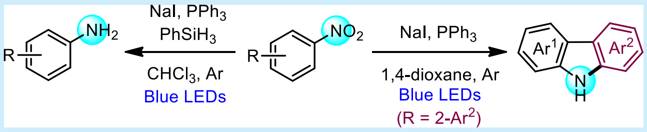
OL Organic Letters

NaI/PPh_3-Mediated Photochemical Reduction and Amination of Nitroarenes

Zhonghua Qu,[#] Xing Chen,[#] Shuai Zhong, Guo-Jun Deng, and Huawen Huang*

Cite This: *Org. Lett.* 2021, 23, 5349−5353

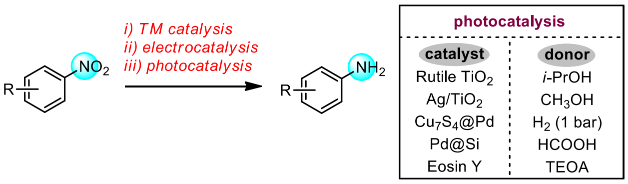
ABSTRACT: A mild transition-metal- and photosensitizer-free photoredox system based on the combination of NaI and PPh_3 was found to enable highly selective reduction of nitroarenes. This protocol tolerates a broad range of reducible functional groups such as halogen (Cl, Br, and even I), aldehyde, ketone, carboxyl, and cyano. Moreover, the photoredox catalysis with NaI and stoichiometric PPh_3 provides also an alternative entry to Cadogan-type reductive amination when *o*-nitrobiarenes were used.



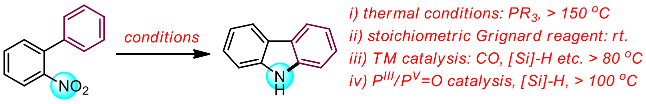
Anilines play fundamentally substantial roles in both academia and industry, which therefore has triggered wide method development of nitroarene reduction.[1] While noncatalytic reduction of nitroarenes using stoichiometric reducing agents provides currently main commercial access to functionalized anilines, these methods suffer from poor selectivity and serious ecological issues.[2] Recent progress on catalytic reduction of nitroarenes mainly depends on transition-metal (TM) catalysis via direct hydrogenation or hydrogen transfer,[3] electrocatalysis along with water oxidation,[4] and sustainable visible-light-induced photocatalysis (Scheme 1a).[5] Of them, the mild photocatalytic process via hole-driven hydrogen transfer with hydrogen donors or hole scavenger is an attractive strategy for reduction of nitroarenes.[6] Hence, three kinds of photocatalytic systems based on photon absorber including plasmonic,[7] semiconductor,[8] and dye-sensitized photocatalyst[9] have been exploited. In most cases, however, the use of transition metals such as copper,[10] silver,[11] and palladium[6b] also lead to the issues of functional group tolerance with respect to, for example, dehalogen[12] and addition upon unsaturated bonds.[13] Recently, Wu and coworkers[14] reported a facile but efficient visible-light-driven photochemical homogeneous nitroarene reduction using eosin Y as photocatalyst and triethanolamine (TEOA) as electron donor. In this system, the aqueous conditions resulted in complete hydrolysis of cyano group and highly excessive amounts of TEOA are required, which may restrict its broader application.

Scheme 1. Catalytic Nitroarene Reduction and Intramolecular Amination (Cadogan Reaction)

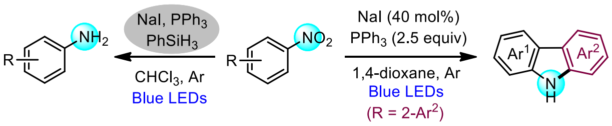
(a) Catalytic nitroarene reduction



(b) Cadogan amination



(c) This work



On the other hand, intramolecular reductive amination of 2-nitrobiarenes, the so-called Cadogan reaction (Scheme 1b), are traditionally achieved under thermal conditions with stoichiometric triphenylphosphine,[15] with recent development of mild process using Grignard reagents[16] and catalytic protocols based on transition-metal catalysts[17] or phosphacycloalkane catalyst.[18] Recently, we discovered mild photocatalytic reductive couplings[19] including the Cadogan amination employing 4CzIPN as the photosensitizor.[19a] Further studies on this project reveal that the photocatalytic reduction of nitroarenes could proceed in the absence of photocatalyst. Herein, we report on these findings to disclose a divergent NaI/PPh_3-mediated photochemical reduction and amination of nitroarenes[20] (Scheme 1c). Salient features of the present reduction protocol include no need for transition-metal catalysts, mild

