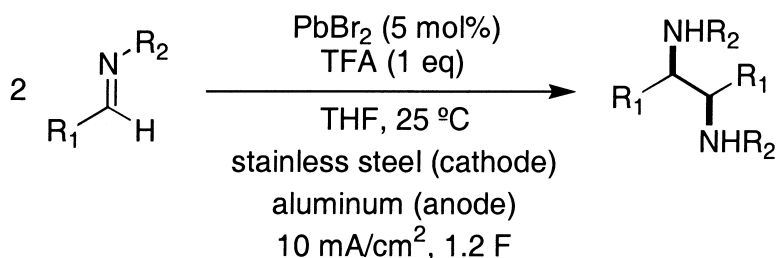


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Parallel Electrosynthesis of 1,2-Diamines

Tung Siu, Wei Li, and Andrei K. Yudin*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

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Parallel reductive hydrocoupling of aldimines was performed to generate vicinal diamines using the spatially addressable electrolysis platform (SAEP). The stainless steel cathodes and sacrificial aluminum anodes were used in this electrosynthesis methodology. Introducing a large substituent on the imino nitrogen atom efficiently controls stereoselectivity of the electroreductive coupling process. This method can now be applied to the generation of libraries of 1,2-diamines, which further expands the techniques of parallel synthesis and combinatorial electrochemistry.

Vicinal diamine functionality is found in many compounds of biological significance.^{1,2} For instance, 1,2-diamines are the key intermediates in the synthesis of bis-thioacetamido chelating agents for ^{99m}Tc, which have found extensive applications as radiopharmaceuticals.³ Biotin (or vitamin H), an essential cofactor in carboxylase-catalyzed reactions, contains the 1,2-diamine moiety.^{4,5} Vicinal diamines have also been used as ligands and chiral auxiliaries in various asymmetric processes⁶ including olefin dihydroxylation⁷ and epoxidation,⁸ Diels–Alder⁹ reactions, aldol¹⁰ condensations, alkylation of aldehydes,¹¹ and cyclopropanation of allylic alcohols.¹²

A number of methods for the preparation of diamines have been developed. These include substitution of β -amino alcohol derivatives¹³ and ring-opening of aziridines¹⁴ or aziridinium ions¹⁵ with nitrogen nucleophiles. Reductive coupling of imines offers an attractive possibility to access a wide range of diamines. A variety of reductants have been used for this purpose, viz., samarium(II) iodide,¹⁶ indium,¹⁷ Pb/Al bimetallic redox system,¹⁸ Zn–Cu couple,¹⁹ niobium(IV) chloride,²⁰ low-valent titanium (LVT),²¹ and cathodic coupling.²² To the best of our knowledge, none of these processes have been extended to parallel synthesis of diamine libraries. This is due to the fact that, with the exception of electrochemistry, most of these techniques involve strong reducing agents, making them impractical in a high-throughput format. Parallel electrochemical reduction of imines may provide a valuable addition to the rapidly expanding repertoire of high-throughput processes.²³ A recent contribution from our laboratory describes the design and applications of the spatially addressable electrolysis platform (SAEP)²⁴ for parallel electrosynthesis. Thus, libraries of α -alkoxycarbamates, α -alkoxyamides, and α -alkoxysulfonamides have been prepared using anodic oxidation in the SAEP format. A multicell electrolysis platform was used for this purpose. We recently extended combinatorial electrochemistry to parallel electrochemical generation of arrays

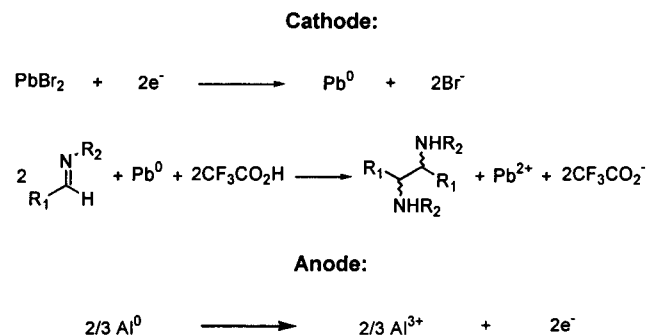
of conducting copolymer film catalysts.²⁵ Here, we demonstrate the application of the SAEP to the parallel generation of vicinal diamines by cathodic hydrocoupling of imines.

