Direct Photochemical Route for Amine- and Catalyst-Free Synthesis of Azoxybenzene and Functional Azoxy Derivatives via Accessible Nitroarene Homocoupling under Ambient Conditions

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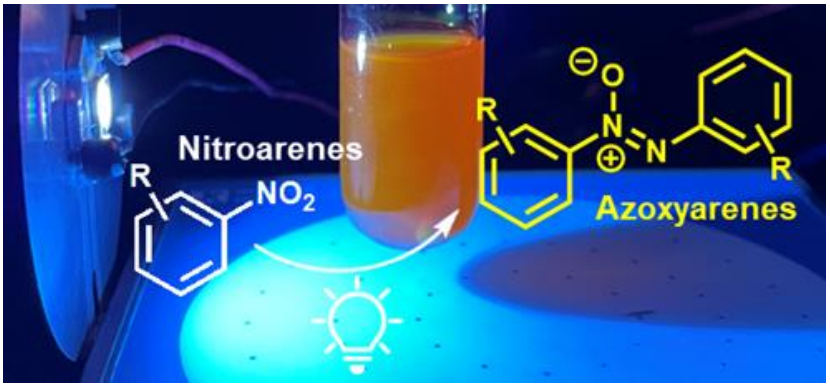


TOC Description: Ultraviolet illumination of nitrobenzenes at 365 nm produces their azoxy counterparts through a direct photochemical route.

Keywords

Nitrobenzene reduction, azoxybenzene, Wallach reaction, nitrobenzene photochemistry

Abstract

We report on a direct photochemical method for the one-pot, catalyst- and additive-free synthesis of azoxybenzene and substituted azoxy derivatives from nitrobenzene building blocks. This reaction is conducted at room temperature and under air, and can be applied to substrates with a wide range of substituents. Yields of products derived from *para*- and *meta*-substituted nitrobenzenes are typically good, while sterically encumbered *ortho*-substituted substrates are not as fruitful. Photochemical Wallach rearrangement of generated azoxybenzenes to *ortho*-hydroxyazoxybenzenes was observed in some cases, most markedly in selected *ortho*-halogenated nitrobenzenes. Overall, this method provides an efficient, green pathway to highly value-added azoxybenzene products.

Introduction

In the past decade, azoxybenzene (diphenyldiazene oxide) has sparked great interest due to its potential applications in organic, medicinal and materials chemistry.[1,2] This compound, which carries an uncommon 1,3-dipolar O–N=N linkage with charges distributed over the three-atom set, is a valuable building block in the preparation of dyes and pigments,[3,4] as well as the development of liquid crystals[4–9] and polymeric materials.[10–12] In synthetic chemistry, the azoxy functionality can be exploited as an *ortho*-directing group in the C–H functionalization of arenes[13–16] and as the precursor for the Wallach rearrangement for the easy preparation of hydroxyazobenzenes.[1,17–22] On the other hand, for medicinal chemistry applications, azoxybenzenes have shown potential for drug delivery,[23] and were recently studied as bioisostere of alkene and amide;[24] remarkably, several azoxyarene analogues of bioactive alkenes and amides showed comparable, promising anticancer activities. It follows that practical, accessible methods for the synthesis of azoxybenzene and functional azoxy derivatives are urgently needed. In general, azoxybenzene is prepared by either oxidation of anilines or reduction of nitroarenes.[1,25] In fact, both processes enable an access route to the condensation between an aryl nitroso compound and an aryl hydroxylamine, which are the participants required to produce azoxybenzene (Figure 1). Unfortunately, both of these processes require harsh reaction conditions, such as high temperature or pressure, that lead to the formation of hazardous or undesirable byproducts following the over oxidation/reduction of the starting materials and the competing formation of diazocompounds.[26]

