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Electrosynthesis of azobenzenes directly from nitrobenzenes

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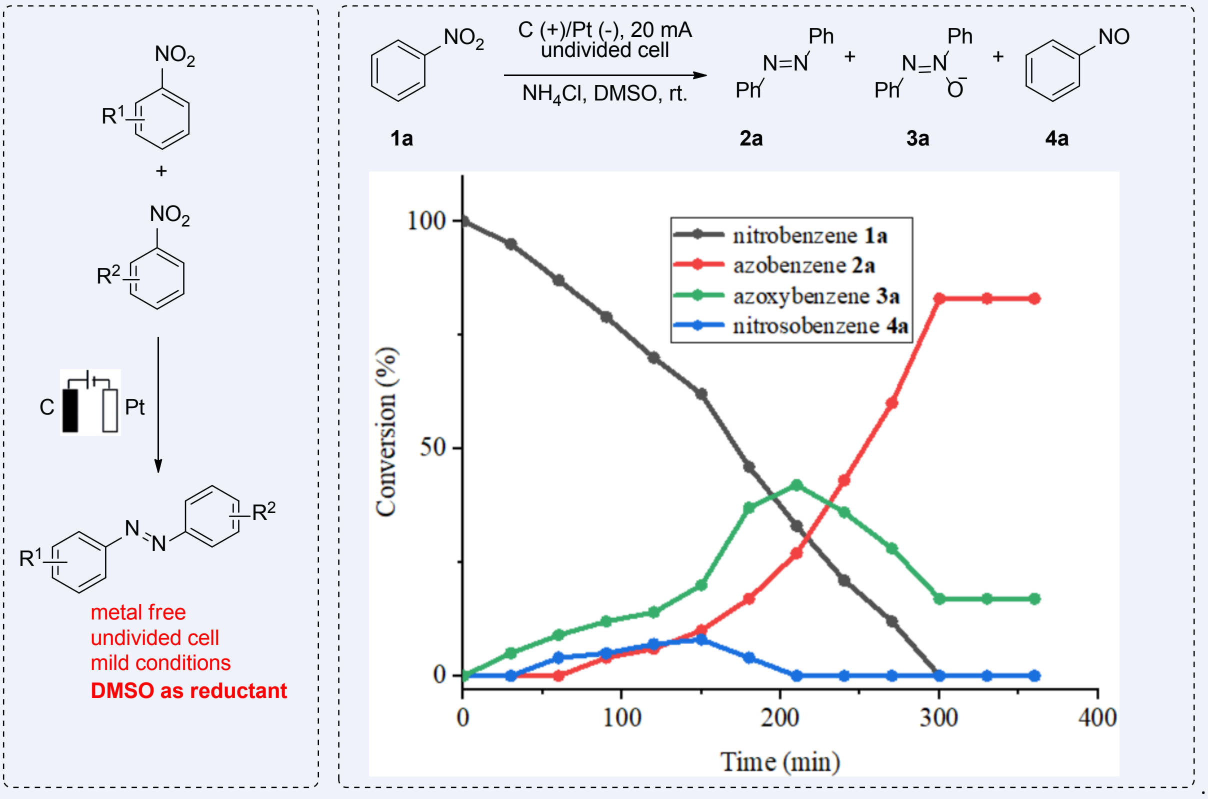
Keywords

Azo compounds | Nitro reduction | Electrochemistry | Nitrobenzenes

Main observation and conclusion

The electrochemical reduction strategy of nitrobenzenes is developed. The chemistry occurs under ambient conditions. The protocol uses inert electrodes and the solvent, DMSO, plays a dual role as a reducing agent. Its synthetic value has been demonstrated by the highly efficient synthesis of symmetric, unsymmetric and cyclic azo compounds.

Comprehensive Graphic Content



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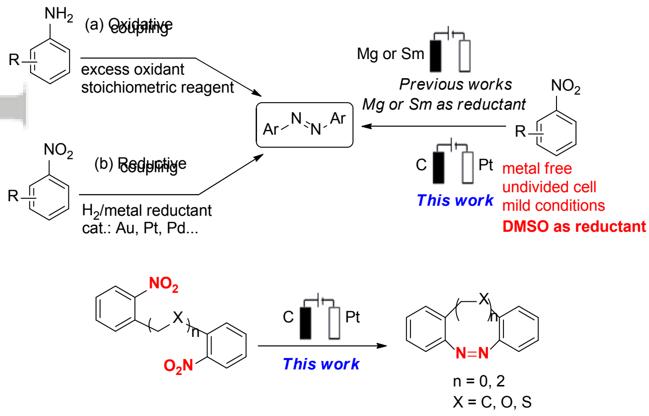
Background and Originality Content

