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Development of Electrochemical Processes for Nitrene Generation and Transfer

Tung Siu, Christine J. Picard, and Andrei K. Yudin*

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

ayudin@chem.utoronto.ca

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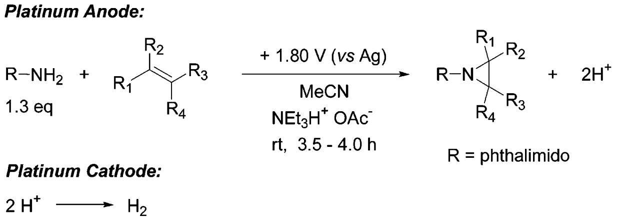

An electrochemical strategy for running nitrogen-transfer reactions on chemically inert anode surfaces has been developed. The generation and trapping of highly reactive nitrene-transfer reagents can be accomplished under mild conditions on platinum electrodes. The key factor that accounts for the high levels of chemoselectivity in this process is the phenomenon of overpotential. We have found that molecules that are similar in terms of propensity toward oxidation can be differentiated on the basis of their affinity to a given electrode surface. Thereby, reactive species can be selectively generated in the presence of acceptor molecules of interest. Specifically, a wide range of structurally dissimilar olefins can be transformed into the corresponding aziridines in the presence of *N*-aminophthalimide. Likewise, nitrene generation in the presence of sulfoxides leads to their chemoselective transformation into the corresponding sulfoximines. In this paper we discuss the underlying mechanistic foundation of these reactions.

Introduction

Due to the fundamental role of electron transfer in redox processes, developing an electrochemical understanding of oxidative atom-transfer reactions that are normally driven by metal reagents may help in designing new, highly efficient processes. The ultimate goal is to find general and practical electrochemical solutions to selective functionalization of hydrocarbons with nitrogen-containing fragments. Another important question is whether direct electron transfer can find broad applications in synthetic organic chemistry. In this regard, understanding ways of electrochemical generation and subsequent trapping of highly reactive atom-transfer species has been of particular interest. Our recent studies defined the scope of electrochemical nitrene transfer to olefins (Table 1) and sulfoxides (Table 2).[1] This strategy allows one to access a wide range of aziridines and sulfoximines, respectively. A variety of substituents around the double bond of the olefin and around the sulfur center of the sulfoxide can be tolerated in the course of these reactions. In the present paper we outline the electrochemical aspects and mechanistic understanding of olefin aziridination and sulfoxide imination processes.

Results and Discussion

Electrochemical Aziridination of Olefins. The aziridination of olefins is of significant current interest due to the enormous synthetic potential of aziridines.[2] These nitrogen-containing heterocycles have approximately 28 kcal/mol of strain[3] and are amenable to ring-opening reactions with a wide range of nucleophiles. Some of these transformations lead to molecules with valuable 1,2-heteroatom relationships, commonly found in natural products and in pharmaceuticals.[4]

Until recently, there have been no examples of catalytic oxidation systems based on readily available oxidants that convert simple amines or amides into active nitrogen-transfer species in the presence of olefins and leave no byproducts. On the other hand, a stoichiometric oxidation

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(1) (a) Siu, T.; Yudin, A. K. *J. Am. Chem. Soc.* **2002**, *124*, 530. (b) Siu, T.; Yudin, A. K. *Org. Lett.* **2002**, *4*, 1839.

(2) McCoull, W.; Davis, F. A. *Synthesis* **2000**, *10*, 1347.

(3) Skancke, A.; van Vechten, D.; Liebman, J. F.; Skancke, P. N. *J. Mol. Struct.* **1996**, *376*, 461.

(4) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.

