

Electrocatalytic Intermolecular Olefin Cross-Coupling by Anodically Induced Formal [2+2] Cycloaddition between Enol Ethers and Alkenes

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Electrochemical reactions have proven to be valuable means for reversing the polarity of alkenes and triggering radical anion- or radical cation-based cyclizing reactions. Anodic olefin coupling initiated by oxidation of electron-rich olefins can provide powerful tools for achieving intramolecular cyclization reactions and building new ring systems. In this case, several combinations of olefins can be introduced in the intramolecular cyclizing system, securing diverse functional groups in the newly cyclized skeletons. Electrocatalytic intermolecular cyclo-dimerization of olefins has been achieved for four-membered-ring formation. On the other hand, it has unfortunately been difficult to achieve electrolytic intermolecular selective cross-coupling of two different olefins to provide the [2+2] cycloadduct. This was disappointing because the electrochemical method might allow for the selective polarity inversion of electron-rich olefins and open the door for the construction of four-membered rings by new combinations of olefins even in neutral conditions. This gave us the incentive to try to determine whether such an electrochemical approach might provide a unique pathway to their selective intermolecular olefin cross-coupling to construct [2+2] cycloadducts between the *in situ*-generated electron-deficient olefins and non-activated ones under the regulation of oxidation potentials and intra- and intermolecular electron transfers. We report herein our initial efforts to develop the novel electrocatalytic intermolecular formal [2+2] cross-coupling of electron-rich olefins.

Initially, the electrolytic cycloaddition between enol ethers **1-3** and allyltrimethylsilane **4** was studied (Fig. 1).

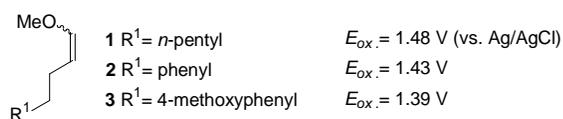


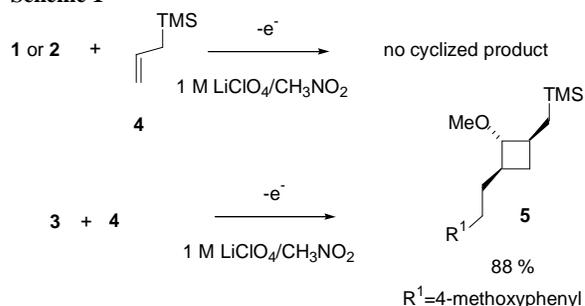
Figure 1. Structures and oxidation potentials of electrolytic substrates.

Anodic oxidation of enol ethers was accomplished using a carbon felt anode, a constant current of 2.5 mA, a carbon felt counter electrode, 1.0 M lithium perchlorate / nitromethane electrolyte solution in an undivided cell. Electrolytic substrates **1** or **2** gave no major cyclized product with **4** in the anodic reaction condition. On the other hand, it was surprising that the anodic activation of the enol ether **3** in the presence of 3 mole equivalents of **4** selectively led to their intermolecular cross-coupling to form corresponding [2+2] cycloadduct **5** in 88 % yield (Scheme 1).

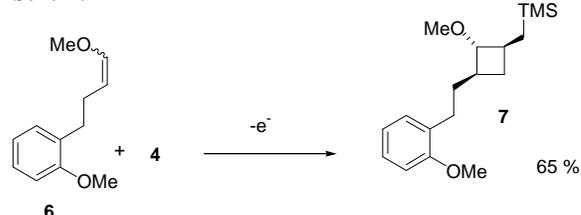
Anodic oxidation of *o*-methoxyphenyl derivative **6** in the presence of **4** also gave the desired cycloadduct **7** (Scheme 2). These reactions clearly show that a methoxyphenyl group in enol ether molecules play an important role in those electrocatalytic cycloadditions. The cycloaddition reaction should be initiated by the anodic oxidation of the enol ether, followed by intermolecular carbon-carbon bond formation. To this end, intramolecular disproportionation between the radical cation and the methoxyphenyl group must have taken place to complete the formation of the four-

membered ring. The *in situ*-generated methoxyphenyl radical cation regenerates the radical cation of the enol ether by intermolecular disproportionation (Scheme 3).

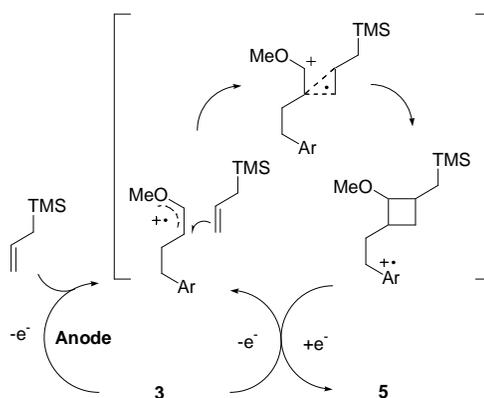
Scheme 1



Scheme 2



Scheme 3. A proposed reaction mechanism of the electrocatalytic intermolecular olefin coupling.



References

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