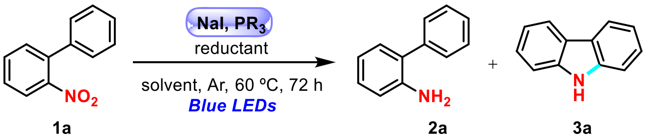
Received: May 16, 2021
Published: June 28, 2021

https://doi.org/10.1021/acs.orglett.1c01654

reaction conditions, ample substrate scope with broad functional group tolerance, high chemoselectivities, and key mechanistic insights in the combinational electron-donor–acceptor (EDA) formation[21] and phosphine catalysis.[22]

To commence our study, 2-nitrobiphenyl (**1a**) was selected as model substrate to evaluate the reaction conditions of divergent reduction upon hydrogenation and amination (Table 1). The synergistic NaI/PPh_3 catalytic system combined with $PhSiH_3$ as hydrogen donor was found to be effective for the reductive hydrogenation. Hence, the 2-aminobiphenyl product (**2a**) was produced with yields ranging from 45% to 98% when performing in different media including DCM, Et_2O, EtOAc, and $CHCl_3$. While the sustainable EtOAc gave excellent yield, $CHCl_3$ was the best solvent (Table 1, entries 1–4). Among other phosphines (Table 1, entries 5–7), while tri-*o*-tolylphosphine did not work, tris(4-fluorophenyl)phosphine and tris(4-methoxyphenyl)phosphine afforded **2a** in good yields. Aliphatic tricyclohexylphosphine also completely prohibited the reduction (Table 1, entry 8). Then some other reductants including TEOA, triethylamine (TEA), and Et_3SiH, dramatically reduced the yields (Table 1, entries 9–11). We also tested other halides instead of NaI, where NaCl, NaBr, KI, and NH_4I were all inferior (Table 1, entry 12). The results of control experiments suggested that NaI, PPh_3, and light stimulation are all critical for the reductive hydrogenation (Table 1, entries 13–15). In comparison, the nitro reduction also proceeded when stoichiometric PPh_3 was utilized in the absence of $PhSiH_3$. To our delight, however, the carbazole product (**3a**) via intramolecular Cadogan amination was formed as the major product (Table 1, entry 16). In this respect, a series of optimizations of reaction conditions were performed for the reductive amination of 2-nitrobiarenes [see the Supporting Information (SI) for details (Table S1)]. The formation of **3a** was obviously improved when the reaction was conducted in 1,4-dioxane, with **2a** further suppressed (Table 1, entry 17). Control experiments reveal that the reaction in the absence of NaI afforded **3a** in only 14% yield (Table 1, entry 18).

Table 1. Optimization of Reaction Conditions[a]

