



Electrochemical double carboxylation of unsaturated C-C bonds with carbon dioxide: An overview

Navid Salehi^a, Bayan Azizi^{b,*}

^a Edare Amozesh va Parvaresh Ziviyeh, Kordestan, Iran

^b College of Health Sciences, University of Human Development, Sulaimaniyah, Kurdistan region of Iraq

ARTICLE INFO

Article history:

Received 8 February 2021

Received in revised form 25 April 2021

Accepted 5 May 2021

Available online 5 May 2021

Keywords:

Carbon dioxide, electrosynthesis, dicarboxylation, dicarboxylic acids, unsaturated C-C bonds.

ABSTRACT

In this review, we try to provide a comprehensive and updated overview of recent advances on the synthesis of dicarboxylic acids through electrochemical decarboxylation of unsaturated hydrocarbons with carbon dioxide. We have classified these reactions based on the type of starting materials. Thus, the review is divided into three major sections. The first section will cover dicarboxylation of alkenes. The second focuses exclusively on dicarboxylation of dienes. The third will discuss dicarboxylation of alkynes.

1. Introduction

Carbon dioxide (CO₂) is the primary greenhouse gas emitted through human activities and caused serious environmental problems [1]. On the other hand, it is an easily accessible, abundant, nontoxic, nonflammable, and renewable source of carbon [2-10]. Therefore, chemical fixation of carbon dioxide into valuable organic compounds is of great importance from the viewpoints of environmental and green chemistry. However, CO₂ is a thermodynamically and kinetically stable molecule which its activation typically requires large energy inputs (e.g., drastic reaction conditions and innovative catalytic processes) [11]. In fact, efficient chemical incorporation of CO₂ is specifically limited to the use of highly reactive molecules such as aziridines [12] and epoxides [13]. Therefore, development of novel strategies for truly efficient chemical transformations of CO₂ is an exceedingly attractive research subject in modern organic synthesis.

Organic electrosynthesis is an extremely versatile and powerful synthetic tool that circumvents the use of expensive catalysts, oxidants or ligands, thus being framed within the principles of green chemistry [14]. In this context, electrochemical methods have been widely used for the synthesis of various value-added chemicals utilizing CO₂ as a C1-building block [15]. Among various electrochemical CO₂-fixation reactions, carboxylation of

carbon nucleophiles by reaction of CO₂ has attracted much attention in recent years. In 2014, De Vos and co-workers highlighted this synthetic strategy in their interesting review paper entitled "electrocarboxylation: towards sustainable and efficient synthesis of valuable carboxylic acids" [16]. However, double carboxylation of unsaturated C-C bonds was omitted. In continuation of our reviews of new methodologies on chemical conversion of CO₂ [17] and modern organic synthesis [18], herein, we will highlight the most important developments on the electrochemical dicarboxylation of unsaturated C-C bonds. The review is divided into three major sections. The first section will cover dicarboxylation of alkenes. The second focuses exclusively on dicarboxylation of dienes. The third will discuss dicarboxylation of alkynes.

2. Double carboxylation of alkene

In 1992, Duñach and co-workers published one of the earliest examples of the dicarboxylic acids preparation through the electro-dicarboxylation of corresponding alkenes with CO₂ [19].

They showed that the treatment of a library of styrene derivative **1** with atmospheric CO₂ in the presence of a catalytic amount of Ni-PMDTA in an undivided cell with magnesium anode and carbon fiber cathode in DMF

* Corresponding author. e-mail: bayan.azizi@uhd.edu.iq