**Electrochemistry**

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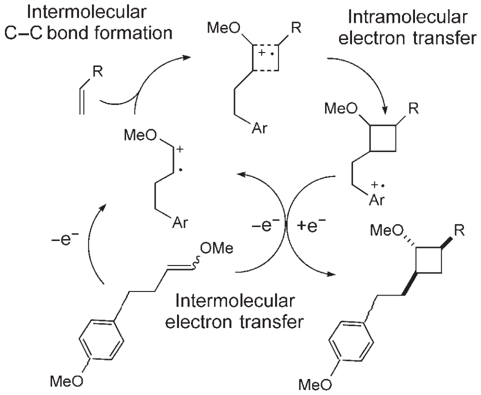
# Electrochemical Enol Ether/Olefin Cross-Metathesis in a Lithium Perchlorate/Nitromethane Electrolyte Solution**

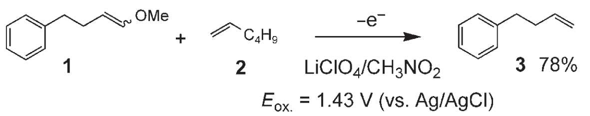
*Teppei Miura, Shokaku Kim, Yoshikazu Kitano, Masahiro Tada, and Kazuhiro Chiba**

Transition-metal-catalyzed olefin cross-metathesis plays an important role in the construction of various carbogenic skeletons by allowing the exchange of substituents between different olefins via an activated key intermediate consisting of a four-membered ring coordinated to a transition metal.[1] Alternatively, electrochemical reactions have proven to be a viable method in triggering reactions between different olefins by reversing the polarity of alkenes[2] and initiating radical anion-[3] (or cation-[4]) based reactions.[5] Electrochemically activated olefin cyclodimerization, for example, can effectively lead to the intermolecular formation of four-membered rings.[6] Moreover, we reported an electrocatalytic intermolecular formal [2+2] cross-coupling of electron-rich olefins (Scheme 1).[7] The anodic oxidation of enol ethers[8] that bear a methoxyphenyl group can be used to trigger an intermolecular formal [2+2] cycloaddition with varied alkenes. In this case, the intermolecular olefin coupling was assisted by a unique lithium perchlorate/nitromethane electrolyte solution[9] and the methoxyphenyl group of the substrates served as an intramolecular electron donor[10] to form the cyclobutane ring. Herein, we describe novel electrochemical olefin cross-metatheses between anodically activated enol ethers and aliphatic alkenes.



**Scheme 1.** Anodic intermolecular formal [2+2] cross-coupling of olefins.

Initially, the electrolytic intermolecular reaction between 4-methoxybut-3-enylbenzene (**1**) and hex-1-ene (**2**) was investigated. The anodic oxidation of enol ether **1** involved a carbon felt anode, a constant potential of 1.43 V (vs. Ag/AgCl), a carbon felt counter electrode, and a lithium perchlorate/nitromethane electrolyte solution (1.0 M) in an undivided cell under argon. Remarkably, the anodic activation of enol ether **1** in the presence of **2** resulted in the formation of but-3-enylbenzene (**3**) in 78 % yield (Scheme 2).



**Scheme 2.** Electrochemical olefin cross-metathesis of 4-methoxybut-3-enylbenzene (**1**) and hex-1-ene (**2**) in lithium perchlorate/nitromethane electrolyte solution.

In our experiments, the reaction was deemed complete after the passage of approximately 1.0 F mole$^{-1}$ of electricity. Under different electrolytic conditions, the desired product was obtained in trace or in unacceptable yields (Table 1). In the absence of electrolysis, a mixture of **1** and **2** in lithium perchlorate/nitromethane electrolyte solution at ambient temperature did not react, even after more than 10 h.

**Table 1:** Electrolytic cross-metathesis of 4-methoxybut-3-enylbenzene (**1**) and hex-1-ene (**2**) under different conditions.

| Electrolyte | Solvent | Electricity [F mole$^{-1}$] | Yield (**3**)[a] [%] |
|---|---|---|---|
| $LiClO_4$ | $CH_3NO_2$ | 1.0 | 78 |
| $LiClO_4$ | $CH_3NO_2$ | 0.5 | 40[b] |
| $LiClO_4$ | $CH_3NO_2$ | 0.3 | 30[c] |
| $LiClO_4$ | $CH_3NO_2$ | 0 | n.d.[d] |
| $Me_4NClO_4$ | $CH_3NO_2$ | 1.0 | 4 |
| $Bu_4NClO_4$ | $CH_3NO_2$ | 1.0 | n.d. |
| $Me_4NClO_4$ | $CH_3CN$ | 1.0 | n.d. |
| $LiClO_4$ | $CH_3CN$ | 1.0 | 3 |

[a] Yields were determined by gas chromatography (n.d. = not detected). [b] 38 % of **1** was recovered. [c] 55 % of **1** was recovered. [d] More than 99 % of **1** was recovered.

Furthermore, the reaction was responsive to a stepwise application of the electricity. Because the amount of the product for each stage remained essentially unchanged during the intervals of electrolysis, an external switch of the electrolysis allows the regulation of the reaction process.