The electroreductive hydrocoupling of imines was first reported by Law in 1912.²⁶ The yields of the vicinal diamines were in the 4–26% range. A copper cathode and divided cell setup were required in order to avoid anodic oxidation of the cathodically generated species. A more efficient procedure for the hydrocoupling of imines, developed by Torii in 1989,²² was based on an undivided cell setup and offered moderate to good yields (56–80%). The electrolysis was performed with a Pt/Pt electrode pair in the presence of TFA. The trifluoroacetate anion was decarboxylated at the anode, thereby preventing reoxidation of the cathodically generated intermediates.

Our goals were to extend parallel electrosynthesis methodology to vicinal diamine synthesis and to optimize electrolysis conditions using the SAEP. In the first trial, we followed the literature procedure²² for the electroreductive hydrocoupling of imine **1** in THF (5 mol % PbBr₂, 1 equiv of TFA, and 0.1 M Bu₄NBr) with platinum electrodes under galvanostatic conditions. However, no diamine product was detected while aniline and benzaldehyde were recovered at the end of reaction. This failure is due to the extremely low current, a result of passivation of the counter electrode (platinum anode) by anodic polymerization of aniline, resulting from hydrolysis of the imine **1**, on the electrode surface. In the literature procedure,²² *N*-benzylimines were used and the hydrolyzed products were not oxidized as easily as trifluoroacetate at the anode.

We then resorted to a sacrificial anode method²⁷ in order to maintain high current density and to prevent the undesired anodic side reactions (Scheme 1). For the platinum/aluminum electrode pair, we obtained the diamine product from imine **1** in 40–50% yield. The current density was maintained at the set value (10 mA/cm²) at the beginning of reaction but gradually dropped toward the end. At the end of the process, a polyaniline film was deposited on the surface of the aluminum anode. To prevent the imine hydrolysis, 4 Å molecular sieves were added to the reaction mixture.

* To whom correspondence should be addressed. E-mail: ayudin@chem.utoronto.ca.

Scheme 1. Electroreductive Hydrocoupling of Imines

Fortunately, the current density was maintained under these conditions at the set value of 10 mA/cm² throughout the electrolysis, leading to a higher isolated yield of the diamine (>70%). TFA was used as a proton source. Other acids were tried but gave unsatisfactory results.

The success of electrochemical reactions crucially depends on the nature of electrodes used.²⁸ With the goal of applying the coupling methodology in a parallel setting, we explored materials less expensive than platinum. We chose stainless steel electrodes and were pleased to find results comparable to results with platinum electrodes. Optimized reaction conditions correspond to a current density of 10 mA/cm², a temperature of 25 °C, a 0.2 M imine concentration, and a total charge of 1.2 F. Under these conditions, the parallel electroreduction of a collection of up to 16 diamines (4 mmol scale) can be completed in 30 min. A common shortcoming of the conventional chemical dimerization of imines using active metals is formation of amines as a result of competitive unimolecular reduction of imines. In our system, the amount of reduced product is less than 5%. One of the reasons for the suppressed unimolecular reduction pathway is the low working potential due to the sacrificial nature of the anode that offers a high degree of selectivity.

Parallel electroreduction results for substrates **1–9** are shown in Table 1. Although imine **1** gave a poor *dl/meso* ratio, in the cases of more sterically demanding benzhydrylbenzylidene amines **2–6**, the *dl* isomers (determined by NMR) of the corresponding vicinal diamines were formed exclusively.²⁹ For the nitro-substituted imines **7** and **8** and *N*-tosylated imine **9**, no diamine products were detected. A cyclic voltammetry (CV) study of substrate **7** shows a reversible redox couple at -1.20 V (vs Ag/AgCl), while the CV of substrate **2** displays an irreversible reduction wave at -1.35 V (vs Ag/AgCl). Apparently, the nitro group is reduced first under these conditions while the imine function remains intact. Since the reduction of the nitro group is reversible, the reduced compound may migrate to the anode and be reoxidized to regenerate the starting material, which was recovered at the end of electrolysis. The reason the tosylated imine does not dimerize under these conditions is most probably due to the reductive cleavage of the S–N bond.³⁰ For ketimines, electrochemical reduction did not proceed to give the desired coupled products. Aliphatic aldimines are also beyond the scope of this process. We have also explored the possibility of one-step electroreduction of 1,2-diamines through in situ generation of the aldimine precursors. For substrates **1–6**, the one-step parallel elec-