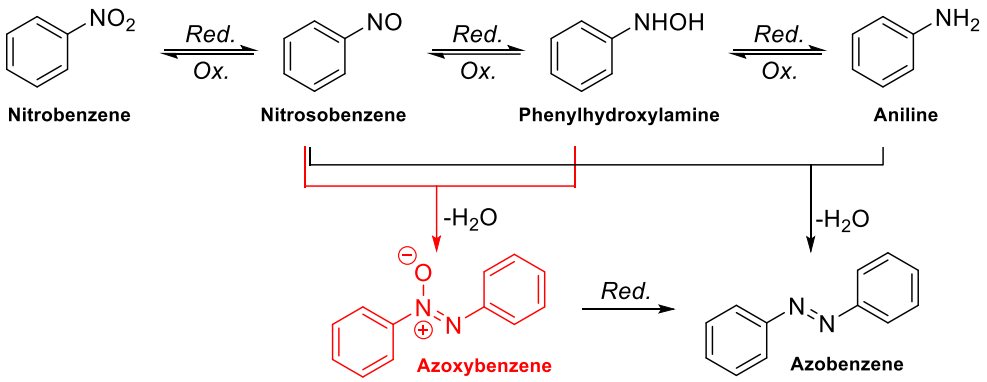


Figure 1. General synthetic pathway for the formation of azoxybenzene/azobenzene from nitrobenzene.

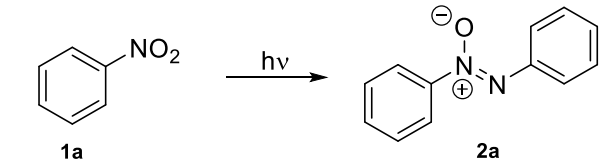
While various attempts have been made for the oxidative coupling of aniline,[3,27–36] for the selective reduction of nitroaromatics to azo and azoxy compounds in particular, several examples have been reported using alcohols as reducing agents[37,38] or catalytic reactions. For instance, the hydrogenation of nitrosobenzene with alcohols catalyzed by Rh(I) produced azoxybenzene along with aldehydic products.[39] Other works reported the use of CeO_2 catalysts,[40] Au nanoparticles supported on mesostructured ceria (Au/meso-CeO_2),[41] or a proline-based gel bound catalyst.[42] Additionally, some notable efforts have focused on the utilization of photocatalytic strategies for coupling of nitroarenes toward the formation of azo- and azoxy- aromatics. Indeed, light-driven reactions can provide a low-cost, mild, and 'tunable' approach to the synthesis of these valuable compounds. For example, azoxybenzenes were synthesized using heterogeneous photocatalysts, such as Au/ZrO_2[43] or Cu nanoparticles on graphene support,[44] graphitic C_3N_4,[45] Pd nanoparticles supported on mesoporous CdS,[46] Ru on CeO_2,[47] Ag-Cu alloy nanoparticles,[48] and the organic photocatalyst Eosin Y.[49] Catalyst-free photochemical reactions can provide even more environmentally friendly synthetic routes. Recently, Tan et al. have reported the one-pot, two-step, catalyst-free photochemical synthesis of azoxy compounds (and imines) by coupling the concomitant reduction of a nitroaromatic precursor with the oxidation of aliphatic amines; specifically, illumination at 400 nm of the nitroarene under Ar leads to H-abstraction from propylamine, eventually generating both key participants (nitrosobenzene and phenylhydroxylamine) through subsequent radical formation and rearrangements.[50] The last step – the condensation between the aryl nitroso and aryl hydroxylamine – works best when conducted in open air or under an O_2 atmosphere.

Inspired by these considerations, we envisioned a highly practical route for the construction of azoxybenzenes, where both key reactive partners originate from the same nitrobenzene building block and are accessed without the assistance of additional catalysts or reagents. In this work, we exploit the established inherent photochemical behaviour of excited nitrobenzene[51] to directly access azoxybenzene in a novel manner. The result is an overall simple (one pot, room temperature, under air, mild illumination conditions) and green (catalyst and amine-free) alternative process for azoxybenzene synthesis. We further applied our method to the targeted synthesis of substituted azoxybenzenes.

Results and Discussion

Photochemical conversion of Nitrobenzene (1a) to Azoxybenzene (2a). In a general reaction, a solution of nitrobenzene was irradiated with ultraviolet light (365 nm, UVA) using a light-emitting diode (LED) for 24 h. We began our studies of this system by first screening various conditions to assess the impact of solvent, concentration, irradiation wavelength, and atmospheric oxygen (Table 1). The best conditions (Entry ***c***, Table 1) were achieved using a 0.15 M solution of nitrobenzene in isopropyl alcohol under air, for which we observed 100% conversion of the starting material and selective formation of azoxybenzene in 93% yield. The reaction was unproductive in benzene (Entries ***g*** and ***h***) and acetonitrile (Entries ***i*** and **j**), and somewhat productive in N,N-dimethylformamide (Entry ***k***); the optimal solvent was clearly isopropanol. Increasing the concentration of nitrobenzene (Entries ***a*** - ***c***) up to full conversion at 0.15 M resulted in improved yield. Running the reaction at 0.05 M under a nitrogen atmosphere (Entry ***d***) gave better conversion than the open-air reaction (Entry ***a***), however the yield of desired product was lower. Finally, under identical conditions otherwise, excitation at 365 nm (Entry ***a***) was more fruitful than excitation at 405 nm (entry ***l***).

