

Electrochemical Debromination of 1-Aryl-1,2-dibromo-2-nitropropanes in Dimethyl Sulfoxide

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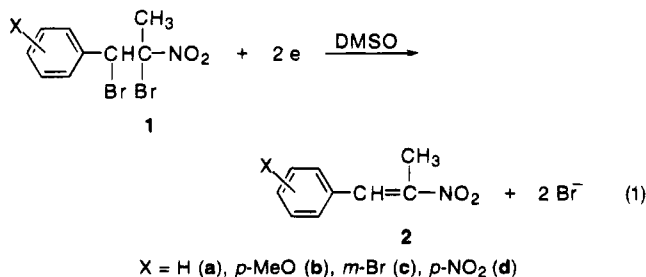
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Electrochemical debromination reactions of *erythro*-dl-1-aryl-1,2-dibromo-2-nitropropanes **1a–d** at a platinum electrode have been investigated by cyclic voltammetry in 0.10 M LiClO₄/DMSO. The reactions produced (*E*)-1-aryl-2-nitropropenes **2a–d** in high yields. The cyclic voltammograms were irreversible and the reduction current decreased as the number of cycles increased. The peak potential for the reductions waves are in the range of –0.51 to –0.56 V (vs Ag/Ag⁺) and show no clear trend with different aryl substituent. The current density increased as the concentration of the substrate increased. The slopes of the plots of log(*I*/*A*) vs log[*C*] are close to unity, indicating unimolecular processes. For all reactions, the Tafel slopes are in the range of 115–125 mV. The logarithm of the ratio *i*_X/*i*_H at –0.16 V did not correlate with the Hammett substituent constants. From these results, the mechanism of these reactions is assessed.

Reductive dehalogenation of vicinal dihalides can be carried out with various reducing agents, such as phosphite, chromous compounds, and zinc.^{1–6} For activated dihalides with electron-withdrawing substituents, milder reducing agents can be utilized.⁷ Thus, if a sufficiently activated vicinal dihalide is reacted with a base with low oxidation potential, the dehalogenation reaction may proceed via a free radical intermediate. Very recently we have investigated the debromination reactions of 1-aryl-1,2-dibromo-2-nitropropanes under various conditions in an attempt to find the first example of elimination reactions that proceed via SET mechanism.^{8,9} However, when the reaction was conducted with 2-nitro-2-propyl anion in DMSO or secondary amines in MeCN, an ionic pathway predominated.⁸ In the accompanying paper, we report the detailed mechanism of debromination reactions of the same substrates promoted by secondary amines in MeCN.⁹

The most favorable condition for SET processes is an electrochemical reaction. The characteristics of SET debrominations should be revealed if the reactions were studied electrochemically. Accordingly, we have investigated the electrochemical debromination of *erythro*-dl-1-aryl-1,2-dibromo-2-nitropropanes **1a–d** at a platinum electrode in DMSO by cyclic voltammetry (eq 1).



Results

Cyclic voltammograms were obtained with Pt working and auxiliary electrodes and Ag/Ag⁺ reference electrode in DMSO containing 1.0 × 10^{–3} M **1a–d** and 0.10 M LiClO₄ at a scan rate of 20 mV s^{–1} between 0.3 V and –0.9 V. In all cases, the waves were irreversible and the reduction wave decreased as the number of cycles increased (plots not shown). The peak potentials at 20 mV s^{–1} are in the range of –0.51 to –0.56 V depending upon the aryl substituent (Table 1). The reduction potentials for 2-bromo-2-nitropropane, benzyl bromide, *p*-nitrobenzyl bromide, and nitrobenzene were also determined under similar conditions and are included in Table 1.

