Accepted Manuscript

Title: Decarboxylative bromination of α,β-unsaturated carboxylic acids *via* an anodic oxidation

Authors: Mei-Xiang Bi, Peng Qian, Yu-Kang Wang, Zheng-Gen Zha, Zhi-Yong Wang

PII: S1001-8417(17)30167-5
DOI: http://dx.doi.org/doi:10.1016/j.cclet.2017.04.030
Reference: CCLET 4066

To appear in: *Chinese Chemical Letters*

Received date: 14-2-2017
Revised date: 19-4-2017
Accepted date: 25-4-2017

Please cite this article as: Mei-Xiang Bi, Peng Qian, Yu-Kang Wang, Zheng-Gen Zha, Zhi-Yong Wang, Decarboxylative bromination of α,β-unsaturated carboxylic acids via an anodic oxidation, Chinese Chemical Lettershttp://dx.doi.org/10.1016/j.cclet.2017.04.030

Original article

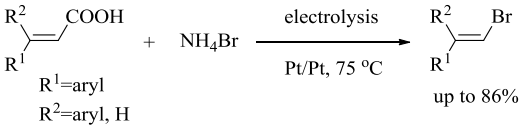
Decarboxylative bromination of *α,β*-unsaturated carboxylic acids *via* an anodic oxidation

Mei-Xiang Bi, Peng Qian, Yu-Kang Wang, Zheng-Gen Zha*, Zhi-Yong Wang*

Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei 230026, China

∗ Corresponding authors.
E-mail addresses: zgzha@ustc.edu.cn (Z.-G. Zha); zwang3@ustc.edu.cn (Z.-Y. Wang)

Graphical Abstract



A novel bromination of *α,β*-unsaturated carboxylic acids was developed *via* a decarboxylation by virtue of a direct anodic electro-oxidation. In this method, ammonium bromide was employed as a bromine source and the reaction features transition-metal-free, short time, and no additional supporting electrolyte.

ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form 19 April 2017
Accepted 21 April 2017
Available online

Keywords: Decarboxylative bromination
α,β-Unsaturated carboxylic acids
Ammonium bromide
Anodic oxidation
Electro-oxidation

ABSTRACT

A novel bromination of *α,β*-unsaturated carboxylic acids was developed *via* a decarboxylation by virtue of a direct anodic electro-oxidation. In this method, ammonium bromide was employed as a bromine source and the reaction features transition-metal-free, short time, and no additional supporting electrolyte.

1. Introduction

Decarboxylative bromination of the carboxylic acids is useful in organic chemistry to obtain bromo-compounds [1]. A number of metal catalysts including mercury, lithium, lead, manganese, silver [2-6] and non-metallic hypervant iodine [7, 8] were employed to access these bromo-compounds. Besides, decarboxylative bromination catalyzed by $NaNO_2$ in combination with HBr in the presence of oxygen was reported previously [9]. However, most of these reactions usually involved heavy metal salts with a little slow process although these methods are highly efficient. As a result, a green alternative methodology for decarboxylative bromination is still desirable.

As far as we know, there has been no report on decarboxylative bromination via an electrochemical oxidation yet. Our group have developed a series of electrochemical routes toward various organic transformations [10-16]. This encourages us to make use of electrochemistry to accomplish a decarboxylative bromination directly. Herein we report an electrochemical decarboxylative bromination of cinnamic acids in aqueous media. This method features transition-metal-free, shorter time and no additional supporting electrolyte.

2. Results and discussion

Initially, the reaction of cinnamic acid **1a** with sodium-bromide in an undivided cell equipped with a pair of C–C electrodes. The mixture was electrolyzed under a constant current of 40 mA with continuous stirring at room temperature for 1 h. Among various