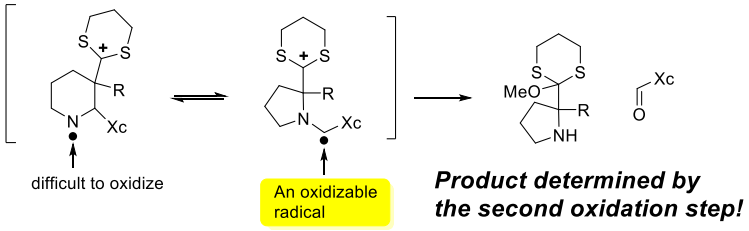
Anodic Cyclizations and Umpolung Reactions Involving Imines.

Zach Medcalf,[&] Essence G. Redd,[%] Jaemyeong Oh,[%] Chang Ji,*[%] and Kevin D. Moeller*[&]

% Department of Chemistry, Texas State University, San Marco, Texas 78666, USA

& Department of Chemistry, Washington University in Saint Louis, Saint Louis, Missouri 63130, USA

TOC Graphic

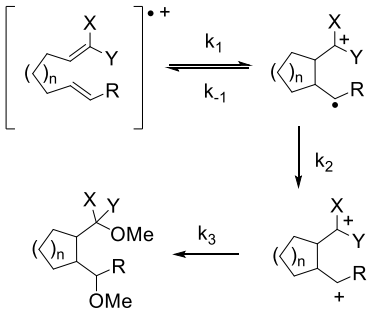


Supporting Information Placeholder

ABSTRACT: Recent discoveries that anodic cyclization reactions rely heavily on the success of a second electron oxidation downstream of the cyclization suggest that this second electron oxidation step can be used to channel a reaction down new synthetic pathways. Here we describe one such application that reverses the normal reactivity of an imine group and sets the stage for the asymmetric synthesis of cyclic amines by anodic cyclization.

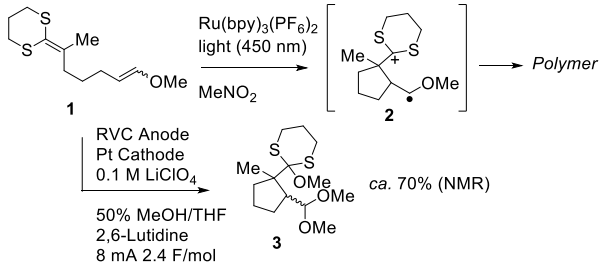
Introduction

Electrochemical methods can be used to reverse the polarity of known functional groups, generate reactive radical ion intermediates, and enable the development of unique pathways to synthetic targets of interest.[1,2] Anodic olefin coupling reactions of the general format shown in Scheme 1 provide an excellent example of such an opportunity.[3] The reactions convert normally nucleophilic electron-rich olefins into reactive intermediates that react with nucleophiles and offer numerous opportunities to construct new bonds and ring systems in novel ways. In addition, the study of anodic olefin coupling reactions has enabled a closer look at how electrochemical reactions can be conducted and the factors that are important for their success.[3]



Scheme 1. A working model for an oxidative cyclization.

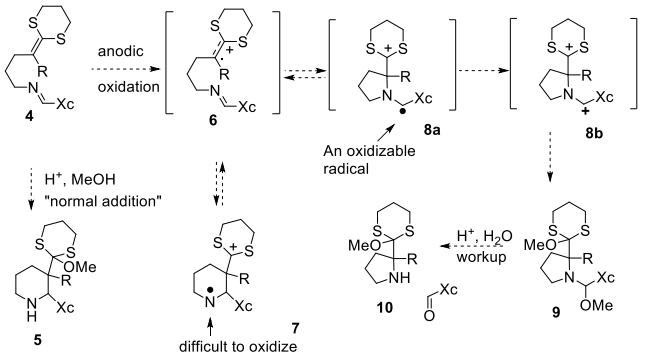
Anodic reactions belonging to this family are controlled by not only the initial oxidation and cyclization steps in the mechanism, but also the removal of a second electron from the molecule downstream of those events (k_2 in Scheme 1).[4] Even anodic cyclization reactions using the best radical cation trapping groups available require a fast second oxidation step. Take for example the chemistry shown in Scheme 2.[5] The chemistry shown highlights a radical cation initiated reaction that was triggered by oxidation of a dithioketene acetal and terminated by trapping of that radical cation with an enol ether. The enol ether was chosen because it is the