The products of the electrochemical reduction of **1b** and **1d** were identified by periodically monitoring the UV absorption of the reaction mixture under the electrochemical condition. Pt gauze (52 mesh) was used as the working electrode, and the peak potential was applied to facilitate the reaction. For both reactions, the UV spectra of the products were identical to those of 1-aryl-2-nitropropenes **2b** and **2d**, respectively. Yields of the debromination products were calculated by comparison of the UV absorption of the infinity samples from the electrochemical reaction with that for the authentic product. The yields are in the range of 80–85%. GC-MS of the isolated product from the electrochemical reaction of a more concentrated solution of **1a** indicated that the debromination product **2a** was the only product.

The peak currents and peak potentials for **1a–d** increased with increasing scan rate (Table 2). Plots of the peak current vs (scan rate)^{1/2} for the reactions of **1a–d** are depicted in Figure 1. They are straight lines for all reactions, indicating that the reaction rates are controlled by diffusion at the peak potential.¹⁰

Steady state current–potential curves were obtained from the cyclic voltammogram of the unstirred solution operated at 1 mV s^{–1}. Tafel plots for the reductions of

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Table 1. Reduction Potentials of Various Compounds in DMSO^{a,b}

compound	E_{pc} , V(vs Ag/Ag ⁺)
PhCH(Br)C(Br)(NO ₂)CH ₃	-0.55 ^c
<i>p</i> -CH ₃ OC ₆ H ₄ CH(Br)C(Br)(NO ₂)CH ₃	-0.55 ^c
<i>m</i> -BrC ₆ H ₄ CH(Br)C(Br)(NO ₂)CH ₃	-0.51 ^c
<i>p</i> -NO ₂ C ₆ H ₄ CH(Br)C(Br)(NO ₂)CH ₃	-0.56 ^c
PhCH ₂ Br	-0.86 ^d
<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Br	-0.86 ^d , -0.93 ^{d,e}
<i>p</i> -NO ₂ C ₆ H ₅	-0.91 ^d
(CH ₃) ₂ C(Br)(NO ₂)	-0.82 ^d

^a [Substrate] = 1.0×10^{-3} M. ^b [LiClO₄] = 0.10 M. ^c Scan rate = 20 mV s⁻¹. ^d Scan rate = 50 mV s⁻¹. ^e See text.

Table 2. Peak Current (I_{pc}) and Peak Potential (E_{pc})^a of 1-Aryl-1,2-dibromo-2-nitropropanes [XC₆H₄CH(Br)C(Br)(NO₂)CH₃]^b in DMSO at Various Scan Rate

scan rate (mV s ⁻¹)	X = H		X = <i>p</i> -CH ₃ O		X = <i>m</i> -Br		X = <i>p</i> -NO ₂	
	I_{pc} (mA)	E_{pc} (V)	I_{pc} (mA)	E_{pc} (V)	I_{pc} (mA)	E_{pc} (V)	I_{pc} (mA)	E_{pc} (V)
5	13.5	-0.44	7.9	-0.14	10.8	-0.31	9.9	-0.39
20	21.0	-0.48	13.5	-0.19	17.6	-0.41	16.3	-0.44
50	30.9	-0.51	20.1	-0.23	25.6	-0.46	23.0	-0.50
100	42.3	-0.54	28.2	-0.27	33.3	-0.50	29.4	-0.54
200	57.4	-0.56	38.3	-0.32	42.7	-0.54	37.5	-0.57

^a All potentials are cited against the Ag/Ag⁺ reference electrode.

^b [Substrate] = 1.0×10^{-3} M, [LiClO₄] = 0.10 M.