Table 1. *i*-PrOH = Isopropyl Alcohol. DMF = *N*,*N*-dimethylformamide. For all the entries below, a solution of nitrobenzene was irradiated for 24 h. After irradiation, the reaction solvent was evaporated under reduced pressure. The crude mixture was then redissolved in CH_2Cl_2 and left to evaporate in the dark for an additional 24 h. We note that purification of Entry ***a*** immediately after evaporation of *i*-PrOH resulted in 61% conversion of nitrobenzene and 47% yield of azoxybenzene. [a]Starting concentration of nitrobenzene. [b]Based on the amount of nitrobenzene recovered from column chromatography. [c]Isolated yield after purification by column chromatography. The identities of all products were confirmed by ^{1}H NMR.



1a
Nitrobenzene

2a
Azoxybenzene

Entry	Solvent	Irradiation Wavelength (nm)	[M][a]	Atmosphere	% Conversion[b]	% Yield[c]
a	*i*-PrOH	365	0.05	Air	68	59
b	*i*-PrOH	365	0.10	Air	87	73
c	***i*-PrOH**	**365**	**0.15**	**Air**	**100**	**93**
d	*i*-PrOH	365	0.05	N_2	85	47
e	*i*-PrOH	-	0.15	Air	0	0
f	*i*-PrOH	-	0.15	N_2	0	0
g	C_6H_6	365	0.05	Air	0	0
h	C_6H_6	365	0.05	N_2	0	0
i	CH_3CN	365	0.05	Air	0	0
j	CH_3CN	365	0.05	N_2	0	0
k	DMF	365	0.15	Air	97	43
l	*i*-PrOH	405	0.05	Air	54	32

These findings can be further understood in the context of the purported reaction pathway. The nitro functional group is typically characterized by lowest energy S_1 (n-π*) and T_1 (n-π*) states, as also shown by the presence of an absorption band at λ_{Abs} = 258 nm in the UV-Vis spectrum of nitrobenzene (Figure S1, Supplementary Information), assigned to the typical n-π* transition for this compound.[51,52] Thus, the photochemistry of the nitro group can find a good model in the photochemistry of the S_1 (n-π*) and T_1 (n-π*) states of the carbonyl group. As such, typical electron transfer or H abstraction processes can be expected. Specifically, the n-π* excitation of nitrobenzene can be considered analogous to that of benzophenone, for which photochemical excitation leads to the formation of a reactive triplet state with unit efficiency.[52] In the presence of isopropyl alcohol, the triplet state of nitrobenzene abstracts H from the solvent, ultimately leading

to the formation of phenylhydroxylamine through a total of four H-atom abstractions, two from the solvent and two from generated radicals,[51] analogous to the processes observed for benzophenone. The light-induced generation of phenylhydroxylamine is then accompanied by two concomitant dark reactions, namely 1) its oxidation to nitrosobenzene and 2) its subsequent condensation with such nitrosobenzene to form azoxybenzene.[51]

After prolonged light exposure of an aerated solution of nitrobenzene in isopropyl alcohol, a bright yellow colour develops (Figure S2), which we attribute to the advancing formation of azoxybenzene. Indeed, the UV-Vis spectrum of a diluted solution of nitrobenzene recorded before and after ultraviolet illumination (Figure S3) shows the appearance of a band at ~320 nm, which corresponds to the absorption maximum of azoxybenzene (compare Figure S1 and Figure S3). Results obtained using 0.10 M and 0.15 M solutions of nitrobenzene (entries ***b*** and ***c*** in Table 1) are also consistent with the aforementioned mechanism, with the production of azoxybenzene being almost quantitative (93% from a 0.15 M solution) when there is enough starting material to enable the formation of phenylhydroxylamine and nitrosobenzene in good concentration. Interestingly, we noticed an increase in the conversion percentage of nitrobenzene (calculated from the weight amount of nitrobenzene recovered from column chromatography) at higher starting concentrations, specifically, 68% at 0.05 M, 87% at 0.10 M, and 100% at 0.15 M, in line with the reported quantum yield of the disappearance of nitrobenzene in *i*-PrOH under UVA irradiation, and the rate constant for hydrogen abstraction.[51,53]