troreduction gave results comparable (listed in Table 1) to results from the two-step method.

In summary, a new technique for parallel electroreduction of vicinal diamines has been developed. Screening of reaction conditions enabled us to perform highly diastereoselective parallel synthesis of diamines using inexpensive stainless steel as cathode and sacrificial aluminum as anode. By introduction of a large substituent group on the imino nitrogen atom, the stereochemistry of diamines can be efficiently controlled.

Experimental Section

General. Aniline, benzhydrylamine, *p*-toluenesulfonamide, benzaldehyde, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, 2-fluorobenzaldehyde, 4-cyanobenzaldehyde, 3-nitrobenzaldehyde, and 4-nitrobenzaldehyde were purchased from Aldrich Chemical Co. Stainless steel (type 304) and aluminum (99+%) electrode materials were purchased from Alfa Aesar. Column chromatography was carried out using 230–400 mesh silica gel. ¹H NMR spectra were referenced to residual CHCl₃ (δ 7.26 ppm), and ¹³C spectra were referenced to CDCl₃ (δ 77.2 ppm). Cyclic voltammetry was conducted on a BAS CV-50W voltammetric analyzer (Bioanalytical Systems, Inc.) equipped with a BAS C3 three-electrode cell stand.

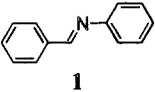
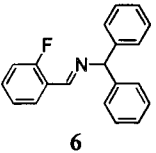
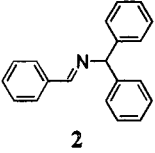
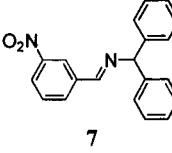
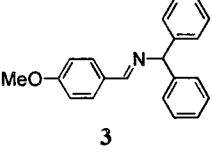
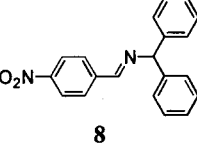
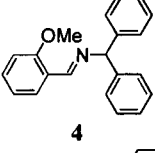
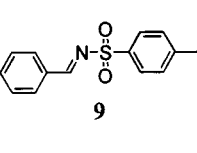
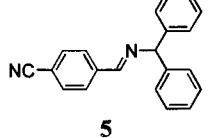
General Procedure for Aldimine Synthesis. Equal molar amounts of aldehyde and amine were mixed in diethyl ether, and MgSO₄ was added. The mixture was stirred for 1 h at room temperature followed by filtration of MgSO₄. The filtrate was concentrated in vacuo, and the crude product was recrystallized from absolute ethanol.

General Procedure for Diamine Synthesis. Parallel electroreduction was conducted using the spatially addressable electrolysis platform (SAEP) (see ref 24 for a detailed description of the instrument). Tubular stainless steel cathodes (7.5 cm² surface area) were used. The electrolyte solution in each 20 mL cell contained the substrate (0.2 M), TFA (0.2 M), PbBr₂ (0.01 M), tetrabutylammonium bromide (Bu₄N⁺Br⁻) as supporting electrolyte (0.1 M), and dry THF as solvent. The SAEP was submerged in a water bath to maintain a temperature of 30 °C. Electrolysis was carried out at constant current until 1.2 F was passed through each cell. After electrolysis, the solvent was evaporated, 5 mL of 5% aqueous HCl was added, and the resulting mixture was stirred for 10 min. Subsequently, 5 mL of 10% aqueous NaOH was added and the solution was extracted with ether (10 mL × 3). The organic phases were combined and dried over MgSO₄. The solvent was evaporated, and the residue was flash-chromatographed on a silica gel column with 1:9 ethyl acetate/hexanes as eluent.