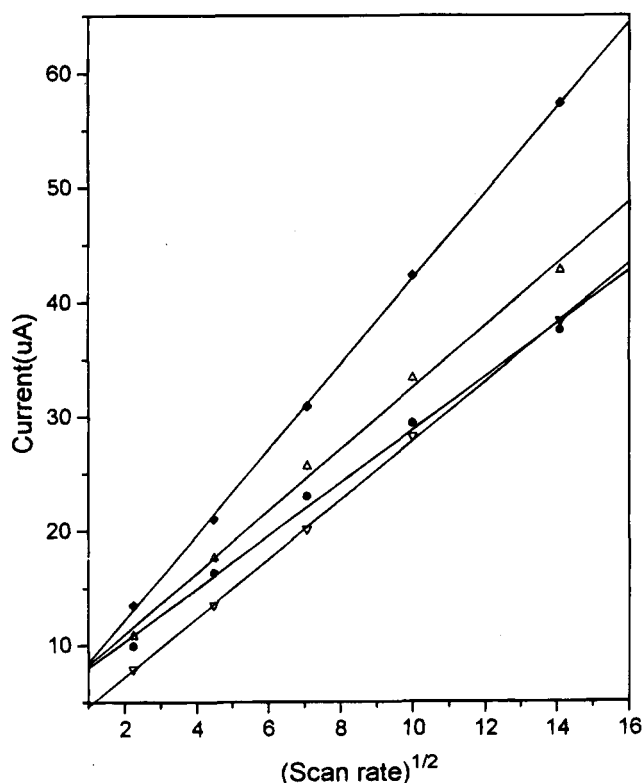


Figure 1. Plots of current vs (scan rate)^{1/2} for electrochemical reduction of XC₆H₄CH(Br)C(Br)(NO₂)CH₃ at peak potential. [X = H (◆), *p*-CH₃O (▽), *m*-Br (Δ), *p*-NO₂ (●)]. [Substrate] = 1.0×10^{-3} M, [LiClO₄] = 0.10 M.

1a–d are shown in Figure 2. The plots are linear at low potential and reach a plateau as the potential reaches a certain limit. The Tafel slopes calculated in the linear region are in the range of 115–125 mV.

Figure 3 shows the Tafel plots for 1c at various concentrations. The slopes are constant but the current density increases as the substrate concentration in-

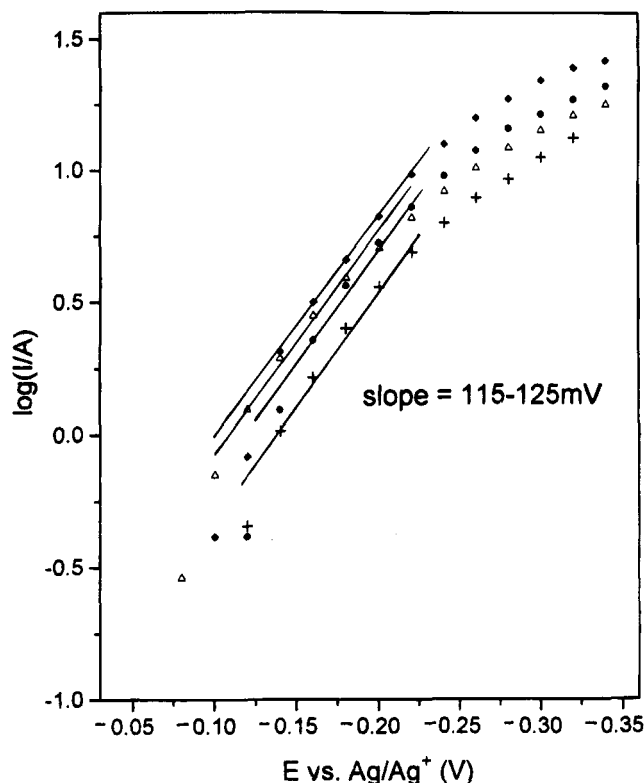


Figure 2. Tafel plots for reactions of XC₆H₄CH(Br)C(Br)(NO₂)CH₃ in unstirred solution. [X = H (◆), *p*-CH₃O (+), *m*-Br (●), *p*-NO₂ (Δ)]. [Substrate] = 1.0×10^{-3} M; [LiClO₄] = 0.10 M; scan rate = 1 mV s⁻¹.