Scheme 2. The need for the removal of a second electron.

best radical cation trapping group that we have studied. In the experiment shown, the desired cyclization reaction was triggered with both a photoelectron transfer reaction and an anodic oxidation.[6] In both cases, the starting material was consumed, a radical cation generated, and a cyclization initiated. However, only the electrochemical reaction effectively led to product. The photoelectron transfer initiated reaction led primarily to polymer. The difference between the two methods was the ability of the electrolysis reaction to rapidly remove a second electron from intermediate **2** following the cyclization. That oxidation drove the reaction to completion. The one-electron photoelectron transfer reaction could not efficiently accomplish the oxidation of intermediate **2** leading to polymerization of the cyclic radical. The result was consistent with a variety of cyclization reactions that all showed the same behavior.[3a,4] A slow second oxidation step led to polymer and reaction mixtures rather than a high yield of the desired cyclization product.

It is tempting to suggest that the importance of the second oxidation step in an anodic cyclization reaction can be used as a design element for introducing new types of selectivity into the reactions. Consider the proposed anodic cyclization shown in Scheme 3. In this process, an electron rich olefin would be oxidized and then the radical cation intermediate trapped by an imine. Typically, cyclization reactions between electron-rich olefins and imines are accomplished by treatment of the substrate with acid. The acid protonates the nitrogen and generates an iminium that is then attacked by the nucleophilic olefin at the carbon of the imine. With the substrate shown in Scheme 3, such a transformation would lead to six-membered ring product **5**. As an alternative, the proposed oxidative cyclization would potentially afford a complementary mode of addition to the imine. The oxidation would generate radical cation intermediate **6** that would in turn add to the imine in one of two possible ways. A cyclization to form six membered ring intermediate **7** in a manner consistent with a "normal addition" to the imine would lead to a six-membered ring product. However, in this case the addition would result in a N-centered radical. This N-centered radical would be much harder to oxidize than an alternative benzylic radical (**8a**) that would be derived from a cyclization leading to a five-membered ring. In this case, the oxidation of **8a** would produce stable iminium ion **8b**. Given the reversibility of radical cation derived cyclizations and the role the second oxidation plays in product determination for such transformations,[3,4] one would expect Curtin-Hammett control of the reaction, a scenario in which the more rapid oxidation of **8a** would drive the reaction to the formation of the five-membered ring product. The oxidation of **8a** to iminium ion **8b** would lead to methanol trapping to form **9**. Product **9** would hydrolyze upon the addition of water during the workup to form the cyclic substituted proline derivative **10** and the aldehyde.

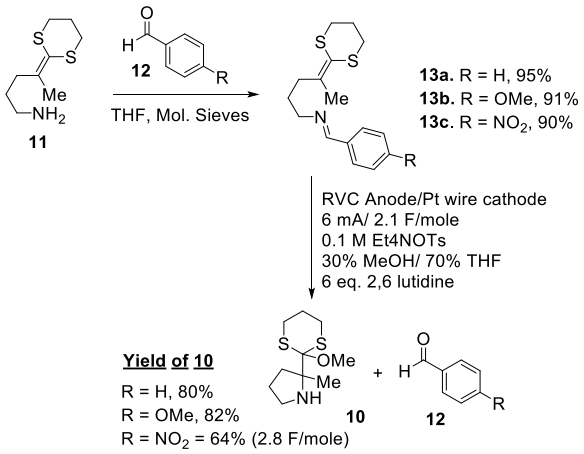


Scheme 3: Using a second oxidation step to change the course of a reaction.

Reactions of this type are particularly attractive because the starting imine can be rapidly constructed in one step from the primary amine used in prior C-N anodic bond forming reactions.[7] The result would be an opportunity to add an auxiliary to the reaction that has the potential to influence the course of the cyclization reaction, potentially introduce selectivity into the product in a manner not available to the amine-based cyclizations, and then automatically recover that auxiliary following the cyclization. However, such a proposal requires that the second oxidation step in the mechanism can be used to drive the reaction in a way that reverses the "normal" addition of a nucleophile to an imine. Is this true? We report herein that the answer to the question is yes.