10.1021/jo048591p CCC: $30.25

TABLE 1. Selected Substrate Scope in Electrochemical Aziridinations of Olefins

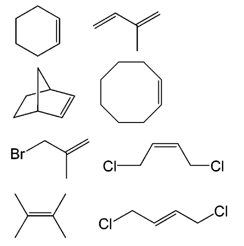
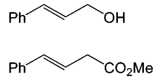
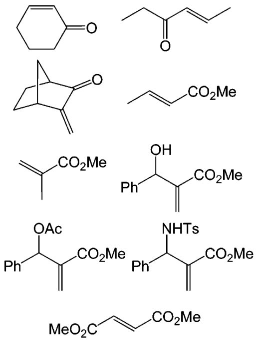
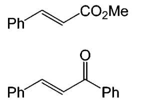
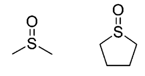
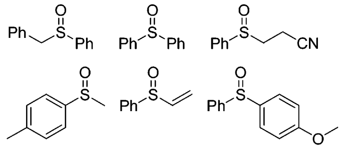
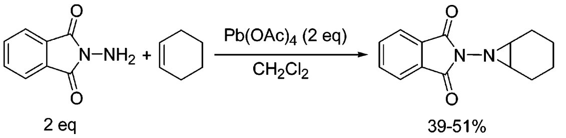
	Aliphatic	Aromatic / Aliphatic
Electron Rich		
Electron Poor		

TABLE 2. Selected Substrate Scope in Electrochemical Imination of Sulfoxides

Aliphatic	Aromatic / Aliphatic
	

system that generates active nitrene precursors from the amine species does exist. Valuable aziridines equipped with an N−N bond can be obtained from olefins using lead tetraacetate as oxidant (eq 1).[5] Unfortunately,



(1)

widespread application of this method is hampered by the use of excess $Pb(OAc)_4$, known for its high toxicity.[6] Because of the broad utility of $Pb(OAc)_4$ as a reagent in organic synthesis, it is desirable to develop systems in which the Pb(IV) species can be replaced by the less toxic reagents. As a general approach to our electrochemical study aimed at understanding the possibilities for catalysis in this system, we first used cyclic voltammetry (CV) to investigate the $Pb(OAc)_4$-mediated nitrene transfer. CV of $Pb(OAc)_2$ in acetonitrile gives a value of +1.60 V (vs Ag/AgCl) for the peak potential that corresponds to the oxidation of Pb(II) to Pb(IV). CV of *N*-aminophthalimide (0.01 M in acetonitrile) shows two irreversible one-electron oxidation processes with anodic peak potentials at +1.35 and at +1.68 V (vs Ag/AgCl). Clearly, only the first electron transfer from *N*-aminophthalimide occurs at a less positive potential than the oxidation of Pb(II); the second electron transfer is in fact more positive. This observation encouraged us to run the electrochemical aziridination with a catalytic amount of $Pb(OAc)_2$. Using 10 mol % $Pb(OAc)_2$ with respect to *N*-aminophthalimide, cyclohexene (1.5 equiv) was transformed into the corresponding aziridine at a constant potential of +1.80 V(Ag wire pseudo reference electrode), and gave a 75% isolated yield of **1**.

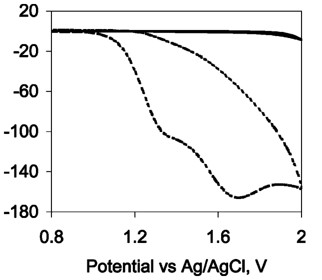


FIGURE 1. Cyclic voltammetry study of *N*-aminophthalimide (dashed line) and cyclohexene (solid line) on a platinum electrode in acetonitrile (0.1 M $HEt_3N^+OAc^-$).

Aware of the relative facility with which olefins may undergo detrimental background oxidation at the anode,[7] we recorded the cyclic voltammogram of cyclohexene under the conditions used in *N*-aminophthalimide oxidation (0.01 M in acetonitrile). The observed anodic current was only −1.3 μA at +1.68 V (vs Ag/AgCl), a small fraction of the current recorded for *N*-aminophthalimide (−152 μA, Figure 1). This clearly indicates that the background oxidation of olefins on platinum electrodes is disfavored under the reaction conditions due to the olefin overpotential. By definition, an overpotential is the "additional potential (beyond the thermodynamic requirement) needed to drive a reaction at a certain rate".[8] Under certain conditions, i.e., electrode material and medium, various substrates possess different overpotentials depending on the nature of the electrode. We hypothesized that the overpotential phenomenon can be used as a guiding principle to selectively oxidize a given species in the presence of a thermodynamically similar acceptor molecule, thus avoiding detrimental background reactions. For instance, selective oxidation of *N*-aminophthalimide at the anode at around +1.60 V should be possible in the absence of $Pb(OAc)_4$. A simple combination of platinum electrodes, triethylamine, and acetic acid has led to a highly efficient, soluble metal reagent-free nitrene transfer from *N*-aminophthalimide to cyclohexene at room temperature (Scheme 1). The reaction utilizes only a small excess of *N*-aminophthalimide relative to the olefin and can be performed in a divided cell using silver wire as a pseudo reference electrode. The pseudo reference electrode was calibrated against the ferrocene/ferricinium couple in the electrolysis medium (E_{pa} = 0.47 V, E_{pc} = 0.30 V).