General Procedure for One-Step Diamine Electroreduction. Equal molar amounts of aldehyde and amine were mixed in dry THF, and MgSO₄ was added to the 20 mL electrolysis cell. The mixture was stirred for 1 h at room temperature followed by addition of TFA (0.2 M), PbBr₂ (0.01 M), and tetrabutylammonium bromide (Bu₄N⁺Br⁻) as supporting electrolyte (0.1 M). The electrolysis and product isolation were performed as described above.

***N*-Benzylidene aniline (1):** ¹H NMR δ 6.5–7.5 (m, 10H), 8.45 (s, 1H).

Table 1. Parallel Electrosynthesis of 1,2-Diamines from Imines

Substrate	Isolated yield of diamine, %	<i>dl:meso</i>	Substrate	Isolated yield of diamine, %	<i>Dl:meso</i>
	77 70 ^a	60:40		67 65 ^a	>99:1
	65 60 ^a	>99:1		NR ^b	--
	57 55 ^a	>99:1		NR ^b	--
	60 62 ^a	>99:1		NR	--
	62 62 ^a	>99:1			

^a Isolated yield for one-step parallel electrosynthesis. ^b 80% of starting material was recovered.

1,2,*N,N'*-Tetraphenylethane-1,2-diamine (mixture of *dl* and *meso* isomers): ¹H NMR δ 4.55 (bs, *dl* + *meso* NH and *dl* NCH), 4.96 (d, $J = 12$ Hz, *meso* NCH), 6.5–7.5 (m, 20H).

Benzhydrylbenzylidene amine (2): ¹H NMR δ 5.62 (s, 1H), 7.2–7.9 (m, 15H), 8.45 (s, 1H). ¹³C NMR δ 78.03, 127.09, 127.81, 128.54, 128.59, 128.64, 130.86, 144.04, 160.89. Mp 94.5–95.0 °C (lit.³¹ 95 °C).

***N,N'*-Dibenzhydryl-1,2-diphenylethane-1,2-diamine:** ¹H NMR δ 2.01 (bs, 2H), 3.66 (s, 2H), 4.42 (s, 2H), 6.7–7.4 (m, 30H). ¹³C NMR δ 63.19, 65.36, 127.32, 127.95, 128.24, 128.43, 128.80, 141.20, 143.15, 144.67. Mp 164–165 °C (lit.³² 162–163 °C).

Benzhydryl-(4-methoxybenzylidene) amine (3): ¹H NMR δ 3.86 (s, 3H), 5.62 (s, 1H), 6.96 (d, $J = 8.7$ Hz, 2H), 7.2–7.5 (m, 10H), 7.84 (d, $J = 8.7$ Hz, 2H), 8.40 (s, 1H). ¹³C NMR δ 55.45, 77.90, 114.04, 126.99, 127.82, 128.49, 130.12, 144.25, 160.16, 161.86. Mp 106–107 °C (lit.³¹ 104–107 °C).

***N,N'*-Dibenzhydryl-1,2-bis(4-methoxyphenyl)ethane-1,2-diamine:** ¹H NMR δ 3.62 (s, 2H), 3.78 (s, 6H), 3.88 (s, 2H), 4.60 (s, 2H), 6.6–7.4 (m, 28H). ¹³C NMR δ 55.27, 63.40, 65.38, 113.44, 127.34, 127.99, 128.38, 129.24, 133.22, 143.64, 145.15, 158.57. Mp 174–175 °C (lit.³² 174–175 °C).

Benzhydryl-(2-methoxybenzylidene) amine (4): ¹H NMR δ 3.88 (s, 3H), 5.67 (s, 1H), 6.9–8.3 (m, 14H), 8.99 (s, 1H). ¹³C NMR δ 55.57, 78.58, 111.07, 120.83, 124.93, 126.93, 127.79, 127.87, 128.47, 132.05, 144.40, 156.77, 159.00. Mp 97.2–98.6 °C (lit.³³ 99 °C).

