

## Review

## Advancements in oxazolidinone synthesis utilizing carbon dioxide as a C1 source

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## ABSTRACT

Carbon dioxide, a natural molecule, has been utilized in the synthesis of chemicals for several decades. Its innocuous chemical properties make it a favorable substance to incorporate in such synthetic processes. Recently, research is being conducted to include carbon dioxide in the production of a specific class of cyclic urethane molecules known as oxazolidinones. Oxazolidinones are important in synthetic and medicinal applications, which necessitate a greener method to produce them. In this review, various synthetic methods including catalytic processes that incorporate carbon dioxide to yield oxazolidinones have been discussed and the results of the research are presented. Emphasis is placed primarily on reactions of carbon dioxide with a variety of aziridines, propargylamines and 2-amino alcohols for the synthesis of oxazolidinones.

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## 1. Introduction

The use of carbon dioxide (CO<sub>2</sub>) for the synthesis of various fine and bulk-chemicals has attracted the interest of various research communities over several decades. CO<sub>2</sub>, one of the major man-made greenhouse gases, is a nontoxic, nonflammable, and inexpensive molecule. It has a large atmospheric abundance of about  $2.3 \times 10^{12}$  t [1], which makes it a viable alternative to other substances that are being depleted. From a green chemical standpoint, it is an invaluable chemical resource based on the facts that CO<sub>2</sub> can be recovered as a by-product of various industrial processes or can be acquired from natural reservoirs and its capability to replace toxic chemicals such as phosgene [2],

cyanic acid [3], and carbon monoxide [4] in various synthetic processes. The industrial syntheses of urea, cyclic carbonates, salicylic acid, and methanol already utilize carbon dioxide as a reactant [5]. Within the scope of green chemistry, CO<sub>2</sub> sequestration has called for the development of new synthetic approaches. 2-Oxazolidinones (OXZs), a class of cyclic urethane molecules known for their synthetic and medicinal applications [6], have attracted the interest of scientific community towards developing new synthetic approaches, especially using CO<sub>2</sub>. Various research efforts have been made in developing synthesis of OXZs using carbon dioxide as a chemical source. In this review, we present a discussion on various approaches adopted for the synthesis of OXZs from different substrates utilizing CO<sub>2</sub>.

The 2-oxo-1,3-oxazolidine ring is a cyclic carbamate skeleton that occupies a special place among heterocyclic compounds. OXZs have been known to be used as chiral auxiliaries since the report of such use of enantiomerically pure 4-substituted oxazolidin-2-ones in asymmetric synthesis by Evans [7]. They are widely used in

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medicine for pharmaceutical preparations [8], in the paint and varnish industry, and in polymer synthesis to prepare foams, coatings, etc. [9]. The polymers containing OXZ rings are known to have effective physicochemical properties including high thermal stability.

Various synthetic organic chemists have put forward considerable efforts in the synthesis of OXZs using various substrates in the presence of CO<sub>2</sub>. Based on the class of substrate used, these can be categorized into three major groups: (i) insertion of CO<sub>2</sub> into the aziridine moiety, (ii) reaction of propargylamines with CO<sub>2</sub>, and (iii) reaction of 2-amino alcohols with CO<sub>2</sub>. This review will briefly discuss existing literature on OXZ synthesis with emphasis on catalysis of the reactions based on these three synthetic methods.

## 2. Oxazolidinone synthesis

### 2.1. Synthesis of oxazolidinones from aziridines and CO<sub>2</sub>

Aziridines are considered to be important three-membered ring functionalities in organic synthesis [10]. Structurally, aziridines are analogous to epoxides with the nitrogen group replacing the oxygen. The chemistry of aziridines has been studied over the last few decades and their applications have been greatly expanded. One such application of aziridines is in the synthesis of OXZs (Fig. 1). A green approach of this synthesis in the presence of CO<sub>2</sub> has been studied by various research groups both in catalytic and non-catalytic pathways.