The nature of the electrode material can be critical in electrosynthesis. For instance, the Kolbe reaction requires smooth platinum or iridium electrodes to give the

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[5] Atkinson, R. S. In *Azides and Nitrenes*; Scriven, E. F. V., Ed., Academic Press: Orlando, FL, 1984; see also references therein.

[6] Daland, R. J. *Lead and Human Health: An Update*; American Council on Science and Health: New York, 2000; see also references therein.

[7] For CV data on various olefins, see: Tsuchiya, M.; Akaba, R.; Aihara, S.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1986**, 1727.

[8] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2000.

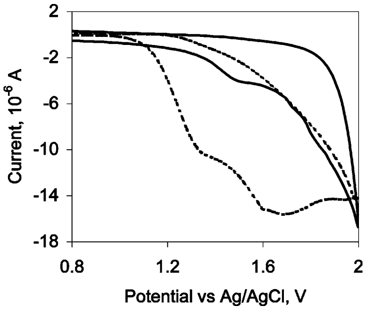
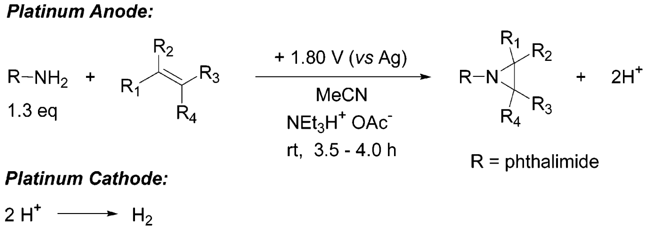


FIGURE 2. Cyclic voltammetry study of *N*-aminophthalimide (dashed line) and cyclohexene (solid line) on a glassy carbon electrode in acetonitrile (0.1 M $HEt_3N^+OAc^-$).

SCHEME 1. Electrochemical Aziridination of Olefins



coupling products, whereas the reactions on graphite lead to products exclusively derived from carbenium ions.[9] In our case, the aziridination reaction did not take place when platinum was replaced by carbon. The CV study (Figure 2) on carbon revealed that the anodic current corresponding to cyclohexene oxidation (-5.3 μA at $+1.68$ V) was comparable to that of *N*-aminophthalimide (-15.6 μA at $+1.68$ V). Such a small difference in electroactivity apparently does not secure high selectivity in *N*-aminophthalimide oxidation, supporting the notion that selectivity can be obtained by maximizing the difference in overpotentials between the substrates.

The choice of the separator material turned out to be crucial to the success of electrochemical nitrene transfer. In certain cases, the use of glass frits resulted in higher cell voltages (the voltage needed to be applied across the cell to maintain the working potential) which exceeded the instrument compliance voltage limit and caused the working potential to be lower than the set value of $+1.80$ V. In such cases, Nafion membranes allowed us to construct cells with lower cell voltages, which enabled scaleup. Aziridination attempts in undivided cells resulted in significant amounts of olefin reduction byproducts.

As a qualitative measure of electroactivity throughout the reaction, we monitored the current/time profile. The poisoning of platinum electrodes is a common problem, and the current/time profile is the easiest and most reliable way of comparing the reaction runs and ensuring that the electrode performance is close to optimal and is reproducible. For instance, Figure 3 features the comparison of current/time profiles for the aziridination on poisoned (sulfided) platinum vs aziridination on flamed platinum. The current/time profiles also facilitate scaleup by providing direct comparison of the electrochemical process efficiency as a function of the electrode surface area, which is particularly important for scaleup.