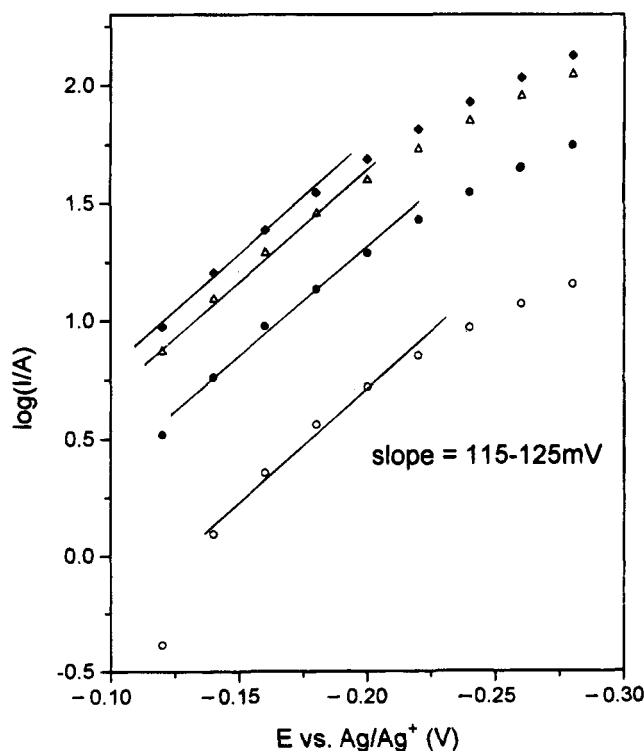


Figure 3. Tafel plots for reactions of *m*-BrC₆H₄CH(Br)C(Br)(NO₂)CH₃ at various concentration in unstirred solution [concn = 1.0×10^{-3} M (○), 5.1×10^{-3} M (●), 1.0×10^{-2} M (Δ), 1.4×10^{-2} M (◆)]. Scan rate = 1 mV s⁻¹.

creases, indicating that not only strongly adsorbed substrates but also those near the electrode surface participate in the reaction. Similar results were observed

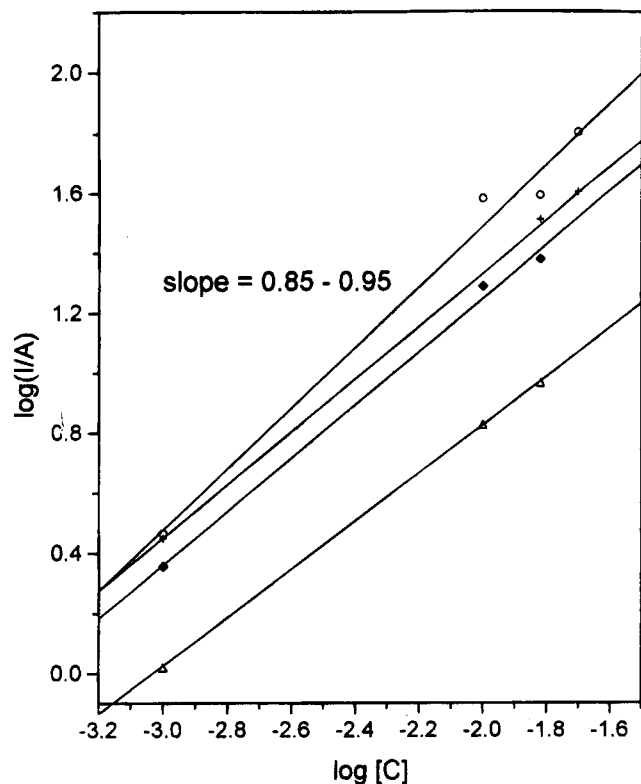


Figure 4. Plots of $\log(I/A)$ vs $\log[C]$ for reactions of $\text{XC}_6\text{H}_4\text{CH}(\text{Br})\text{C}(\text{Br})(\text{NO}_2)\text{CH}_3$ in unstirred solution [$\text{X} = \text{H}$ (\circ), $p\text{-CH}_3\text{O}$ (Δ), $m\text{-Br}$ (\blacklozenge), $p\text{-NO}_2$ ($+$)]. [Substrate] = 1.0×10^{-3} M; $[\text{LiClO}_4] = 0.10$ M; scan rate = 1 mV s^{-1} .