Results and Discussion

The effort to study the proposed anodic cyclization reactions began with the synthesis of an initial set of substrates that were designed to probe the compatibility of the chemistry with imines having different electronic properties. To this end, the imines were generated by condensing an amine substrate with either benzaldehyde or an electron-rich or electron-poor benzaldehyde derivative. For the derivatives, the substituents were placed at the para position of the aromatic ring so that they would have maximum influence on the second oxidation step of the reaction (Scheme 4). The anodic cyclization of all three arylimine substrates proceeded nicely using electrolysis conditions that are typically used for a variety of anodic cyclization reactions. Such reactions benefit from high surface area carbon electrodes that are compatible with the rapid removal of a second electron,[8] and MeOH/THF electrolyte solutions that use tetraethylammonium tosylate as an electrolyte to reduce the amount of methanol at the anode surface. Reducing the amount of methanol at the anode surface buys time for the cyclization reaction. The reactions also benefit from the use of low current densities that serve to keep the concentration of the highly reactive radical cation at a minimum. This prevents dimerization and polymerization reactions that can arise from the radical cation interemediate. A base (2,6-lutidine) was used as a proton scavenger in order to prevent methanolysis of the acid-labile ketene dithioacetal at the surface of the anode. For these reactions, the use of LiOMe in pure methanol solvent that was employed for the anodic cyclizaton of amine **11** was avoided in order to ensure more time for the cyclization in case the reaction with the imine was slower.



Scheme 4. A test with an initial set of substrates.

Oxidation of both the substrate with the simple benzaldehyde derived imine and the substrate derived from the 4-methoxybenzaldehyde proceeded to the product in high yield while consuming only the theoretical amount of current. In both cases, the second oxidation step involving intermediate **8** following the cyclization was expected to be fast. When an electron-poor aryl ring was used (**13c**), the anodic cyclization reaction led to a lower yield and a reduction in the overall current efficiency of the process. The need for more current was consistent with earlier cyclization reactions where a slower second oxidation step was encountered.[4] In an undivided cell, a slow second oxidation of the cyclic intermediate can lead to re-reduction, reformation of the substrate, and a reduction in current efficiency. In such cases, the use of a divided cell improves the current efficiency of the reaction even if the yield of product is not improved due to polymerization pathways.[4] While the drop in current efficiency in the current case was not as large as in those past cases, this was not a surprise since the neighboring amine lone pair in intermediate **8** would ensure a successful second oxidation step to make the iminium ion needed to form the cyclization product **9** in spite of the electron-poor aryl ring.

Cyclic voltammetry data confirmed that the difference between the cyclizations was due to the second oxidation step and not the cyclization reaction itself. In Figure 1, the cyclic voltammetry data is presented for a substrate having an isolated dithioketene acetal moiety (D), a substrate having only an imine derived from benzyladehyde and a primary amine (E), and the three cyclization substrates **13a-c** (A-C). Each of the electrolysis substrates has an oxidation potential that was roughly equal and significantly less positive than either of the isolated functional groups. The observations were consistent with an oxidation of the ketene dithioacetal group with a Nernstian shift occurring for all three cyclization substrates. The magnitude of the Nernstian shift being similar for all three cyclization substrates indicated that the cyclizations were all fast, occurred at or near the electrode surface, and proceeded at roughly the same rate.[7] Hence, the difference observed for the substrate with the p-nitro group was not the rate of the cyclization reaction, but rather the presence of the nitro-group slowing the reaction "downstream" of that cyclization, a suggestion most consistent with the presence of the nitro-group slowing the second oxidation step in the mechanism involving intermediate **8**.

The rate of the cyclization reactions also indicated that the earlier precautions of using less methanol and a weaker base to "buy-time"for the cyclizations was not necessary. Indeed, when substrate **11** was oxidized using the same conditions as the previous amine cyclizations (LiOMe base instead of 2,6-lutidine and pure methanol solvent),[7] the reaction led to a nearly identical yield of product (80%).