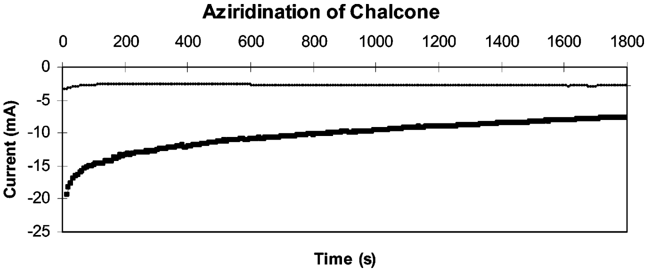


FIGURE 3. Current/time profiles of aziridination of chalcone on poisoned (sulfided) platinum (thin line) vs aziridination on flamed platinum (thick line).

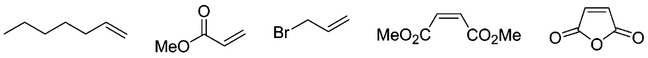


FIGURE 4. Olefins that are inert in electrochemical aziridination.

In sharp contrast to the metal-based nitrene transfer, both electron-rich and electron-poor olefins can be converted to aziridines with high efficiency. For certain monosubstituted terminal olefins (Figure 4), the electrochemical aziridination was not successful although the redox behavior of these olefins is not significantly different from that of the others. Surprisingly, dimethyl maleate was found to be inert toward electrochemical aziridination, while the corresponding *trans*-isomer, dimethyl fumarate, gave an excellent yield of the aziridine. In all cases with inert olefins, *N*-aminophthalimide was completely converted to phthalimide (precipitated from the reaction mixture) and the olefins were recovered quantitatively. This observation suggests that the electrochemical oxidation does take place but the active nitrogen-transfer species is not intercepted by the olefin. This is clearly a relative rate phenomenon, rather than a consequence of platinum surface poisoning with "inert" olefins. Indeed, a 1:1 mixture of 1-hexene and chalcone gave an 83% yield of chalcone-derived aziridine while 1-hexene remained unreacted.

Electrochemical Imination of Sulfoxides. The nitrene transfer to sulfur was investigated similarly to aziridination.[10] The redox behavior of sulfoxides on platinum was first studied using cyclic voltammetry (Figure 5). At $+1.68$ V, tetramethylene sulfoxide (0.01 M in acetonitrile) produces a considerably smaller anodic current (-7.52 μA) than the current recorded for *N*-aminophthalimide (-152 μA). This is a sign of kinetically sluggish background oxidation of sulfoxides to sulfones on a platinum anode, which enables direct electrochemical nitrogen transfer to sulfoxides.

The nature of the electrode material is crucial to the success of this process as well. CV (Figure 6) of tetramethylene sulfoxide (0.01 M in acetonitrile) on a glassy

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[9] Torii, S.; Tanaka, H. In *Organic Electrochemistry*, 4th ed.; Lund, H., Hammerich, O., Eds.; Marcel Dekker: New York, 2001; Chapter 14.

[10] (a) Ohashi, T.; Masunaga, K.; Okahara, M.; Komori, S. *Synthesis* **1971**, *96*. (b) Colonna, S.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2120. (c) Kim, M.; White, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 1172. (d) Kemp, J. E. G.; Closier, M. D.; Stefanich, M. H. *Tetrahedron Lett.* **1979**, 3785.

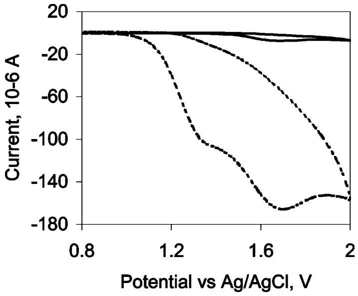


FIGURE 5. Cyclic voltammetry study of N-aminophthalimide (dashed line) and tetramethylene sulfoxide (solid line) on a platinum electrode in acetonitrile (0.1 M $HEt_3N^+OAc^-$).