To further confirm the photochemistry at play, we irradiated a solution of nitrobenzene in isopropyl alcohol under N_2 atmosphere, by using a fused silica cell equipped with a round quartz stem (7 mm OD) which was degassed and immediately sealed off prior to ultraviolet illumination. According to the previously published mechanism,[51] the quantum yield of photolysis of nitrobenzene is ~30% higher under an inert atmosphere than in aerated solutions, which can be easily attributed to a lower probability of triplet quenching by oxygen; this is reflected in our observed conversion of nitrobenzene in these two cases (Entry ***a*** vs. Entry ***d***). After irradiation, the solution was treated according to our general protocol: evaporation of isopropyl alcohol under reduced pressure, redissolution in CH_2Cl_2 and slow evaporation under air. In view that one of the key aforementioned dark reactions is promoted in air-saturated solutions (i.e., oxidation of phenylhydroxylamine to nitrosobenzene) we expected to obtain a lower yield of azoxybenzene in the oxygen-free reaction (Entry ***d***) as compared to the oxygen-containing one (Entry ***a***) despite the

higher conversion of nitrobenzene in the former; results show that this is indeed the case (47% and 59%, respectively). These findings also suggest that the two so-called dark reactions begin during the irradiation period, as nitrobenzene is gradually transformed into phenylhydroxylamine.

Reactions conducted in the absence of light (Entries ***e*** and ***f***) validate that the photochemical excitation of the substrate is definitely required to initiate the reaction. On the other hand, irradiation with blue light at 405 nm (Entry ***l***) led to an observed 54% conversion of nitrobenzene and 32% isolated yield of azoxybenzene, consistent with the lower absorptivity of the former at this wavelength.

Additional mechanistic insights were provided by investigating solvent dependence. For this purpose, we tested our reaction by using solutions, both aerated and degassed, of nitrobenzene in benzene (Entries ***g*** and ***h***), acetonitrile (Entries ***i*** and ***j***) and *N*,*N*-dimethylformamide (Entry ***k***). Indeed, the quantum yield of the photolysis of nitrobenzene is strongly dependent on the rate of H abstraction from the solvent as the primary step.[51] Accordingly, no reaction was observed when nitrobenzene was dissolved in either acetonitrile or benzene, where hydrogen abstraction from nitrobenzene is unlikely (note that, between the two, benzene is normally considered the better hydrogen donor due to its lower bond dissociation energy for the homolytic cleavage of the C-H bond).[54] However, we isolated two main products from the reaction in DMF: azoxybenzene and azobenzene in comparable yields (43% and 36%, respectively, with azobenzene formed by azoxybenzene reduction - ^{1}H NMR in Figure S4). This outcome was not entirely unforeseen, considering that i) the photochemical reduction of azoxybenzene to azobenzene is a known process in the presence of solvents that enable hydrogen abstraction,[1,55] and ii) amide solvents have been repeatedly shown as non-innocent participants, as both hydrogen and electron donors in photoredox catalysis, often eliminating the need for additional sacrificial reagents.

Intriguingly, ultraviolet irradiation of nitrobenzene also yielded trace amounts of 2-(phenyldiazenyl)phenol (2-hydroxyazobenzene, **3a**) i.e., the product of a Wallach rearrangement of azoxybenzene (Figure 2). Specifically, we observed the presence of a signal at ~13 ppm in the ^{1}H NMR of a crude reaction (Figure S5 reports a zoomed spectrum of entry ***a***, unpurified). The formation of 2-hydroxyazobenzene by irradiation of azoxybenzene was first observed by Cumming and Ferrier in 1925 by irradiating a solution of azoxybenzene in ethanol with UV light,[18] and later confirmed by Badger and Buttery in 1954[21] and Lewis and Reiss in 1966.[22] In 1985, Shine, Subotkowski and Gruszecka[20] confirmed that the photochemical pathway to the Wallach

rearrangement involves the formation of an oxadiazole-like intermediate (Figure 2) and that the transposition has an intramolecular character, ultimately leading to the known *ortho*-hydroxy product. To confirm our observations, we irradiated a solution of pure azoxybenzene (0.15 M) in isopropanol at 365 nm for 24 h. The absorption spectrum of the solution recorded before and after ultraviolet irradiation show the unmistakable appearance of a bathochromically shifted band (Figure S6). Following workup and purification we were able to isolate the 2-(phenyldiazenyl)phenol Wallach-rearranged product (^{1}H NMR in Figure S7) in 65% yield.

