

SYNLETT Spotlight 187

The Electron: The Simplest Chemical Reagent¹

Compiled by Mohammad Rafiee

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Mohammad Rafiee was born in Malayer (Iran) in 1979. He completed his M.Sc. (2002) and is currently working towards his Ph.D. in Electrochemistry, under the supervision of Prof. D. Nematollahi at Bu-Ali Sina University in Hamadan. His research interests include Electrochemical synthesis and Electroanalysis.

Faculty of Chemistry, Bu-Ali Sina University, Hamadan 65174 Iran
E-mail: m-rafiee@basu.ac.ir



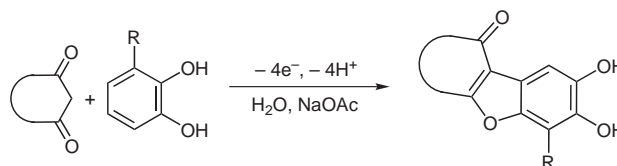
Introduction

In this manuscript some new aspects of electroorganic synthesis as a powerful method in organic chemistry are presented. Since the development of the Kolbe reaction in 1854 electrosynthesis has become more and more important in organic chemistry due to its following characteristics: unique selectivity because of in situ formation of an active species at the interface, inversion in polarity by transfer of electron and variability in product formation by control of potential.² The most dominant advantage of using this chemical reagent are its adaptability to technology and flexibility in use. The use of water or ionic liquids

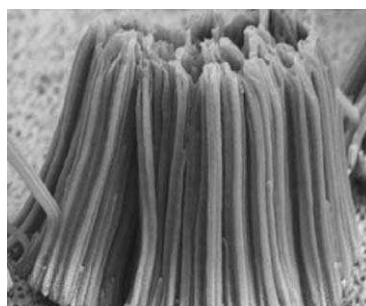
instead of toxic solvents, room temperature condition, high energy efficiency and using the electrode as electron source instead of toxic reagents are in accord with the principle of green chemistry.^{3a} Using nanomaterials in the electrode and the synthesis of nanomaterials based on electrochemical polymerization are interfaces with nanotechnology.⁴ The use of modified electrodes or electrochemical mediators increases product yields.⁵ Also, modification with enzymes provides highest chemo-, regio- and stereoselectivity, which is compatible with scopes of biochemistry.⁶

Abstracts

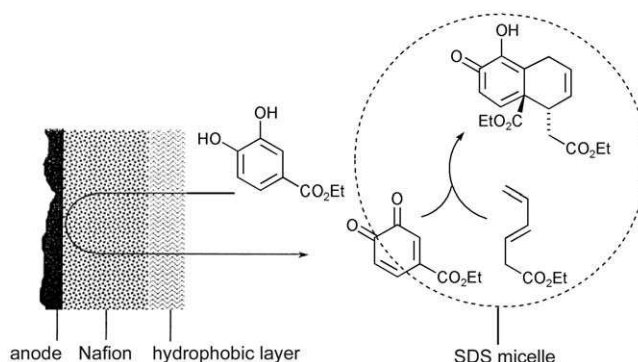
A) Nematollahi's research group works on the development of electrochemical methods for the synthesis of new organic compounds.³ Electrochemical oxidation of benzenedioles in the presence of β -diketones as a facile and green method was used for the synthesis of new benzofuran derivatives in aqueous solutions with high atom economy and safe waste under ambient conditions.^{3a}



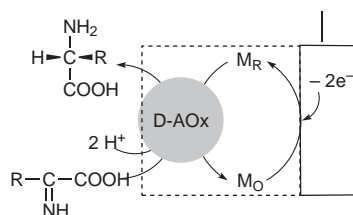
B) Nanotubes and nanowires of conducting polymers such as polypyrrole and polyaniline were synthesized by using nanoporous templates such as alumina through electrochemical polymerization. Their dimensions were about 100 nm to 20 μ m. These tubes show an enhancement of the electronic conductivity compared to bulk materials. They also show better properties (morphology, degree of delocalization and conductivity) compared to those tubes synthesized by a chemical method with the same templates.⁴



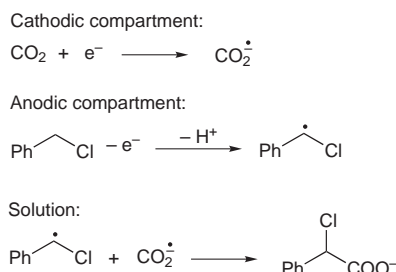
C) Chiba et al. showed that modified electrodes enhanced the product yield. For example, Diels–Alder reaction of in situ generated quinones with dienes is accomplished in excellent yields in an aqueous sodium dodecyl sulfate solution by selective electrooxidation on a glassy carbon electrode modified by cation-exchange resin.⁵