Azobenzene derivatives are an important class of molecules, which are widely used in dyestuffs, colourants, photoresponsive materials, and therapeutic drugs.[1] Recently, due to the strong coordination ability of nitrogen atom, many chemists utilized the azo group as a directing group for *ortho* C-H functionalization.[2] Accordingly, all sorts of preparation methods for the synthesis of these compounds have been developed. The traditional synthetic method is primarily based on coupling of aryl diazonium salts with nucleophiles.[3] Yet this method requires preparation of reactive diazonium salts by oxidation of the corresponding aromatic amines with nitrous acid. Due to the electrophilic substitution mechanism, this kind of reaction is limited to the combination of electron rich and electron deficient aromatic substrates. Significant progress has been achieved by employing direct dehydrogenation of aromatic anilines or diarylhydrazines (Scheme 1 a).[4] Yet these methods suffer from major issues such as using excessive additives and oxidants or hard preparation of starting materials. The direct dehydrogenation of diaryl hydrazines with the liberation of molecular hydrogen would be an alternative method for preparing aromatic azo compounds. [5]

Nitroarenes are easily accessible and stable compounds, and can be converted into functionalized amines by reduction reaction.[6] In this regard, our group demonstrated a series of protocols by direct amination of nitroarenes to form corresponding amines or *N*-containing heterocycles.[7] Likewise, preparation of azobenzenes through a reduction of nitrobenzenes with reducing reagents is highly attractive (Scheme 1, b).[8] But this approach is limited to operations that require stoichiometric amounts of metal reductant or high-pressure hydrogen as a reducing reagent. For example, Guo and coworkers reported a Cu/graphene photocatalytic reduction coupling reactions of aromatic nitro compounds to corresponding azo compounds. [9]

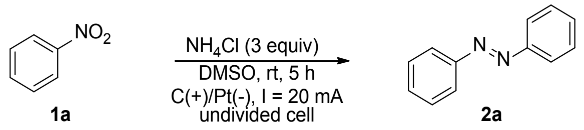
Scheme 1. Previous reports on catalytic approaches to the synthesis of azobenzene derivatives.



Electrochemical synthetic methods have been considered as a green and viable synthetic tool since it employs electrons as reagents to avoid waste production.[10] The nitroaryl electroreduction has attracted considerable attention over the past decade, especially for the synthesis of anilines.[11] To date, very few examples have been reported on the use of electrochemistry to synthesize azobenzenes from nitroarenes. In 2006, Kim and co-workers employed magnesium electrodes for the direct reduction of nitrobenzenes to synthesize azobenzenes.[12] Noteworthy, this reaction suffers from the use of a sacrificial Mg electrode and narrow substrate scope. In 2017, Mellah carried out the same reaction, using stoichiometric Sm as a reagent that was electrogenerated from Sm anode.[13] As part of our continuing efforts in molecular synthesis using nitroarenes as the readily available coupling partners, herein, we report an environment-friendly and efficient electrochemical strategy for the reductive coupling of nitroarenes into azobenzenes under mild reaction conditions. Notably, this method uses inert electrodes while the solvent, DMSO, plays a dual role as a reducing agent, therefore, providing a green synthetic approach for azobenzene derivatives.

Results and Discussion

Table 1 Optimization of the reaction condition^a.



Entry	Variation from the standard reaction conditions	Yield^b (%)
1	none	76
2	NH_4Br instead of NH_4Cl	20
3	NH_4OAc instead of NH_4Cl	25
4	TBAB instead of NH_4Cl	n.r.
5	$^nBu_4NBF_4$ instead of NH_4Cl	40
6	DMF instead of DMSO	trace
7	EtOH instead of DMSO	trace
8	Pt as anode	38
9	10 mA instead of 20 mA, 10 h	trace
10	25 mA instead of 20 mA, 4 h	51
11	no NH_4Cl	n.r.
12	no electric current DMSO	n.r.