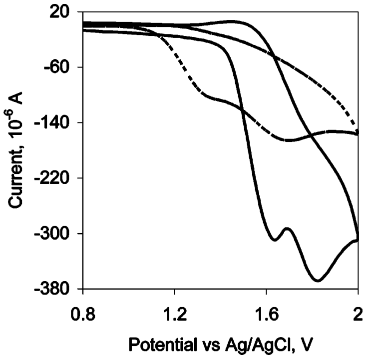
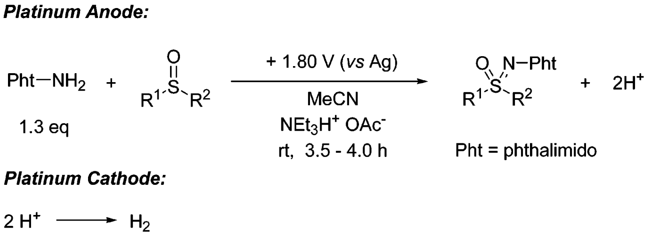


FIGURE 6. Cyclic voltammetry study of N-aminophthalimide (dashed line) and tetramethylene sulfoxide (solid line) on a glassy carbon electrode in acetonitrile (0.1 M $HEt_3N^+OAc^-$).

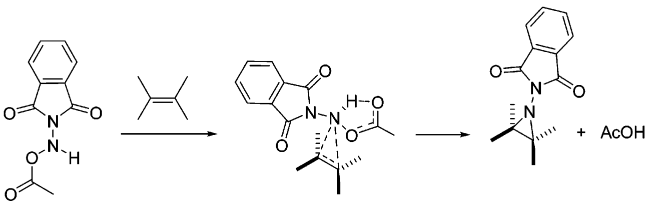
SCHEME 2. Electrochemical Imination of Sulfoxides



carbon electrode shows two irreversible oxidation processes with peak potentials at +1.64 and +1.82 V and a considerably higher anodic current (−272 μA) than that of N-aminophthalimide at +1.68 V (−15.6 μA). Not surprisingly, the bulk electrolysis of tetramethylene sulfoxide in the presence of N-aminophthalimide on graphite gave tetramethylene sulfone as the major product with no evidence of sulfoximine formation.

On the other hand, the electrolysis conditions on platinum were similar to those of aziridination (Scheme 2). A small excess of N-aminophthalimide relative to sulfoxide was used. The electrolysis was performed in a divided cell using silver wire as a pseudo reference electrode. No special precautions to exclude moisture or air were taken. The reaction was stopped when the cell current dropped to less than 5% of its original value. There was no evidence for the background formation of sulfone byproduct. The oxidative imination of sulfides (resulting in sulfimines) was also attempted using this methodology. However, due to the less positive oxidation potential of sulfides compared to N-aminophthalimide, a mixture of products consisting mainly of sulfoxide and sulfoximine was obtained.

SCHEME 3. Mechanism of the Nitrene Transfer to Olefins



The electrochemical nitrene-transfer process was found to be stereospecific. An enantiomerically enriched (93% ee of the (R)-enantiomer)[13] sample of methyl p-tolyl sulfoxide was electrolyzed under the same conditions as above. The ee value measured for the product sulfoximine **20** was the same (97%) within the error of HPLC analysis, and the X-ray structure (see the Supporting Information) of the product showed retention of configuration, indicating that no racemization occurred during nitrene transfer.

Mechanistic Apects of the Electrochemical Aziridination Process. The mechanism of $Pb(OAc)_4$-mediated olefin aziridination with N-aminophthalimide and other N-amino heterocycles has been studied by Atkinson and co-workers.[11] It is believed that the oxidation of N-aminophthalimide by $Pb(OAc)_4$ generates an N-acetoxyamino intermediate, which is stable enough to be observed by NMR at low temperature (<5 °C). Addition of olefins to this intermediate at elevated temperature is known to result in aziridines (Scheme 3). In the absence of olefins, the N-acetoxyamino intermediate dimerizes to generate tetrazene, which then decomposes to phthalimide by extrusion of N_2. Fuchigami and coworkers[12] showed that electrochemical oxidation of N-aminophthalimide using Bu_4NBF_4 or $LiClO_4$ as supporting electrolyte at 0 °C gave tetrazene as the main product and 10−20% phthalimide. It is believed that the electrochemically generated N-nitrene intermediate inserts into the N−H σ-bond of N-aminophthalimide to afford the tetrazane product (Scheme 4). The tetrazane is further oxidized to give tetrazene. In our case, the crucial role of the acetate anion is to prevent the unwanted nitrene dimerization pathway. The necessity of acetate (or other carboxylate) anions for the aziridine generation implies that a similar N-acetoxyamino intermediate is involved in our reaction. This is also evidenced by the correlation between aziridine yields and acetate concentrations (Table 3). In the case of inert olefins (Figure 4), the nitrene transfer is slow and an alternate path (A, likely proceeding via two consecutive α-hydride eliminations) depicted in Scheme 4 predominates to give phthalimide as the reaction product, leaving the olefin intact. Therefore, we believe that the key role of the acetate anion is to intercept the Pt−N species obtained after the first α-hydride elimination, leading to the N-acetoxy species.