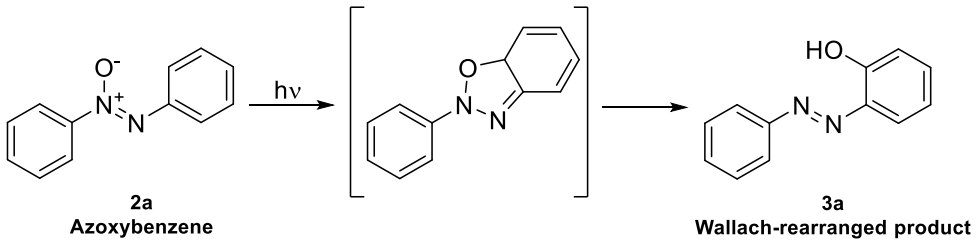


Figure 2. Observed photo-Wallach rearrangement of azoxybenzene.

Synthesis of Substituted Azoxybenzenes (Substrate Scope and Limitations). We probed the scope and limitation of this mild, direct photochemical route to azoxybenzenes as a means to 1) determine the extent to which azoxy derivatives could be productively accessed using this method, and 2) understand the impact of sterics and electronics on this reaction. The results of this investigation can be seen in Figure 3. In all cases, the only materials observed in appreciable amounts (> 5%) at the conclusion of the reaction were the indicated products and the starting nitroarene. Products were isolated using column chromatography.

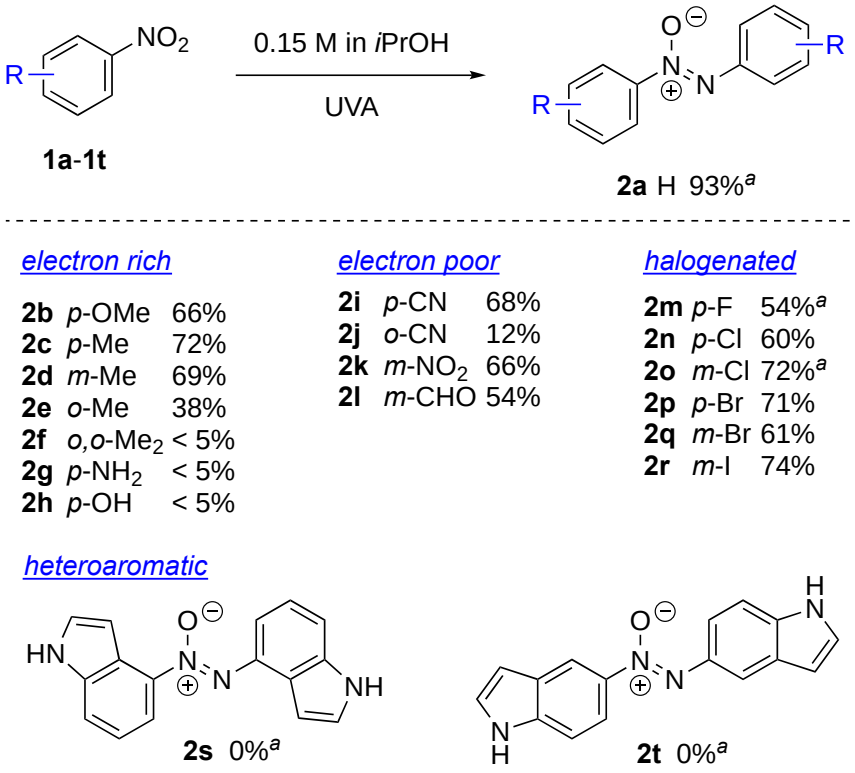


Figure 3. Substrate scope for the synthesis of azoxybenzenes via reductive homocoupling of nitroarenes. The general procedure described above was applied. If not noted, reactions were irradiated for 48 hours. Yield reported as isolated yield after purification by column chromatography. The identity of each product was confirmed by ^{1}H NMR, ^{13}C NMR and GC-MS (see Supplementary Information). [a]Reaction irradiated for 24 hours.