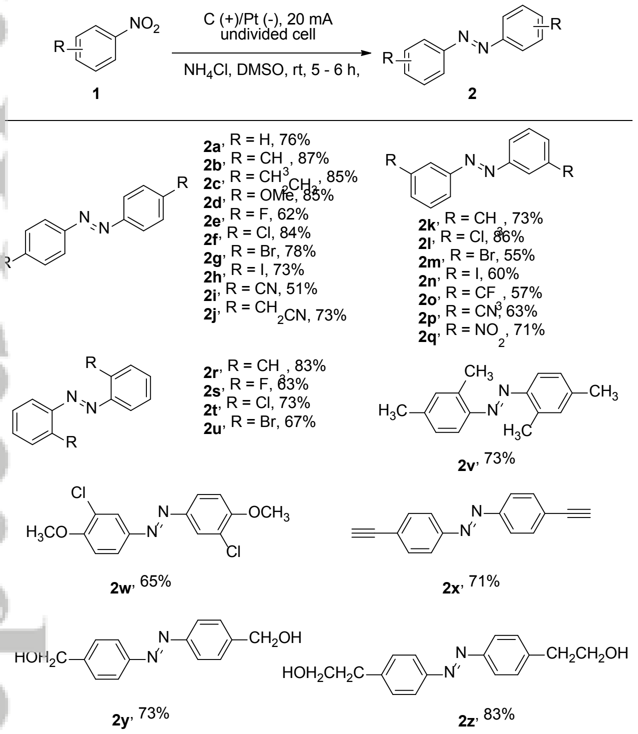
^{a}Reaction conditions: anode: graphite rod (6 mm) and cathode: Pt foil (1.0 x 1.0 cm^2), constant current = 20 mA, **1a** (0.5 mmol), NH_4Cl (1.5 mmol), DMSO (8 mL) in an undivided cell, rt, air, 5 h. ^{b} Isolated yield based on **1a**

We primary chose nitrobenzene **1a** as the substrate for reductive homodimerization with carbon/platinum electrodes and NH_4Cl electrolyte to determine the optimized conditions. Nitrobenzene **1a** reacted efficiently in an undivided cell with 20 mA for 5 h, azobenzene **2a** was synthesized in 76% isolated yield (Table 1, entry 1). Then we investigated the influence of electrolytes such as NH_4Br, NH_4OAc, TBAB (*n*-Bu_4NBr) or *n*-Bu_4NBF_4, it was found to be ineffective for this electrochemical reduction reaction (Table 1, entries 2-5). The employment of other media such as DMF and EtOH also failed to give acceptable yield of azobenzene **2a**, which indicates DMSO may play roles more than solvent (Table 1, entries 6-7). During the optimization process, (methylsulfonyl) methane was detected by GC-MS when utilizing DMSO. When a reticulated Pt was used as the anode, the yield of azo product **2a** was dramatically decreased (Table 1, entry 8). Either lower (10 mA) or higher (25 mA) constant current (compared to 20 mA) leads to lower yields (Table 1, entries 9-10). We did not observe azo product **2a** when the reaction was carried out in the absence of current or electrolyte (Table 1, entries 11-12).

Under the optimized conditions, we investigated various aromatic nitro compounds for this reductive homocoupling reaction (Scheme 2). A 76% isolated yield of azo product **2a** was achieved using nitrobenzene (**1a**) as model substrate. Electron-rich aromatic nitro compounds, such as methyl, ethyl and methoxy groups in the *para* position, reacted smoothly to furnish the corresponding azo products **2b-2d** in excellent yields. Halo-substituted nitrobenzenes (**1e-1h**) could also be used. It should be noted that the use of 4-iodo-nitrobenzene **1h** gave access to product **2h** in 73%

yield and C–I bond is suitable for this reaction system. An isolated yield was reduced to 51% using 4-nitrobenzonitrile (**1i**) as the reactant. Interestingly, steric factors do not seem to play a role, whether the substituents were at ortho or *meta* position. For example, *p*-methylnitrobenzene (**1b**), *m*-methylnitrobenzene (**1k**), *o*-methylnitrobenzene (**1r**) proceeded smoothly to give the corresponding azo products in 73–87% yields. Nitrobenzenes with two functional groups also reacted well giving the aromatic azo products in good yields (**2v** and **2w**). It is noteworthy that the ethynyl group is well tolerated under this reaction condition, and the ethynyl-substituted aromatic azo compounds **2x** could be used for further Sonogashira coupling or addition reactions. In this reaction, sensitive and active hydroxy group substituent on benzene ring was well tolerated, yielding azobenzene products (**2y** and **2z**) in good yields.