To further probe the involvement of acetate in the electrochemical aziridination, we performed oxidation of

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[11] Atkinson, R. S.; Grimshire, M. J.; Kelly, B. J. *Tetrahedron* **1989**, *45*, 2875.

[12] Fuchigami, T.; Sato, T.; Nonaka, T. *Electrochim. Acta* **1986**, *31*, 365.

[13] Chilmonczyk, Z.; Egli, M.; Behringer, C.; Dreiding, A. S. *Helv. Chim. Acta* **1989**, *72*, 1095.

SCHEME 4. Electrochemical Oxidation of *N*-Aminophthalimide

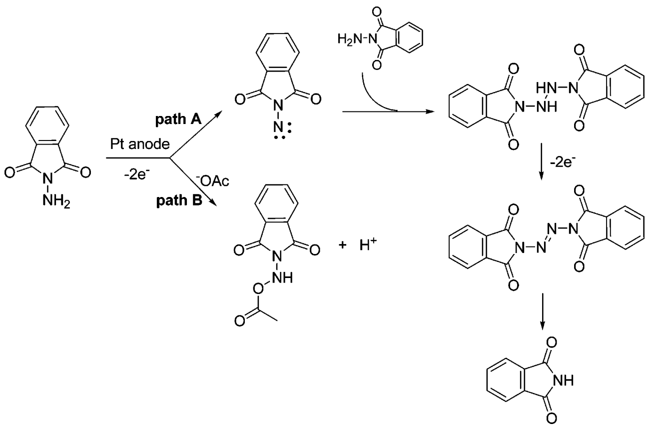

TABLE 3. Cation and Anion Effects in Electrochemical Aziridination with 1.0 mmol Cyclohexene, 1.3 mmol *N*-Aminophthalimide, and Supporting Electrolyte

supporting electrolyte	amt of supporting electrolyte (mmol)	yield of aziridine (%)	amt of phthalimide (mmol)
$LiClO_4$	1.0	0	1.06
Bu_4NBF_4	1.0	0	1.11
Et_4NOTs	1.0	0	1.03
1:1 Et_3N/CF_3CO_2H	1.0	90	0.33
1:1 $Et_3N/ClCH_2CO_2H$	1.0	87	0.33
Me_4NOAc	1.0	85	0.39
Et_4NOAc	1.0	81	0.37
Bu_4NOAc	1.0	83	0.37
1:1 $Et_3N/HOAc$	0.20	55	0.64
1:1 $Et_3N/HOAc$	0.50	69	0.51
1:1 $Et_3N/HOAc$	2.0	83	0.40
1:1 $Et_3N/HOAc$	5.0	89	0.32

N-aminophthalimide in the presence of cyclohexene with supporting electrolytes other than triethylammonium acetate. The results are shown in Table 3. With $LiClO_4$, Bu_4NBF_4, and Et_4NOTs as supporting electrolytes, no aziridine was detected while phthalimide was isolated in high yields (80−85%).

More mechanistic evidence has been obtained by comparing the stereochemical outcomes of electrochemical and chemical ($Pb(OAc)_4$-mediated) aziridinations. Dreiding and co-workers[13] showed that the $Pb(OAc)_4$-promoted aziridination is stereospecific; i.e., (*E*)-olefins afford only *trans*-aziridines and (*Z*)-olefins only *cis*-aziridines. In our study, the NMR analysis and X-ray analysis (see the Supporting Information) of **1** showed exclusive formation of the *trans*-aziridine. The electrochemical aziridination of (*Z*)-1,2-dichloro-2-butene was also stereospecific (Table 4, entries 2 and 3). Furthermore, the diastereoselectivities of the electrochemical and chemical approaches were comparable (Table 4, entries 4 and 5). The *syn*-aziridine (see the Supporting Information for the X-ray analysis) was exclusively obtained from olefin **3**. Taken together, these facts provide additional evidence that speaks in favor of the *N*-acetoxy intermediate.

