

Euroorganicchemistry 2019: Anodic electro oxidation a key tool in the synthesis of natural quinones and kinetic study - Guillermo A. Guerrero Vásquez - BetaTec Hop products Ltd

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Abstract

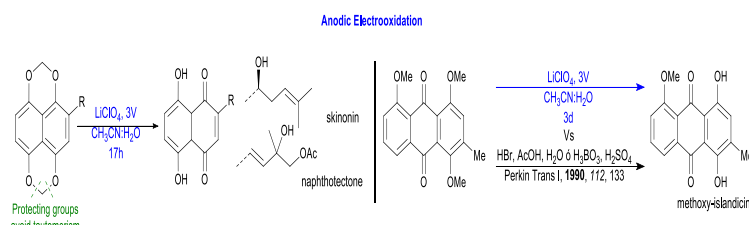
The formation of natural occurring quinones from protected intermediates compounds, involves a series of steps of oxidation and deprotection, whose limitations are the number of steps that involve a reduction in the yields and sensitive of the intermediate quinones to the Lewis acids¹.

The anodic electrooxidation methodology has showed to be an efficient procedure to generate the final deprotection and oxidation treatment² that involved available starting materials in any organic chemistry laboratory. Experimental set-up was made with graphite electrodes under argon by using mixtures of LiClO₄ (0.01 M) in H₂O/CH₃CN (1:1) as the electrolyte.

When methoxy moiety is used as protective group, reaction proceeds in two steps. First step of oxidation: electrolysis at 1.71 V for 21 h to generate a quantitative mixture of structural isomers. Second step of demethylation and tautomerization: electrolysis at 3.09 V for 7 h transformed the structural isomers into the desired quinone target. By contrast, when using methylenedioxy as protector, no intermediate was observed by TLC. Both steps proceed at 1.7 V for 17 h to the clean conversion into quinones moiety. The reaction yields oscillate between 64-96%.

Quinones crudes prepared by this methodology can be used directly in the following reaction steps. In addition, quinones can be easily purified by using a Sephadex LH-20 column with isocratic H₂O/CH₃CN mixtures. The main problem is the retention of naftazarine derivatives in the stationary phase of the columns, which generates a reduction in the reaction yields (see table 1).

A complementary study of chemical kinetics suggests a first order reaction and that this reaction is governed by a radical reaction.



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- (a) K. C. Nicolaou, D. Hepworth, *Angew. Chem. Int. Ed.* **1998**, *37*, 839-841. (b) G. A. Guerrero-Vásquez, F. A. D. Galarza, C. K. Z. Andrade, J. M. G. Molinillo, F. A. Macías, *Eur. J. Org. Chem.* **2016**, 1599-1605. (c) G. A. Guerrero-Vásquez, C. K. Z. Andrade, J. M. G. Molinillo, F. A. Macías, *Eur. J. Org. Chem.* **2013**, 6175-6180.

Electrosynthesis, a historically powerful tool for the assembly of variety of industrial-scale inorganic or organic materials, has experienced a renaissance over the last ten years with research efforts seeking a dual production platform for molecules and energy carriers. most well-known characteristic of the catechols is that they will be easily oxidized mainly thanks to their antioxidant activity and low oxidation potentials. most well-known characteristic of the catechols is that they will be easily oxidized mainly thanks to their antioxidant activity and low oxidation potentials. one among the foremost important parameters in antioxidant activity is that the oxidation potential of the specified antioxidant; an implication of this study is that the possibility of synthesis of structure and pH tunable compound with both catechol and diphenylamine groups. The antioxidants activity of those compounds are going to be a topic of interest, considering the likelihood of formation of both phenoxyl and aminylradicals.

Additionally, we've reported the quantitative study of reaction of o-quinones with N-methylaniline at various pH values.

Biography

Guillermo A. Guerrero Vásquez was born in Tolima, Colombia. He received his B.Sc in Chemistry in 2007 from the University of Quindio, Colombia and was awarded a M.Sc. 2009 and Ph.D. 2015 in organic chemistry both from University of Cadiz, Spain under the supervision of Prof. Francisco A. Macias and Prof. Jose M. G. Molinillo.

His Ph.D. obtained a international mention for the stage of six months with the professor Brian M. Stoltz at California Institute of Technology, USA as visiting student researcher in 2012. He conducted postdoctoral studies firstly with Prof. Jacques Lebreton and Dr. Sylvain Collet at the University of Nantes, France in 2015-2016 and then with Prof. Francisco R. Sarabia at University of Malaga, Spain in 2016-2017. Currently he is working in the Chemistry department at BetaTec Hop products Ltd., in Worcestershire, UK. His research interests include synthetic methodology, natural product synthesis and all aspects of medicinal chemistry.