***N,N'*-Dibenzhydryl-1,2-bis(2-methoxyphenyl)ethane-1,2-diamine:** ¹H NMR δ 2.4 (b, 2H), 3.38 (s, 2H), 3.43 (s, 6H), 4.51 (s, 2H), 6.6–7.4 (m, 28H). ¹³C NMR δ 55.11, 63.98, 64.03, 110.45, 126.54, 127.26, 127.62, 127.98, 128.08, 128.18, 144.24, 145.55, 158.69. HRMS ($M - H$)⁺: 603.3035 (calcd mass 603.3012, C₄₂H₃₉N₂O₂). Mp 133–134 °C.

4-Benzhydryliminomethyl benzonitrile (5): ¹H NMR δ 5.66 (s, 1H), 7.2–8.0 (m, 14H), 8.45 (s, 1H). ¹³C NMR δ 78.16, 114.21, 118.623, 127.39, 127.71, 128.70, 128.98, 132.50, 143.40, 159.06. Mp 117–118 °C.

***N,N'*-Dibenzhydryl-1,2-bis(4-cyanophenyl)ethane-1,2-diamine:** ¹H NMR δ 2.0 (b, 2H), 3.75 (s, 2H), 4.35 (s, 2H), 6.8–7.6 (m, 28H). ¹³C NMR δ 63.49, 64.71, 111.82, 127.04, 127.63, 128.70, 129.19, 132.25, 142.32, 143.44, 146.26. HRMS ($M + H$)⁺: 595.2835 (calcd mass 595.2862, C₄₂H₃₅N₄). Mp 202–203 °C.

Benzhydryl-(2-fluorobenzylidene) amine (6): ¹H NMR δ 5.65 (s, 1H), 6.9–8.3 (m, 14H), 8.79 (s, 1H). ¹³C NMR δ 78.53, 115.79, 124.41, 127.17, 127.76, 128.24, 128.29, 128.59, 132.44, 154.19, 160.01, 165.03. Mp 94.5–96.0 °C.

***N,N'*-Dibenzhydryl-1,2-bis(2-fluorophenyl)ethane-1,2-diamine:** ¹H NMR δ 2.1 (b, 2H), 4.12 (s, 6H), 4.49 (s, 2H), 6.9–7.4 (m, 28H). ¹³C NMR δ 64.05, 115.12, 115.57, 124.09, 126.98, 127.13, 127.79, 128.40, 128.62, 128.81, 143.23, 144.68. HRMS ($M - H$)⁺: 579.2633 (calcd mass 579.2612, C₄₀H₃₃F₂N₂). Mp 169–170 °C.

Benzhydryl-(3-nitrobenzylidene) amine (7): ¹H NMR δ 5.68 (s, 1H), 7.2–8.3 (m, 13H), 8.50 (s, 1H), 8.68 (s, 1H).

^{13}C NMR δ 78.06, 123.29, 125.32, 127.40, 127.74, 128.71, 129.70, 134.04, 138.11, 143.40, 158.39. HRMS: 316.1211 (calcd mass 316.1212, $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$). Mp 136–137 °C.

Benzhydryl-(4-nitrobenzylidene) amine (8): ^1H NMR δ 5.68 (s, 1H), 7.2–7.5 (m, 10H), 8.01 (d, $J = 8.8$ Hz, 2H), 8.28 (d, $J = 8.8$ Hz, 2H), 8.51 (s, 1H). ^{13}C NMR δ 78.25, 123.96, 127.44, 127.74, 127.82, 128.68, 128.73, 129.25, 143.34, 158.66. Mp 135–136 °C (lit.³¹ 134–135 °C).

N-Benzylidene-toluene-4-sulfonamide (9): ^1H NMR δ 2.44 (s, 3H), 7.2–8.0 (m, 9H), 9.03 (s, 1H). ^{13}C NMR δ 21.76, 126.63, 128.24, 129.27, 129.93, 131.42, 132.61, 135.02, 144.70, 170.23. Mp 108–109 °C (lit.³⁴ 109–110 °C).

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