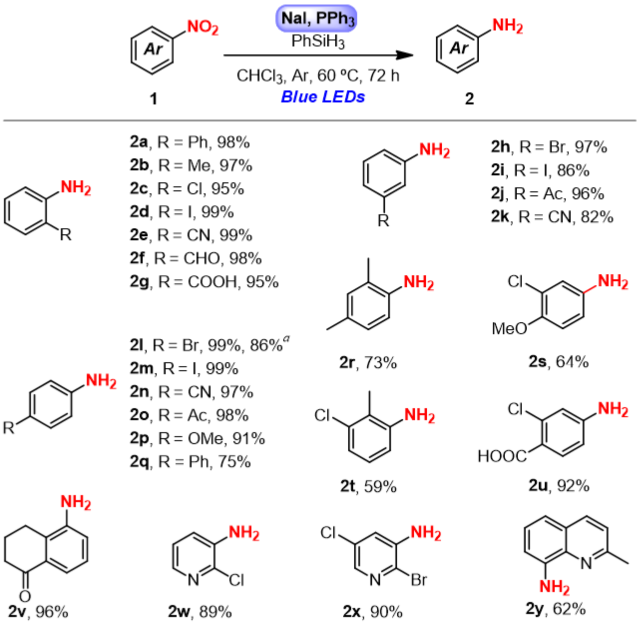


entry	PR_3	reductant	solvent	yield[b] (%)	
				2a	3a
1	PPh_3	$PhSiH_3$	DCM	60	trace
2	PPh_3	$PhSiH_3$	Et_2O	45	trace
3	PPh_3	$PhSiH_3$	EtOAc	90	nd
4	PPh_3	$PhSiH_3$	$CHCl_3$	98	nd
5	$P(o\text{-tol})_3$	$PhSiH_3$	$CHCl_3$	trace	trace
6	$P(p\text{-FPh})_3$	$PhSiH_3$	$CHCl_3$	80	trace
7	$P(PMP)_3$	$PhSiH_3$	$CHCl_3$	75	trace
8	PCy_3	$PhSiH_3$	$CHCl_3$	trace	trace
9	PPh_3	TEOA	$CHCl_3$	12	trace
10	PPh_3	TEA	$CHCl_3$	trace	trace
11	PPh_3	Et_3SiH	$CHCl_3$	10	trace
12[c]	PPh_3	$PhSiH_3$	$CHCl_3$	<20	nd
13[d]	PPh_3	$PhSiH_3$	$CHCl_3$	nd	nd
14		$PhSiH_3$	$CHCl_3$	24	nd
15[e]	PPh_3	$PhSiH_3$	$CHCl_3$	trace	nd
16[f]	PPh_3		$CHCl_3$	16	52
17[f]	PPh_3		dioxane	8	82 (78)
18[e,f]	PPh_3		dioxane	trace	14

[a] Reaction conditions: **1a** (0.2 mmol), NaI (40 mol %), PPh_3 (20 mol %), reductant (2 equiv), solvent (2.0 mL), irradiation with a 35 W blue LEDs at 60 °C for 72 h under argon atmosphere; [b] Yield determined by GC analysis of the crude reaction mixture using 1,3,5-trimethylbenzene as the internal standard, and yield in parentheses indicates isolated yield. [c] NaCl, NaBr, KI, or NH_4I instead of NaI. [d] Reaction in dark. [e] Without NaI. [f] 2.5 equiv of PPh_3.

With the established reductive reactivities by the visible-light-induced NaI/PPh_3 catalytic system, we first extended it to aniline formation from substituted nitroarenes especially with reducible functional groups (Scheme 2). The substrates bearing either electron-withdrawing or electron-donating groups worked well to exclusively afford the corresponding aniline products. The reducible carbon–halogen bonds other than nitro remained without any detectable collapse with Cl (**2c**, **2s**, **2u**), Br (**2h**, **2l**), or even I (**2d**, **2i**, **2m**). Among others including aldehyde (**2f**), ketone (**2j**, **2o**, **2v**), carboxyl (**2g**, **2u**), and cyano (**2e**, **2k**, **2n**), the reduction also occurred only in the nitro group. In other words, 100% nitro reductive selectivities were observed in all examples of competitive reduction. Incomplete conversion of some nitroarenes was observed to result in lower than 90% yield (**2i**, **2k**, **2q**–**2t**). Notably, nitropyridines bearing chloro and bromo also proceeded through exclusive nitro reduction (**2w**, **2x**). Finally, 8-nitroquinoline worked with moderate conversion (**2y**). However, other nitro heterocycles, such as those containing thiazole, imidazole, indazole, etc., failed to give the corresponding reduction products in this system.

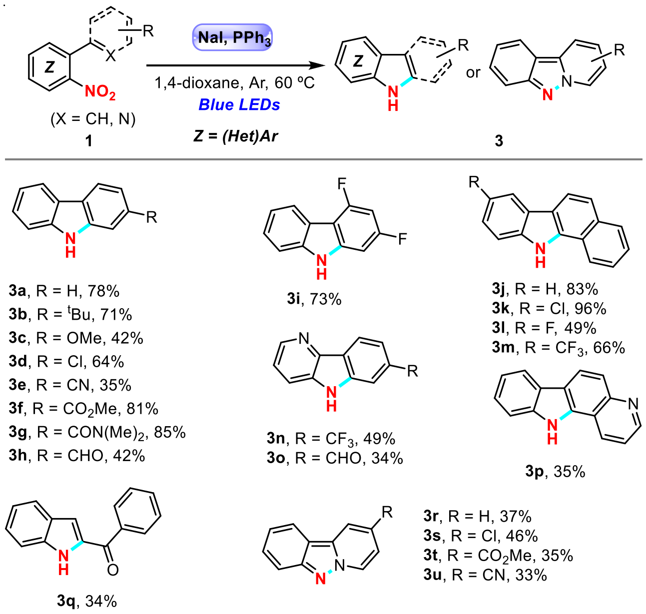
Scheme 2. NaI/PPh_3-Mediated Photochemical Reduction of Nitroarenes



[a] Isolated yield of 10 mmol scale reaction.