Table 3. Reduction Current and Relative Rates of Electrochemical Reactions of 1-Aryl-1,2-dibromo-2-nitropropanes [$\text{XC}_6\text{H}_4\text{CH}(\text{Br})\text{C}(\text{Br})(\text{NO}_2)\text{CH}_3$] in DMSO at -0.16 V^a

X	i_X (μA)	relative rate ^b
H	0.70	1.0
$p\text{-CH}_3\text{O}$	0.25	0.36
$m\text{-Br}$	0.55	0.79
$p\text{-NO}_2$	0.68	0.97

^a [Substrate] = 1.0×10^{-3} M, $[\text{LiClO}_4] = 0.10$ M, scan rate = 1 mV s^{-1} . ^b Relative rate = i_X/i_H (see text).

for other substrates. Plots of $\log(I/A)$ vs $\log[C]$ are shown in Figure 4. In all cases, the slopes are close to unity, indicating unimolecular processes.¹¹⁻¹⁴

The relative rates of the electrochemical reactions of **1a-d** were calculated by the ratio i_X/i_H , where i_X and i_H represent the reduction currents of substituted and unsubstituted substrates, respectively.¹¹⁻¹⁴ The reduction currents and the relative rates at -0.16 V are summarized in Table 3. The $\log(i_X/i_H)$ are plotted against the σ values of the substituents in Figure 5. The rate data correlate nonlinearly with Hammett substituent constants.

Discussion

The electrochemical reduction of *erythro-dl*-1-aryl-1,2-dibromo-2-nitropropanes **1a-d** in DMSO produced (*E*)-

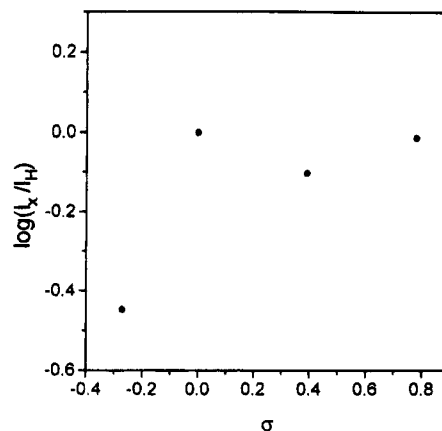


Figure 5. Hammett plot for electrochemical debromination of $\text{XC}_6\text{H}_4\text{CH}(\text{Br})\text{C}(\text{Br})(\text{NO}_2)\text{CH}_3$ in DMSO at -0.16 V . [Substrate] = 1.0×10^{-3} M; $[\text{LiClO}_4] = 0.10$ M; scan rate = 1 mV s^{-1} .

1-aryl-2-nitropropanes **2a-d** in high yields. Since the reaction must proceed by the electron transfer mechanism, the most important mechanistic questions are the rate equation, the rate-determining step, the reaction site, and the nature of the reactive intermediates. The kinetic order of the reaction was determined by measuring the current density at different substrate concentrations. The current density increases as the concentration of the substrate increases, indicating that not only strongly adsorbed substrates but also those near the electrode participate in the reaction. Moreover, the slopes of the plots of $\log \text{ mV s}^{-1}$ vs $\log[C]$ are near unity (Figure 4), consistent with unimolecular processes.¹⁵

That the first electron transfer step is rate determining has been demonstrated by the cyclic voltammetric experiments. For all reactions, the cyclic voltammograms were irreversible and the reduction current decreased as the number of cycles increased. This result indicates that the reduced species must have decomposed before the anodic potential is applied and that the first step is rate limiting. The conclusion is supported by the Tafel slopes, which can be expressed as $0.0591/\alpha n$, where α and n represent the transfer coefficient and the number of electrons which are transferred. Considering that α is usually taken as 1 for reversible and 0.5 for irreversible electron transfer, respectively, the observed Tafel slopes of 115–125 mV can only be explained if the reduction proceeds by irreversible SET mechanism.¹¹⁻¹⁴

