

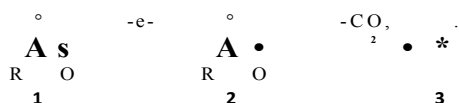
ELECTROCHEMICAL ACTIVATION OF AROMATIC ACIDS: NEW WAY OF ACCESS TO BENZOYLOXY RADICALS

S. Kaumbekova, M. Sultanov, S. Zhumagali, A. Baibek, K. Lam*

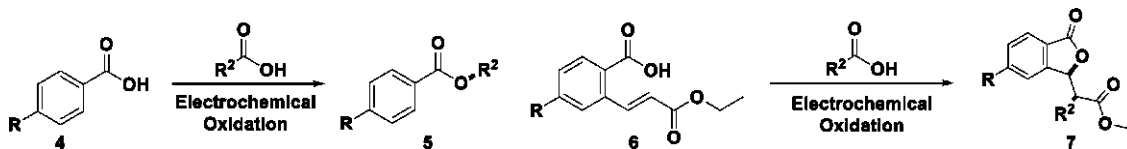
School of Science and Technology, Nazarbayev University, Astana, Kazakhstan; *kevin.lam@nu.edu.kz

Introduction. Electrochemistry is a powerful tool in organic chemistry even though its full potential is largely underestimated. Indeed, most organic electrosyntheses are not only more ecologically friendly but also far cheaper than more conventional chemical reactions.

Methodology. To the best of our knowledge, only few methods for generating benzyloxy radicals have been reported in the literature. Generation of oxygen-centered radicals very often implies the synthesis of moderately stable compounds [1] or the use of toxic strong oxidants [2]. As a result, benzyloxy radicals have been rarely used as chemical reagents but most of the time as a radical-chain initiator. The use of the Kolbe reaction, in order to generate benzyloxy radicals, would represent not only a greener and safer but also a cheaper alternative to the traditional chemical methods. The Kolbe electrolysis usually allows the generation of carbon-centered radicals, in a very simple manner: the carboxylate **1** is electrochemically oxidized into the carboxyl radical **2** which usually rapidly loses carbon dioxide to form the radical **3** [3]. However, to the best of our knowledge, the Kolbe reaction has never been used to generate oxygen-centered radical.



Results. Although aromatic carboxylates have been reported to not undergo Kolbe reaction [4], much to our surprise, previous results showed that electrolysis of benzoic acid **4**, in presence of an excess of aliphatic acid, leads cleanly to the formation of the ester **5** which presumably results from a recombination between a benzyloxy radical and a radical formed by the Kolbe decarboxylation of the aliphatic acid. Such process indeed allows the formation of esters under very mild conditions but more importantly, this would also represent a new easy way to prepare lactones **7**. In fact, the reaction is quite robust and could be performed under air, in neutral or slightly acidic wet methanol.



Acknowledgments. We thank Nazarbayev University for supporting this project under the grant № KФ-14/01.

References.

- (a) D. H. R. Barton, J. M. Beaton, L. E. Geller, M. M. Pechet, *J. Am. Chem. Soc.* **1960**, *82*, 2640. (b) A. L. J. Beckwith, B. P. Hay, G. M. Williams, *J. Chem. Soc., Chem. Commun.* **1989**, 1202. (c) D. J. Pasto, F. Cottard, *Tetrahedron Lett.* **1994**, *35*, 4303.
- (a) T.-L. Ho, *Cerium(IV) Oxidation of Organic Compounds in Organic Synthesis by Oxidation with Metal Compounds* (Eds.: W. J. Mijs, C. R. H. I. De Jonge), Plenum, New York, **1986**, pp. 569–631. (b) V. M. Micovic, R. I. Mamuzic, D. Jeremic, M. Lj. Mihailovic, *Tetrahedron* **1964**, *20*, 2279. (c) J.-M. Surzur, M.-P. Bertrand, *Bull. Soc. Chim. Fr.* **1973**, 1861.
- (a) H. J. Schafer, *Top. Curr. Chem.* **1990**, *152*, 91. (b) H. J. Schafer in *Comprehensive Organic Synthesis* (Ed.: B. M. Trost, I. Fleming), Pergamon, **1991**, *Vol. 3*, p. 633
- H. J. Schafer, *Top. Curr. Chem.* **1990**, *152*, 91