Subsequently, the generality and substrate scope of the NaI/PPh_3-mediated reductive aminations of *o*-nitrobiarenes were probed (Scheme 3). Moderate to good yields were obtained

Scheme 3. NaI/PPh$_3$-Mediated Photochemically Reductive Amination of 2-Nitrobiarenes



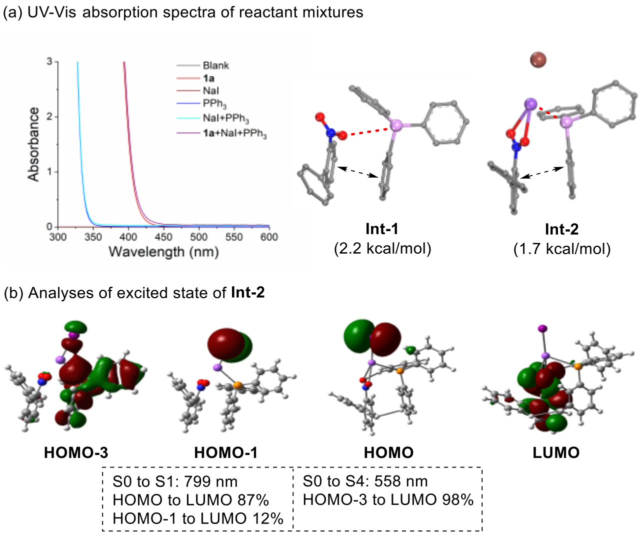


Figure 1. (a) UV–vis absorption spectra of reactant mixtures, (b) Predicted excited states molecular orbital diagrams of **Int-2**.

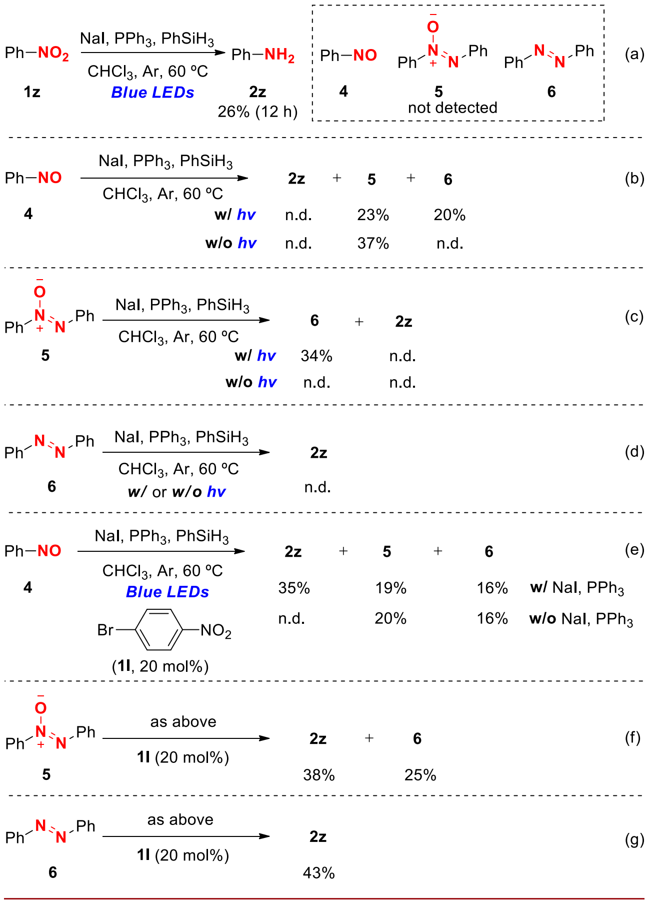
when substituted *o*-nitrobiarenes were employed, with a range of compatible functionalities including chloro, cyano, ester, amide, and formyl (**3a**–**3h**). The C–F amination did not occur when *o*-fluorophenyl was attached (**3i**). Then 11*H*-benzo[*a*]carbazoles were generated in moderate to excellent yields when the reactants bore a naphthyl moiety (**3j**–**3m**). Notably, 2-(5-chloro-2-nitrophenyl)naphthalene afforded the corresponding benzo[*a*]carbazole (**3k**) in almost quantitative yield (96%). Among others, aza-carbazoles (**3n** and **3o**) were smoothly delivered from the starting 3-nitro-2-phenylpyridines, albeit in relatively low yield. Moreover, aza-benzo[*a*]carbazole **3p** produced in 35% yield. While *o*-nitrostilbenes did not work, *o*-nitrochalcone could proceed through reductive amination to afford the 2-benzoylindole product **3q**. Finally, pyrido[1,2-*b*]indazole products were generally formed in modest yields when 2-(2-nitrophenyl)pyridines were employed (**3r**–**3u**). Notably, majority of starting materials was recovered in the cases of those with low yields such as **3c** and **3n**–**3u**. The aniline side products were generally formed in trace amounts. We also tried to modify the reaction conditions to improve the reactivity of these reactants, but we failed.