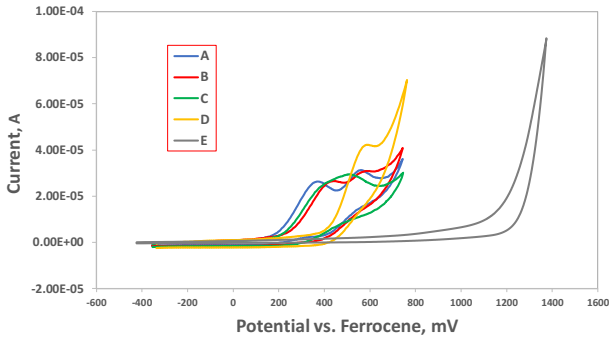


Figure 1: Cyclic voltammograms of (A) 2.2 mM *N*-[(4-methoxyphenyl)methylene]-4-(1,3-dithian-2-ylidene)-1-pentanamine **13b**, (B) 2.2 mM *N*-(phenylmethylene)-4-(1,3-dithian-2-ylidene)-1-pentanamine **13a**, (C) 2.2 mM *N*-[(4-nitrophenyl)methylene]-4-(1,3-dithian-2-y//lidene)-1-pentanamine **13c**, (D) a substrate having only a ketene dithioacetal, 3.2 mM 5-(*tert*-butyldimethylsilyloxy)-2-(1,3-dithian-2-ylidene)pentane, and (E) a substrate having only a benzaldehyde derived imine, 2.8 mM *N*-(phenylmethylene)-1-pentanamine at glassy carbon electrode with a scan rate of 25 mV s^{-1} in 30% MeOH/70% THF containing 0.1 M Et_4NOTs.

As in the earlier amine cyclizations, the use of a less electron-rich olefin was not compatible with reaction because of the low oxidation potential associated with the cyclic amine product. In those cases, the Nernstian shift associated with the substrate was not sufficient to drop the oxidation potential of the substrate below that of the product (ca. + 0.46 V vs. ferrocene).[7] When a methoxy enol ether substrate that has an oxidation potential about 300 mV higher than that of the ketene dithioacetal was used as a substrate for the cyclization, the reaction led to a large number of products.

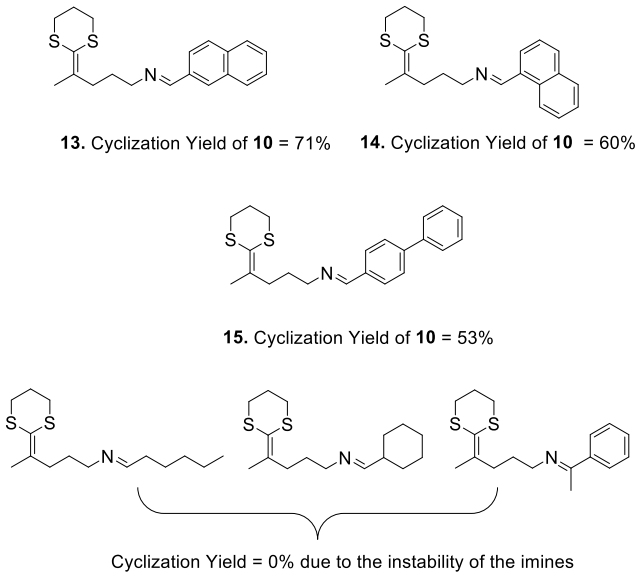
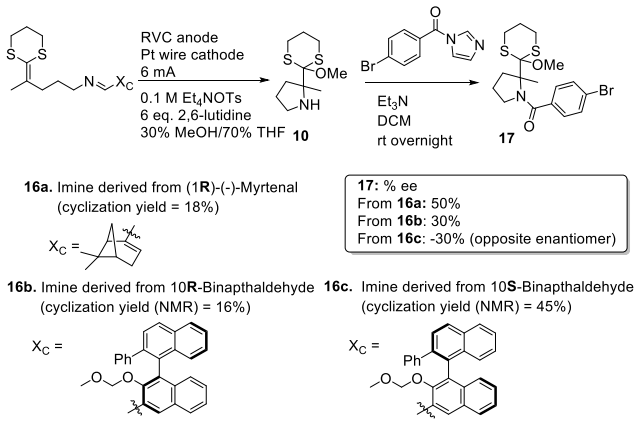


Figure 2. Varying the structure of the imine.