The next question is which of the benzyl bromide or bromonitropropyl moieties would be reduced preferentially. The question may be answered by comparing the reduction potentials. For all reactions, the peak potentials for the reduction waves are in the range of -0.51 to -0.56 V (Table 1). The values are very similar and show no clear trend with different aryl substituents. Similarly, the peak potential for benzyl bromide and *p*-nitrobenzyl bromide are nearly the same, although the latter shows second reversible wave at a more negative potential which can be attributed to the reduction of the nitro group (Table 1). This result indicates that the reduction potential for the benzyl bromide moiety is relatively insensitive to the electron-withdrawing ability of the aryl substituent. Therefore, it is difficult to interpret the

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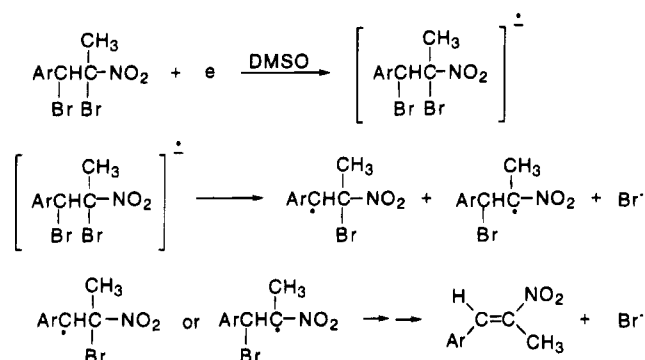
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Scheme 1



small differences in peak potentials for **1a–d** in terms of a substituent effect. On the other hand, the reduction potential for 2-bromo-2-nitropropane is slightly less negative than that for benzyl bromide. However, since the difference in the peak potential is very small, it seems most reasonable to assume that the initial electron transfer occurs at the both sites, although the former might be slightly favored.

The relative rates of the reactions did not correlate with Hammett substituent constants (Figure 5). One plausible interpretation for the nonlinear Hammett plot might be that the reaction site changes from C-1 to C-2 as the electron-withdrawing ability of the aryl substituent increases. If the electron transfer occurred at the benzyl bromide moiety, a modest ρ value should be observed because the electron density increases at the benzylic position in the transition state. On the other hand, if the bromonitropropyl moiety were reduced preferentially, the ρ value should be near zero because the reaction site is insulated from the effect of the substituent in the β -aryl ring by the sp^3 -hybridized carbon. This would predict that the Hammett ρ value should change from a positive value to near zero, as observed. However, it is not clear why the reaction site should change as such. Alternatively, the result can also be interpreted with a negative deviation of the data for **1b** from the near-zero slope. If the *p*-methoxy group stabilizes the reactant by donating electron density to the benzylic carbon which must be highly electron deficient due to the presence of the electron-withdrawing groups, the activation energy for **1b** could be higher than other substrates to retard the rate. However, in view of the similar reduction potential for both sites (vide supra), the origin of the nonlinear Hammett plot may be more complex than these interpretations.

The combined results reveal that the most reasonable mechanism for the electrochemical debromination reaction of **1a–d** appears to be the EC mechanism shown in Scheme 1. The dibromides **1a–d** will accept an electron from the cathode to form the anion radical in the rate-determining step. Since both of the C–Br bonds are relatively weak, the most likely reaction of the anion radical would be to lose bromide and to form an alkyl radical. Considering that the unpaired electron should remain on the same side of the scissible bond throughout the fragmentation processes, either the benzylic radical or the nitroalkyl radical would be produced depending upon which site is reduced initially.¹⁶ The alkyl radicals would then expel a bromine radical to afford **2a–d**.

Alternatively, they may be reduced further before losing bromide ion or undergoing disproportionation to produce the alkene and the dibromide.¹⁷ The stereospecificity of the reaction is retained despite the presence of the free radical intermediate, because the *E* isomer is much more stable than the *Z* isomer. However, the detailed mechanism of the decomposition of the radical anion cannot be determined experimentally because it occurs after the rate-determining step.