Conclusions

The present study illustrates the use of an overpotential as a means of bypassing the requirement for stoichiometric or catalytic amounts of oxidants and metal additives in organic redox reactions. The differentiation of substrates is based on their behavior at the electrode/solution interface. This strategy has been applied to electrochemical nitrogen transfer to olefins and sulfoxides, resulting in synthetically useful aziridines and sulfoximines, respectively. The electrochemical aziridination process gives good to excellent yields for both electron-rich and electron-poor olefins. The range of olefins compares favorably with the metal-catalyzed aziridination processes, which usually have limited substrate scope.

Identifying other nitrogen sources for electrochemical nitrene transfer will further broaden the utility of this process. In this regard, cyclic voltammetry will continue to be an invaluable tool that can be used to select the nitrene precursor molecules with higher overpotentials than the nitrene acceptors (e.g., olefins and sulfoxides). The parallel electrosynthesis methodology[14] may be promising to further identify appropriate nitrogen sources.

Experimental Section

***N*-Aminophthalimide.**[15] To hydrazine monohydrate (4.4 g) in 95% ethanol (80 mL) was added powdered phthalimide (12 g), and the mixture was stirred at room temperature for 2 min. The resulting spongy mass was quickly heated and refluxed for 3 min while ammonia was evolved. Cold water (250 mL) was added at once, and *N*-aminophthalimide crystallized during 1 h. Recrystallization from 95% ethanol gave white needles (5.6 g, 43%, mp 223−224 °C).

CV Experiments. A platinum disk (0.07 cm^2) electrode, a platinum wire (0.1 mm diameter) electrode, and a Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. The substrate concentration of 0.01 M in acetonitrile with 0.1 M $Et_3HN^+OAc^-$ as supporting electrolyte was used, and the potential was swept between 0.0 and +2.0 V at a rate of 200 mV/s.

Electrochemical Aziridination. (a) A 0.5 mmol Scale. A two-compartment divided cell with a glass frit was used. The anodic compartment was charged with 41 mg (0.5 mmol) of cyclohexene, 105 mg (0.65 mmol) of *N*-aminophthalimide, and 10 mL of 0.05 M $Et_3N/HOAc$ in acetonitrile. Another 10 mL of 0.05 M $Et_3N/HOAc$ in MeCN was added to the cathodic compartment. Flat platinum foils (1.25 × 2.5 cm, 99.99%) were used as working and auxiliary electrodes. The platinum electrode foils were placed parallel to each other (4.5 cm apart), and this arrangement was rigidly fixed throughout the process by supporting the electrodes using custom-made Teflon holders. Silver wire (1.5 mm diameter, 99.99%) was used as a pseudo reference electrode and was placed 0.5 cm away from the middle of the anode plate. The electrolysis was performed at +1.80 V at ambient temperature and was stopped when the cell current dropped to less than 5% of its initial value. The contents of the anodic compartment were collected and concentrated in vacuo. The residue was washed with water and extracted with dichloromethane (3 × 5 mL). The organic phases were combined, dried over $MgSO_4$, concentrated, charged onto a silica gel column, and eluted using EtOAc/hexane (1:4), which afforded 7-phthalimido-7-azabicyclo[4.1.0]-heptane (**1**) as a yellow solid (111 mg, 85%).