Interestingly, the best-observed yield was for the formation of the unsubstituted compound **2a**. The reaction tolerated milder electron-donating groups well (**2b**-**2d**), but it suffered in correlation with steric crowding of the nitro group (**2e**, **2f**) and failed when the electron-donating groups were protic (**2g**, **2h**). Electron-withdrawing groups in the *para* (**2i**) or *meta* (**2k**, **2l**) positions did not preclude reasonable conversion to product, and in fact we were surprised to observe the conversion of *meta*-dinitrobenzene (**1k**) was fairly efficient (66%) and minimal side products were observed. As with the electron-donating groups, we observed that *ortho*-substitution with an electron-withdrawing group (**2j**) was highly deleterious for this reaction. *Para*- (**1m**, **1n**, **1p**) and *meta*-halonitrobenzenes (**1o**, **1q**, **1r**) were converted to the product in good yields. However, *ortho*-chloro and -bromo substrates (**1u**, **1v**) gave the Wallach-rearranged hydroxyazobenzenes (**3u**, **3v**) (Figure 4) as the only observed product of the reaction, presumably accessed by the photochemical process described above (Figures S8 and S9). Trace (< 5%) amounts of Wallach products were observed

in unsubstituted nitrobenzene (**1a**), certain electron-poor substrates (**1j**, **1l**), and selected other halogenated nitrobenzenes (**1n**, **1o**, **1q**). The placement of the halogen at the *ortho* position seems to have a stereoelectronic effect that strongly promotes this rearrangement. While halogen bonding between a nitrogen and an *ortho*-halide would result in a lowering of the HOMO and facilitation of this rearrangement,[56,57] it is unlikely to occur due to the highly directional nature of halogen bonds.[58] Crystal structures of *ortho*-bromo- and *ortho*-chloroazobenzenes do display halide–*ortho*-diazo-nitrogen distances that are less than the sum of their respective van der Waal radii,[59] meaning that in solution either 1) there will be an electrostatic interaction between those two groups (i.e., a directionally non-classical halogen bond)[60] or 2) *ortho*-halogenated azobenzenes (and thus azoxybenzenes) will be twisted out of plane in solution. Either case could result in elevated reactivity of the azoxybenzene, and may help to explain why we observe spontaneous Wallach rearrangements in these cases. It is also worth noting that conversion of *ortho*-halogenated nitrobenzenes to product in this reaction correlates inversely with the size of the halide (i.e., Cl > Br > I) and is likely reflective of the impact of increasing steric hindrance surrounding the nitro group on azoxybenzene formation (as seen in compounds **1e** and **1f**).

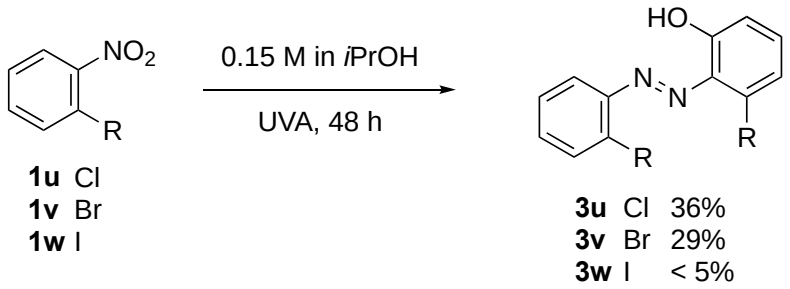


Figure 4. Unexpected Wallach products of the attempted homocoupling of *ortho*-halonitrobenzenes.

Conclusions

Significant synthetic effort has been made in the past to access azoxybenzenes, which are industrially useful synthetic molecules, in a practical fashion and under mild synthetic conditions. In this work, we have demonstrated a green and straightforward approach to the efficient and selective synthesis of azoxybenzenes via the uncatalyzed, photochemical homocoupling of nitrobenzenes. Yields are generally good, and in cases of low yield unreacted starting material can be mostly recovered. The reaction suffers proportionally to steric hindrance around the nitro group,

and the method is not useful for substrates bearing protic electron-donating substituents nor for the two nitroheteroarenes examined. In some cases, we observed spontaneous photo-Wallach rearrangement to produce an asymmetric hydroxylated azobenzene product: this was mostly a very minor component of reaction mixtures, if observed, but for two *ortho*-halogenated substrates (**1u**, **1v**) it was the major product.

We envision this reaction being exceptionally useful for scientists looking for straightforward ways to prepare symmetrically substituted azoxybenzenes. It also serves as an entry to Wallach rearrangement products, and may encourage future work in this area in terms of either synthetic method development and/or applications of these products. This method also demonstrates the value of revisiting established photochemistry in the context of synthetic organic chemistry with the goal of reducing the unnecessary use of catalysts or co-reagents. This mindset may lead to the development of more sustainable, green, and industrially/medicinally useful chemical transformations.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgments

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