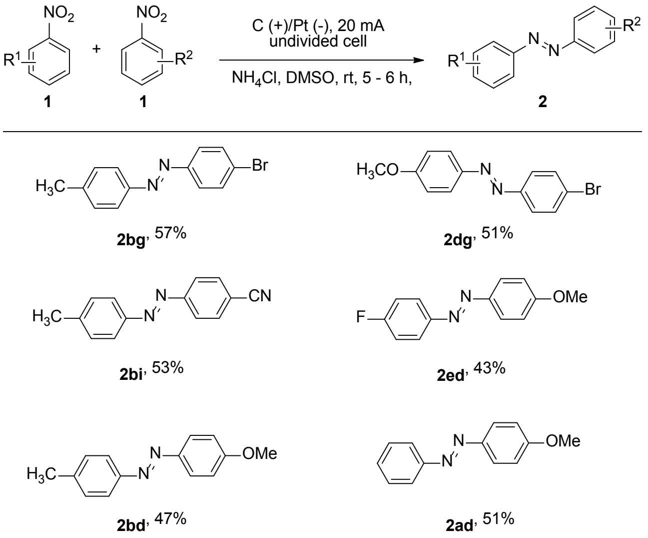
Scheme 2 Symmetric aromatic azo compounds under standard conditions^{a}.



^{a} Reaction conditions: anode: graphite rod (6 mm) and cathode: Pt foil (1.0 x 1.0 cm^2), constant current = 20 mA, **1a** (0.5 mmol), NH_4Cl (1.5 mmol), DMSO (8 mL) in an undivided cell, rt, air, 5 h. ^{b} Isolated yield based on **1a.**

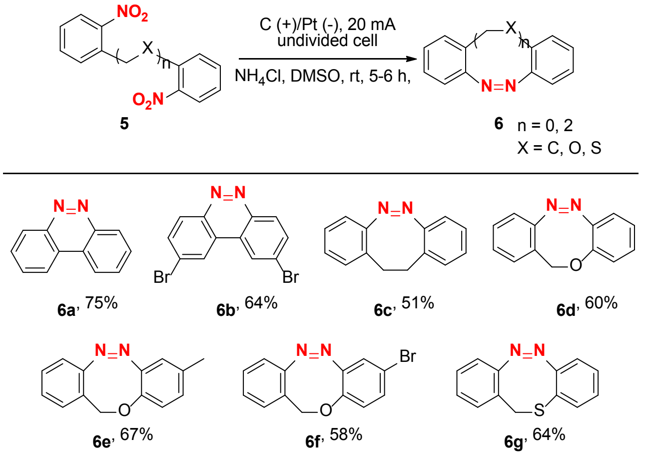
Next, the formation of unsymmetric aromatic azo compounds were also explored (Scheme 3). Unsymmetric azo product **2bg** as a major product was selectively achieved in 57% yield when *p*-methylnitrobenzene (**1b**) was reacted with equimolar amount of 4-bromonitrobenzene (**1g**). Similar yield was obtained when 4-methoxyaniline (**1d**) was treated with 4-bromoaniline (**1g**). This heterocoupling approach is also applicable for the synthesis of push-pull-type azobenzenes **2bi** and **2ed** in moderate yields. The cross-dimerization reactions of an electron-rich *p*-methoxy nitrobenzene (**1d**) with *p*-methylnitrobenzene (**1b**) and nitrobenzene (1a) also lead to give unsymmetric azobenzenes **2bd** and **2ad** in 47% and 51% yield, respectively.

Scheme 3. Unsymmetrically substituted Azo Compound preparation under Standard conditions.



Reaction conditions: anode: graphite rod (6 mm) and cathode: Pt foil (1.0 x 1.0 cm^2), constant current = 20 mA, **1** (0.25 mmol), NH_4Cl (1.5 mmol), DMSO (8 mL) in an undivided cell, rt, air, 5-6 h. Isolated yields.

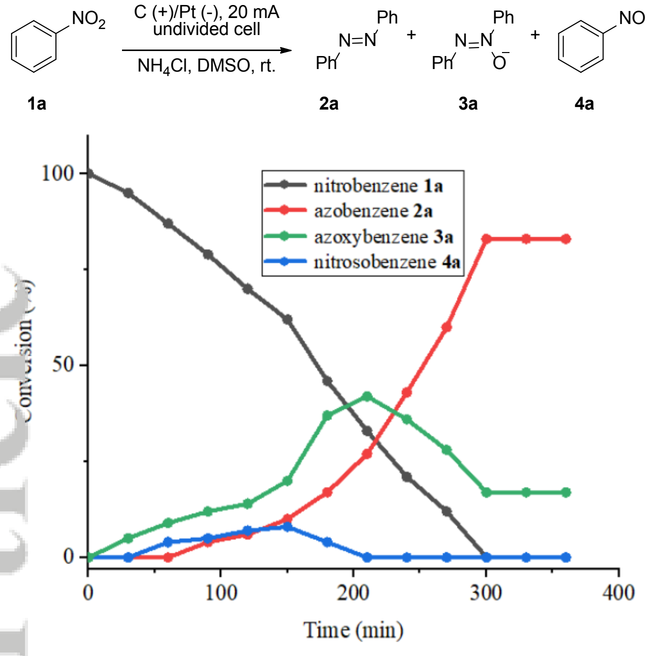
Scheme 4. Control experiments under various conditions.