(b) A 5 mmol Scale. A three-compartment divided cell equipped with a Nafion membrane placed between the working and auxiliary electrode compartments was used. The reference

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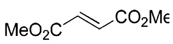
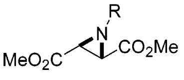
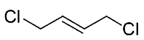
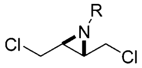
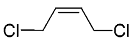
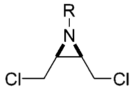
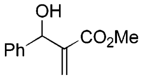
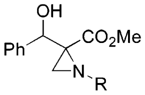
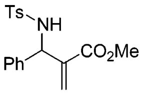
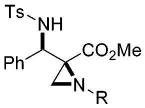
[14] (a) Siu, T.; Li, W.; Yudin, A. K. *J. Comb. Chem.* **2001**, *3*, 554. (b) Yudin, A. K.; Siu, T. *Curr. Opin. Chem. Biol.* **2001**, *5*, 269. (c) Siu, T.; Yekta, S.; Yudin, A. K. *J. Am. Chem. Soc.* **2000**, *122*, 11787. (d) Siu, T.; Li, W.; Yudin, A. K. *J. Comb. Chem.* **2000**, *2*, 545.

[15] Drew, H. D. K.; Hatt, H. H. *J. Chem. Soc.* **1937**, 16.

TABLE 4. Comparison of Electrochemical and Chemical Aziridinations of Olefins

Entry	Substrate	Product	Configuration of aziridine	
			electrochemical method (yield, %)	chemical method[a]
1		 **1**	*trans*[b] (92)	*trans*
2		 **2a**	*trans* (76)	*trans*
3		 **2b**	*cis* (73)	*cis*
4		 **3a**	4.4:1 d.r. (73)	4.2:1 d.r. 3.8:1 d.r.[c]
5		 **3b**	*syn*[b] (78)	*syn*

[a] All aziridination reactions with $Pb(OAc)_4$ were studied by NMR in CD_3CN. The products were not isolated, and their configurations were determined by comparison with the products from electrochemical reactions. [b] X-ray structure. [c] NMR study in $CDCl_3$.

compartment was separated from the anodic (working) compartment by a glass frit. The anodic compartment was charged with 1.04 g (5 mmol) of *trans*-chalcone, 1.05 g (6.5 mmol) of *N*-aminophthalimide, and 100 mL of 0.05 M Et_3N/HOAc in acetonitrile. A 40 mL sample of 0.05 M Et_3N/HOAc in MeCN was added to the cathodic compartment, and 6 mL of 0.05 M Et_3N/HOAc in MeCN was added to the reference compartment. Platinum foils (anodic, 2.5 × 5 cm; cathodic, 2.5 × 2.5 cm, 99.99%) were used as working and auxiliary electrodes. The platinum electrode plates were placed parallel to each other (11 cm apart), and this arrangement was fixed throughout the process. Silver wire (1.5 mm diameter, 99.99%) was used as a pseudo reference electrode. Electrolysis was performed at +1.80 V at ambient temperature and was stopped when the cell current dropped to less than 5% of its initial value. The contents of the anodic compartment were collected and concentrated in vacuo. The residue was washed with water and extracted with dichloromethane (3 × 30 mL). The organic phases were combined, dried over Na_2SO_4, concentrated, charged onto a silica gel column, and eluted using EtOAc/hexane (1:4), which afforded 2-(2-benzoyl-3-phenyl-aziridin-1-yl)-isoindole-1,3-dione (**8**) as a yellow solid (1.2 g, 65%).

Electrochemical Sulfoximination Procedure. The anodic compartment was charged with 1.0 mmol of sulfoxide, 210 mg (1.3 mmol) of *N*-aminophthalimide, 78 mg (1.3 mmol) of acetic acid (glacial), 130 mg (1.3 mmol) of triethylamine, and 20 mL of acetonitrile. Portions of 0.05 M AcOH in MeCN were added to the cathodic (20 mL) and reference (4 mL) compartments. Platinum foils (2.5 × 2.5 cm, 99.99%) were used as working and auxiliary electrodes. Silver wire (1.5 mm diameter, 99.99%) was used as a pseudo reference electrode. Electrolysis was performed at +1.80 V at ambient temperature and was stopped when the cell current dropped to less than 5% of its original value. The contents of the anodic compartment were collected and concentrated in vacuo. The residue was washed with water and extracted with dichloromethane (3 × 5 mL). The organic phases were combined, dried over $MgSO_4$, concentrated, charged onto a silica gel column, and eluted using EtOAc/hexane to afford the sulfoximine.

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Supporting Information Available: Experimental procedures and characterization data for the new compounds (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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