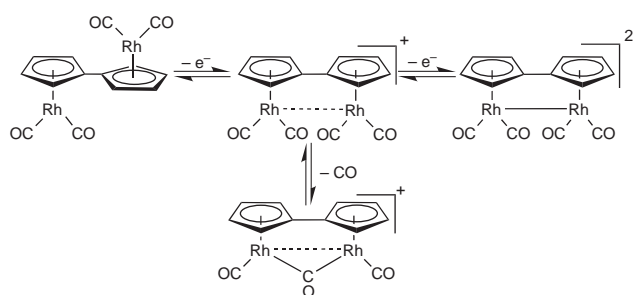
D) Immobilization of enzymes and electron mediators on the surface of the electrode led to asymmetric electrochemical reactions.^{6a} For example, asymmetric synthesis of amino acids has been successfully achieved by electrochemical reduction of an imino acid using an electrode modified with amino acid oxidase and electron mediator. Enantiomeric excesses close to 100% were achieved.^{6b}



E) Paired electrosynthesis is a unique example of reaction design in organic and inorganic synthesis. In this method both reactive species that form at the anode and the cathode participate in desired reactions.⁷ For example, reduction of CO₂ to the anion radical at the cathode and oxidation of benzyl chloride at the anode produce α -chlorophenylacetic acid (36%) and α -phenylacetic acid (47%).^{7b}



F) Geiger and his research group work on the synthesis and electrochemistry of some interesting organometallic compounds. The anodic oxidation of compounds having two Rh-containing moieties linked by a fulvalendiyl dianion has been studied in varying electrolyte media. The effects of the supporting electrolyte and solvent were studied on stabilization of 1⁺- and 2⁺-cations and it was shown that the medium effect is a powerful method for manipulating the equilibrium concentrations of the various redox states that make up a multiple-electron-transfer process.⁸



References

- (1) The title of this spotlight derives from an expression used by Prof. W. E. Geiger.
- (2) Shono, T. *Electroorganic Synthesis*; Academic Press: San Diego, **1991**.
- (3) (a) Nematollahi, D.; Rafiee, M. *Green Chem.* **2005**, *7*, 638. (b) Nematollahi, D.; Rafiee, M. *J. Electroanal. Chem.* **2004**, *566*, 31. (c) Nematollahi, D.; Habibi, D.; Rahmati, M.; Rafiee, M. *J. Org. Chem.* **2004**, *69*, 2637. (d) Nematollahi, D.; Goodarzi, H. *J. Org. Chem.* **2002**, *67*, 5036. (e) Nematollahi, D.; Workentin, M. S.; Tammari, E. *Chem. Commun.* **2006**, 1631.
- (4) (a) Yang, S. M.; Chen, K. H.; Yang, Y. F. *Synth. Met.* **2005**, *152*, 65. (b) Joo, J.; Park, K. T.; Kim, B. H.; Kim, S. M.; Lee, S. Y.; Jeong, C. K.; Lee, D. H.; Park, D. H.; Yi, W. K.; Lee, S. H.; Ryu, K. S. *Synth. Met.* **2003**, *7*, 135. (c) Park, D. H.; Kim, B. H.; Jang, K. M.; Bae, K. Y.; Lee, S. J.; Joo, J. *Synth. Met.* **2005**, *153*, 341.
- (5) Chiba, K.; Jinno, M.; Nozaki, A.; Tada, M. *Chem. Commun.* **1997**, 1403.
- (6) (a) Yuan, R.; Watanabe, S.; Kuwabata, S.; Yoneyama, H. *J. Org. Chem.* **1997**, *62*, 2494. (b) Kawabata, S.; Iwata, N.; Yoneyama, H. *Chem. Lett.* **2000**, *2*, 110.
- (7) (a) Otero, M. D.; Batanero, B.; Barba, F. *Tetrahedron Lett.* **2005**, *46*, 8681. (b) Otero, M. D.; Batanero, B.; Barba, F. *Tetrahedron Lett.* **2006**, *47*, 2171.
- (8) Nafady, A.; Chin, T. T.; Geiger, W. E. *Organometallics* **2006**, *25*, 1654.