With the established reactivities of our mild visible-light-driven nitroarene reduction mediated by NaI/PPh$_3$, we were attracted to depict its photoactivating action models. First, we performed UV–vis spectroscopic absorption experiments on various combinations of **1a**, PPh$_3$, and NaI in a solution of the same concentration as the real reaction mixture (Figure 1a). The results reveal that the combination of PPh$_3$ and NaI features the same absorption with PPh$_3$, only in the UV (<360 nm). With the participation of *o*-nitrobiphenyl, either single component or combinations display an absorption in the visible region with an onset around 440 nm. Further, we did density functional theory (DFT) calculations to support the proposed photoactivating action models (Figure 1b). Without the iodide additive, the electron-poor nitroarene **1a** and the electron-rich PPh$_3$ interact via a Coulombic attraction with a P–O distance of 3.57 Å and a π–π interaction with a shortest π-stacking distance of approximately 3.44 Å. This assembly leads to the formation of the atom transfer complex **Int-1**. It is calculated to be endergonic by 2.2 kcal/mol, which is much lower than the generation of dioxazaphosphetane intermediate from trialkyl phosphines including Radosevich's phosphacycle.[15,22] On the other hand, the additional NaI seems to affect the interaction of **1a** and PPh$_3$ slightly, but the Coulombic interaction of it with both **1a** and PPh$_3$ forms a new atom transfer complex (**Int-2**) (endergonic by 1.7 kcal/mol). The complex **Int-2** is expected to absorb photons to initiate the first deoxygenation process.[23] Moreover, the time-dependent DFT (TD-DFT) calculation on the excited state of **Int-2** assigned a S_0-to-S_4 excitation, which was predicted to be 558 nm. This peak has almost exclusively charge-transfer excitation characteristic (98%) from I-PPh$_3$ fragment to PhNO$_2$ fragment (HOMO-3 to LUMO).

To obtain more mechanistic information on the NaI/PPh$_3$-mediated reduction of nitroarenes, some control experiments were carried out. First, aniline (**2z**) was found to be the only reduction product within 12 h with major nitrobenzene (**1z**) recovered, while potential intermediate products such as nitrosobenzene (**4**), azoxybenzene (**5**), and azobenzene (**6**) were not observed (Scheme 4a). Moreover, when these compounds instead of **1z** were subjected to the standard conditions, the target aniline was not formed in all cases with or without light stimulation (Scheme 4b–d). These results suggest that the presence of nitroarenes could probably be a critical factor for the late-stage reduction of intermediate products. Hence, compounds **4**–**6** were treated with additional 1-bromo-4-nitrobenzene in catalytic amounts (Scheme 4e–g). Aniline was indeed generated as the major product in those reactions. We speculate that the combination of nitrobenzene, NaI, and PPh$_3$ forms a EDA complex[20a] that absorbs photons to not only decompose into nitrosobenzene or the Ph-N(OH) intermediate but also transfer energy to enable late-stage reduction of intermediate products.[4a]

In summary, the combination of nitroarenes with NaI and PPh$_3$ was found to generate an EDA complex that absorbs photons to enable reductive hydrogenation of nitroarenes. This mild photoredox catalytic system has been demonstrated to be highly selective for nitro reduction because a pad of reducible functional groups are accommodated in it. With stoichiometric

Scheme 4. Control Experiments



amounts of PPh$_3$ playing dual roles of initiator for energy transfer and electron donor, the photocatalyst-free NaI/PPh$_3$-based photocatalysis has also been used as an efficient method for Cadogan-type reductive amination of *o*-nitrobiarenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01654.

> Experimental procedures, characterization data, computational details, and ^{1}H NMR and ^{13}C NMR spectra for all products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Huawen Huang − *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China;* orcid.org/0000-0001-7079-1299; Email: hwhuang@xtu.edu.cn

Authors

Zhonghua Qu − *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China*

Xing Chen − *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China*

Shuai Zhong − *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China*

Guo-Jun Deng − *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China;* orcid.org/0000-0003-2759-0314

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c01654

Author Contributions

[#]Z.Q. and X.C. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support by the National Natural Science Foundation of China (22071211), the Science and Technology Planning Project of Hunan Province (2019RS2039), Hunan Provincial Natural Science Foundation of China (2020JJ3032), and the Collaborative Innovation Center of New Chemical Technologies for Environmental Benignity and Efficient Resource Utilization is gratefully acknowledged.

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