With the initial experiment in place, the scope of the imines that can be used was examined (Figure 2). For each of the reactions, the cyclic ketene dithioacetal was used due to its stability, ease of synthesis, and known compatibility with the cyclizations. Since the use of the imine did not appear to significantly alter the anodic cyclization relative to the previous amine cyclizations, and the aldehyde portion of the imine is not incorporated into the product, the goal of the study was not to explore the nature of the products that could be made but rather to identify the types of auxiliaries that could be used to influence future reactions. With this in mind, two factors governed the choice of substrates; one the possibility for using a chiral auxiliary to control absolute stereochemistry of the products generated and two the recent observation that electrochemical reactions involving substrates with aryl rings can be confined to the surface of an electrode.[9] Both developments would offer new opportunities to introduce selectivity into an anodic cyclization reaction.

The oxidations were all run using the conditions shown in Scheme 4. Two conclusions were quickly reached. First, the reactions tolerated the use of more conjugated aryl rings such as napthlene rings even when the imine was more hindered (**14**), as well as the use of a biphenyl ring (**15**). In this way, the reaction proved compatible with the types of aryl rings that are found in chiral auxiliaries,[10] used to optimize guest-host interactions,[11] and known to have affinity towards aryl-ring based anodic surfaces.[9] Second, the use of a simple alkyl imines and imines derived from ketones were not successful because the imines were not stable enough for the electrolysis reaction. While it may be possible to alter the electrolysis in a manner that enables the use of these more sensitive substrates, it is clear that at the present the use of imines derived from aryl aldehydes provide the best path forward for introducing new types of selectivity into the anodic cyclization reactions.

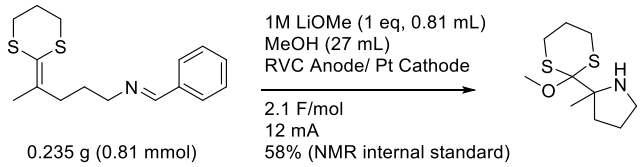
In an exploratory study, the reaction was shown to be compatible with the use of chiral imines (Scheme 5).[12] To this end, three



Scheme 5. Reactions using chiral imines.

substrates (**16a-c**) were prepared and oxidized. Following the cyclization reaction, the product amine was converted into an amide for HPLC analysis on a chiral column. Each of the chiral imines used did influence the absolute stereochemistry of the reaction with the myrtenal-based imine leading to a 50% e.e. of the major product and the binapthaldehyde imines leading to a 30% e.e. of the major product. As expected, the two different enantiomers of the binapthaldehyde did afford the opposite enantiomer of the product obtained. While the yields for the cyclizations were low, they were not optimized further at this point due to the level of asymmetric induction obtained. Typically, such low yields reflect the imine not being stable to the reaction conditions. While such scenarios can frequently be optimized, this would be ideally done after screening for a more optimal chiral auxiliary.

Finally, we demonstrated that the reaction could be run on a larger scale than that used to pioneer the initial cyclization reactions (Scheme 6). For simplicity, the scaled reaction was run using



Scheme 6. Reaction on a 235 mg scale.

methanol with lithium methoxide serving as both the base to neutralize the acid generated at the anode and the electrolyte needed for the reaction. While the yield of the process was lower than the optimized conditions used for the pioneering reactions, the ability to avoid the use of an external electrolyte and 2,6-lutidine as an additive made up for this difference.

Conclusion

We have found that the second oxidation step in an anodic cyclization reaction can serve as a driving force to provide products that reverse the normal addition of a nucleophilic olefin to an imine. The result is an opportunity to temporarily place an aryl ring into a reaction that affords a cyclic amino acid derivative. Efforts to utilize that aryl ring to introduce new types of selectivity into anodic cyclization reactions are underway.

ASSOCIATED CONTENT

Supporting Information

Sample experimental procedures for the site-selective reactions are included. This material is available free of charge via the Internet at http://pubs.acs.org."

Data Availability

All data underlying this study are available in the published article and its online supplementary material."

AUTHOR INFORMATION

Corresponding Authors

Kevin D Moeller: moeller@wustl.edu
Chang Ji: cj22@txstate.edu

Notes

The authors declare no competing financial interests.

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