc)_2$ and $K_2S_2O_8$ as the oxidant yielding **5a** in 79% isolated yields.[19c]



Scheme 2. Diversification of azobenzene derivatives.

To better understand the reaction mechanism, a series of control experiments were carried out. In the absence of the catalysts or under the dark conditions, no formation of product was observed. This clearly confirms that all the key reaction components are essential for the success of the present ADH reaction. Performing the reaction under air/oxygen atmosphere, 66% yield of **2a** was observed. Importantly, there is no formation of dihydrogen was observed on GC, and indeed the product formation is mainly due to the oxidative pathway.[11-12] Cyclic voltammetry experiment of **1a** and **1c** shows the oxidation potential of the two compounds are +0.58 V *vs*. SCE, and +0.66 V *vs*. SCE, respectively. The reduction potentials $E^{III/II}$ and $E^{II*/I}$ of tris(2,2′-bipyridine)ruthenium, $[Ru(bpy)_3]^{+2}$ were determined to be +1.29 V *vs*. SCE, and +0.77 V *vs*. SCE, respectively.[20] The reduction potential $E^{III/II}$ (**III**) of $Co(dmgH)_2(py)Cl$ and the oxidation potential $E^{III/II*}$ of $[Ru(bpy)_3]^{+2}$ were reported as -0.67 V *vs*. SCE,[21] and -0.81 V *vs*. SCE, respectively.[20] Thus, it is expected that the excited state of $*[Ru(bpy)_3]^{2+}$ could transfer an electron to Co^{III} while hydrazobenzene **1a** could transfer an electron to $[Ru(bpy)_3]^{3+}$ and in this way the catalytic cycle will be completed, and thus may follow the oxidative quenching mechanism.

Based on the above experimental observation, and recent literature precedents[20] on dual catalysis[21] and hydrogen evolving reactions by proton reduction cobalt complexes,[22] we have proposed a plausible mechanism as follows (Scheme 3). Under the visible-light irradiation the photocatalyst, $[Ru(bpy)_3]^{2+}$ generates the excited state $*[Ru(bpy)_3]^{2+}$ which can reduce Co^{III} to Co^{II} *via* the single electron transfer (SET) through oxidative quenching and lead to $[Ru(bpy)_3]^{3+}$. Then, the formed $[Ru(bpy)_3]^{3+}$ is reduced by **1a** to regenerate $[Ru(bpy)_3]^{2+}$ and an amine radical cation **1a'**. This radical cation **1a'** can undergo hydrogen-atom transfer with Co^{II} to produce the intermediate **2a'** and a highly reducing Co^{I} or can directly produce Co^{III}-H intermediate. Subsequently, the highly reducing Co^{I} species immediately reacts with a H^+ ion (released from **1a'**) to give Co^{III}-H intermediate. This Co^{III}-H intermediate may react with the second proton (released from **2a'**) releasing a molecule of H_2 and Co^{III} or may undergo reduction to Co^{II}-H followed by protonation to release a H_2 molecule and Co^{II}. However, the homolytic cleavage that involving the two Co^{III}-H intermediate to evolve hydrogen gas could also not be ruled out.[22-23]



Scheme 3. Plausible reaction mechanism for ADH of hydrazobenzene (**1a**).

In conclusion, we have developed a dual transition-metal catalyzed acceptorless dehydrogenation of hydrazobenzene derivatives to the corresponding azobenzenes with the liberation of hydrogen gas. This unprecedented ADH strategy was achieved under environmentally benign conditions by merging the visible-light photoredox catalysis with Co-based proton reduction catalysis at room temperature under base-, and oxidant-free conditions. Interestingly, reversible hydrogen storage/release phenomenon on hydrazobenzene/azobenzene couple is also demonstrated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental and spectroscopic data, copies of ^{1}H, and ^{13}C NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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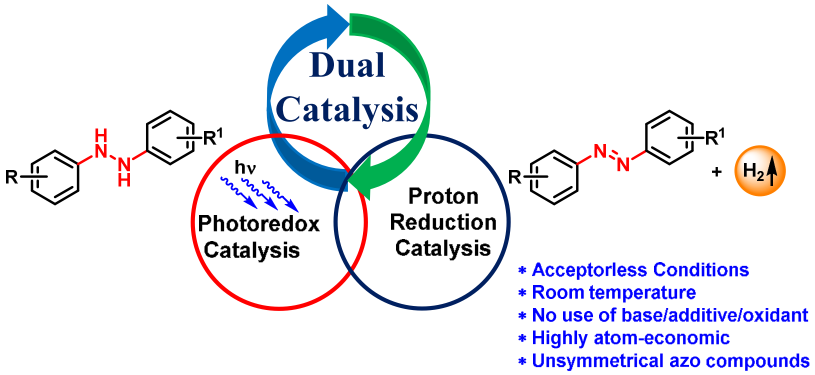
SYNOPSIS TOC



- Acceptorless Conditions
- Room temperature
- No use of base/additive/oxidant
- Highly atom-economic
- Unsymmetrical azo compounds