Reaction conditions: anode: graphite rod (6 mm) and cathode: Pt foil (1.0 x 1.0 cm^2), constant current = 20 mA, **5** (0.5 mmol), NH_4Cl (1.5 mmol), DMSO (8 mL) in an undivided cell, rt, air, 5-6 h. Isolated yields.

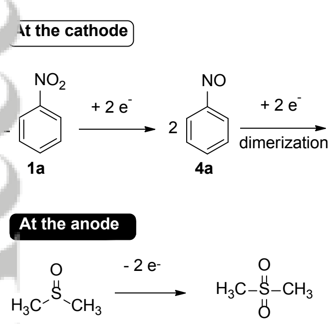
Furthermore, the treatment of 2,2'-dinitro-1,1'-biphenyl (**5a**) gave intramolecular cyclization product (**6a**) in 75% yield. The target product (**6b**) can be obtained when using 4,4'-dibromo-2,2'-dinitro-1,1'-biphenyl. It is noteworthy that eight membered ring product 6c was obtained when using 1,2-bis(2-nitrophenyl)ethane (**5c**). Other eight membered ring products **6d-6g** can also be obtained in moderate yields (Scheme 4). We also conducted cyclic voltammetry (CV) experiments (see Supporting Information, Fig S3). The reductive peak of **1b** was recorded at -1.143 V vs SCE and **5a** at -1.280 V vs SCE in ethanol.

Scheme 5. Time-conversion plot for the catalytic reduction of nitrobenzene into azobenzene.



In order to better understand this potential reaction pathway, we then carried out reaction time tracking experiment of nitrobenzene (**1a**) conversion to azobenzene (**2a**) through gas chromatography (GC) analysis (Scheme 5). In the early stage of electrochemical reduction coupling reaction, the concentration of raw material nitrobenzene (**1a**) decreased continuously, while the concentration of azo product azobenzene (**2a**), intermediate product azoxybenzene (**3a**) and nitrosobenzene (**4a**) increased slowly. Meanwhile, the highest conversion of nitrobenzene (**4a**) was 8% in 150 min, and then it was completely converted after 210 min. At the same time, the intermediate product azoxybenzene (**3a**) reached a threshold of 42% conversion, and then the concentration decreased to 18%. The evolution of the concentration of azoxybenzene (**3a**) and nitrosobenzene (**4a**) suggests a reaction pathway, in which the nitroaromatic compound is initially reduced to nitrosobenzene (**4a**), which quickly dimerize to form azoxybenzene (**3a**), and finally to the corresponding azobenzene (**2a**).

Scheme 6. Possible reaction pathway.



On the basis of our experimental results and precedent reports, a possible mechanism for this reaction is proposed, as depicted in Scheme 6. Reduction of nitrobenzene (**1a**) at cathode could generate a nitrosobenzene (**4a**) intermediately, and then the dimerization was occurred quickly to form azoxybenzene (**3a**), followed by a further reduction to generate target product azobenzene (**2a**). At the anode, the solvent DMSO was oxidized to give (methylsulfonyl)methane, which was detected by GC-MS.

Conclusions

In summary, we demonstrated an efficient and low energy-consuming electrochemical reduction procedure for nitro to construct a N=N double bond under mild reaction conditions. This protocol was carried out under ambient conditions in DMSO and provided a straightforward route for the synthesis of symmetric, unsymmetric and cyclic azo compounds.

Experimental

General procedure for the electrochemical reaction

In an undivided three-necked flask (25 mL), 4-methylnitrobenzene (0.5 mmol, 69 mg), NH$_4$Cl (1.5 mmol, 81 mg) and DMSO (8 mL) were continuously added. The flask was equipped with platinum plate electrode (1.0×1.0 cm^2) as the cathode and graphite rod (Φ = 6 mm) as the anode. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under air at room temperature for 5 h. After the reaction was complete, the mixture was diluted with water (30 mL) and then extracted by EtOAc (10 mL×3). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, filtered, concentrated in vacuo and the crude product was obtained. The pure product was obtained by silica gel chromatography using petroleum ether/ ethyl acetate (100:1) as eluent.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2021xxxxx.

Acknowledgement

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Electrosynthesis of azobenzenes directly from nitrobenzenes

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