The electrochemical enol ether/olefin cross-metathesis can also be extended to the combination of simple alkyl enol ethers and alkenes. For example, anodic oxidation of 1-methoxy-tridec-1-ene (**4**) in the presence of **2** afforded the desired tridec-1-ene (**5**) in 76 % yield (Scheme 3).

To gain insight into the reaction mechanism, the anodic activation of enol ether **1** was carried out with deuterium-

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[*] T. Miura, Dr. S. Kim, Prof. Y. Kitano, Prof. M. Tada, Prof. K. Chiba
Laboratory of Bioorganic Chemistry
Tokyo University of Agriculture and Technology
3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509 (Japan)
Fax: (+81) 42-360-7167
E-mail: chiba@cc.tuat.ac.jp

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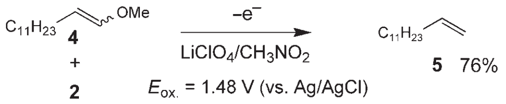
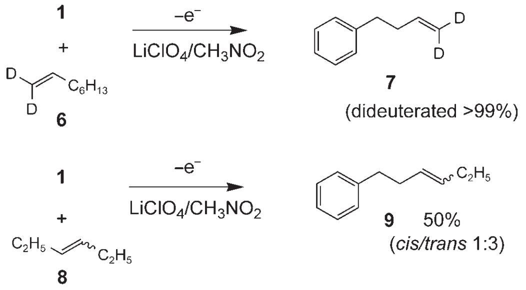


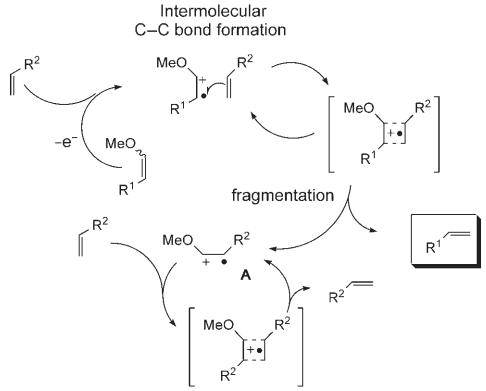
**Scheme 3.** Electrochemical olefin cross-metathesis between alkyl enol ether **4** and hex-1-ene (**2**).

labeled olefin **6** (Scheme 4). The formation of almost completely dideuterated product **7**[11] helped to verify our proposed cross-metathesis pathway. Moreover, under the same reaction conditions, an internal olefin, hex-3-ene (**8**), resulted in the carbon-chain-elongated product **9**.



**Scheme 4.** Electrochemical olefin cross-metathesis of enol ether **1** with deuterated olefin **6** or internal olefin **8**.

Notably, these electrochemical enol ether/olefin cross-metathesis reactions also give rise to a trace amount of the alternate fragment as the enol ether—for example, **4** was detected in the electrochemical reaction mixture of **1** and **5** along with main product **3**. Accordingly, a radical-cation-assisted fragmentation must have taken place to complete the formation of the metathesis products. The radical cation (fragment **A**) generated in situ from the enol ether could regenerate the radical cation of the starting enol ether by intermolecular electron transfer. On the other hand, the presence of a methoxyphenyl group should complete the formation of the corresponding four-membered ring. Except for specific enol ethers with neighboring oxidizable moieties that exhibit oxidation potentials of reasonable relative values, most enol ethers, however, should form the cross-metathesis products without completion of the intramolecular electron-transfer-assisted cyclobutane formation. In a cyclic voltammetry study, the anodic oxidation peak of **1** appeared at 1.43 V (vs. Ag/AgCl) with no cathodic peak.[12] The oxidation current of enol ether **1** was observed in the region 0.8–1.55 V (vs. Ag/AgCl). Anodic oxidation of the mixture of **1** and **2** in lithium perchlorate/nitromethane at around the lowest potential of the region (0.8–1.0 V vs. Ag/AgCl) also gave the desired product **3**. On the other hand, aliphatic alkene **2** in lithium perchlorate/nitromethane gave no clear oxidation peak in the region 0–1.6 V (vs. Ag/AgCl). The results suggest that cross-metathesis is initiated by anodic oxidation of the enol ether, followed by the formation of the key intermediate—a four-membered radical-cation ring—from the activated enol ether and alkene (Scheme 5).



**Scheme 5.** Proposed reaction mechanism of electrochemical olefin cross-metathesis.

In conclusion, anodic-oxidation triggers olefin cross-metathesis reactions between enol ethers and alkenes in a lithium perchlorate/nitromethane electrolyte solution. Intermolecular reactions allow the exchange of carbon fragments between even simple alkyl enol ethers and alkenes. Because the oxidation potentials of enol ethers are relatively low, the reaction may involve inter- and intramolecular enol ether/olefin cross-metathesis, thus avoiding overoxidation of substrates. In this reaction system, the synergistic effects of the electrochemical activation of the enol ether and the stabilization of the radical-cation intermediates in a suitable electrolyte solution should effectively help to form the active key intermediate. Efforts to expand the scope of this electrochemical methodology for the synthesis of various alkenes and to extend the work to intramolecular reactions are currently underway.

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