Experimental Section

Materials. DMSO was distilled from CaH_2 . Reagent-grade LiClO_4 was used without further purification. 1-Aryl-1,2-dibromo-2-nitropropanes **1a–d** and 1-aryl-2-nitropropene **2a–d** were available from previous work.⁸ Fresh solutions of **1a–d** were prepared by dissolving **1a–d** and LiClO_4 (0.10 M) in DMSO before use and deaerated by bubbling the solution with argon for at least 1 h.

A platinum wire (1.0 mm, diameter, 99.99%, Aldrich) and platinum gauge (52 mesh, 99.9%, Aldrich) were used as the working electrodes in the cyclic voltammetry and electro spectroscopy, respectively. The Pt wire and Ag/Ag^+ were used as the counter and reference electrodes, respectively. These electrodes were electrochemically polished in 1 M $\text{H}_2\text{SO}_4(\text{aq})$. After the electrodes were withdrawn from the solution, they were immediately washed with a stream of doubly distilled water and DMSO.

Apparatus and Measurements. Cyclic voltammetric experiments were performed by using an EG & G Princeton Applied Research Co. (PARC) Model 273 potentiostat/galvanostat. Voltammograms were recorded on an EG & G PARC Model 8900 X–Y recorder using EG & G PARC Model 270 software program. The reference and counter electrodes were prepared by inserting Ag wire (1.0 mm, diameter, 99.99%) and Pt wire (1.0 mm diameter, 99.99%) into the glass tubes (5.0 mm diameter) containing 0.1 M AgNO_3 in DMSO and the electrolyte solution, respectively. The junction device for the two electrodes were Pt wire and Vycor tips, respectively. Pt wire (1.0 mm, diameter, 99.99%) or Pt gauge (52 mesh, 99.9%) were used as the working electrodes in the cyclic voltammetry and electro spectroscopy, respectively. The three electrodes and a deaeration tube were inserted into the quartz cuvette containing ca. 2.5 mL of sample. The in situ cell was sealed with Teflon tape and Parafilm and deaerated for at least 1 h before use. All measurements were made under positive pressure of argon. UV–vis spectra were obtained with a Hewlett-Packard 8452A diode array spectrophotometer. All potentials cited were against the Ag/Ag^+ reference electrode.

Cyclovoltammograms were recorded at scan rate of 20 mV s^{-1} between 0.3 V and -0.9 V (vs Ag/Ag^+ reference electrode) to avoid complications caused by the reduction of 1-aryl-2-nitropropene at -1.05 to -1.35 V. The effect of scan rate on the peak potential was determined by varying the scan rate between 5 and 200 mV s^{-1} .

Steady state current–potential curves were obtained from the cyclovoltammogram of the unstirred solution operated at 1 mV s^{-1} . The Tafel plots were obtained at different substrate concentrations to determine the kinetic order.

Product Studies. The products of the electrochemical reduction of **1b** and **1d** were identified by periodically monitoring the UV absorption of the reaction mixture under the electrochemical conditions. Pt gauge (52 mesh) was used as the working electrode and the peak potential were applied to facilitate the reaction. For both reactions the UV spectra of the products were identical to those of 1-aryl-2-nitropropenes **2b** and **2d**. The yields of the debromination products were calculated by comparison of the UV absorption of the infinity sample from the electrochemical reaction with that for the

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authentic product. The yields were 80 and 85% for **1b** and **1d**, respectively.

The product of the electrochemical reaction of *erythro-dl*-1,2-dibromo-2-nitro-1-phenylpropane (**1a**) was also identified by GC-MS. The electrochemical reduction was conducted with 0.02 g of **1a** in 10 mL DMSO as described above. The solutions were diluted with water and extracted several times with cyclohexane and CH₂Cl₂. The GC-MS of the isolated product revealed that 2-nitro-1-phenylpropene was the only product.

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