In 1976, use of iodine (I<sub>2</sub>) for the synthesis of OXZs from aziridines and CO<sub>2</sub> was reported by Soga et al. [11]. In a simple synthesis of OXZs from molecules like aziridines, 2-methylaziridine was made with yields of OXZs as high as 80.5%. A regioselective synthesis of OXZs using organoantimony halides was reported by Nomura et al. [12]. Organoantimony halides reportedly aided in the cycloaddition by  $\alpha$ -cleavage. Organotin halides were also studied in this same report. Due to their stronger Lewis acidity as compared to organoantimony compounds, they were reported to cause dimerization of aziridines under the applied reaction conditions.

After over a decade, nickel (Ni) complexes of cyclam or bipyridine ligands were studied for the efficient catalytic insertion of the carbon dioxide into aziridines [13]. Under the electrochemical conditions, these catalysts were found to be effective with regioselectivities of 60–86%. The experimental conditions were mild, CO<sub>2</sub> pressure at 1 atm and room temperature, which provides a “greener” chemical approach from previously existing harsh methods. Another research group led by Kawanami et al. discovered an effective use of I<sub>2</sub> as an active Lewis acid catalyst for the regiospecific synthesis of OXZs in supercritical CO<sub>2</sub> [14]. This study shows a decrease in the yield of the OXZ product with increase in CO<sub>2</sub> pressure. Kawanami et al. stated a probable explanation to this anomaly was due to the variation of CO<sub>2</sub> content in the different phases of the reaction medium (liquid or supercritical). The source of OXZ reduction could be from the decrease in polarity of the solvent medium. At the given temperature, the polar liquid phase containing only the co-solvent would change to a less polar phase made up of CO<sub>2</sub> and co-solvent. This further increase in pressure results in increase of non-polar CO<sub>2</sub> content, which prevents the formation of the OXZ product.

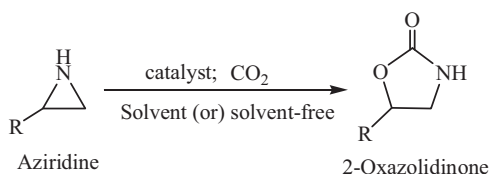


Fig. 1. Synthesis of 2-oxazolidinones from aziridines.

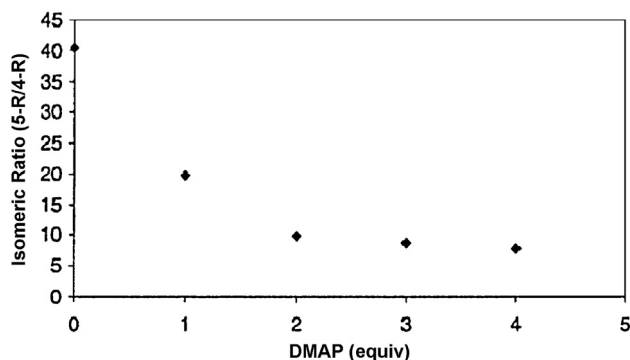


Fig. 2. Ratio of 5-substituted to 4-substituted isomers in the reaction of CO<sub>2</sub> and *N*-propyl 2-phenylaziridine as a function of DMAP concentration. Reprinted with permission from Miller and Nguyen (2004). Copyright (2004) American Chemical Society.

In 2004, a binary complex of (salen)chromium(III) (Cr) and 4-dimethylaminopyridine (DMAP) [15] was reported by Miller and Nguyen to effectively catalyze the coupling of CO<sub>2</sub> and aziridines under mild reaction conditions. This study reported for the first time an effective catalyst for the synthesis of OXZs with the formation of large excess, about 40:1, of the 5-substituted isomer over the 4-substituted OXZ for a wide range of substrates. This study indicates that contrary to the analogous epoxide/CO<sub>2</sub>, this aziridines/CO<sub>2</sub> coupling does not need a co-catalyst to proceed. An interesting influence of catalyst/co-catalyst ratio on the yield of the 5-substituted compounds was observed (Fig. 2). At the optimum ratio of catalyst to co-catalyst (i.e. 2), the ratio of 5-substituted to 4-substituted isomers was observed to be 8:1. While in the absence of the co-catalyst, as studied using *N*-propyl-2-phenylaziridine, the ratio of isomers was found to be 40:1, favoring 5-phenyl-*N*-propyloxazolidinone.

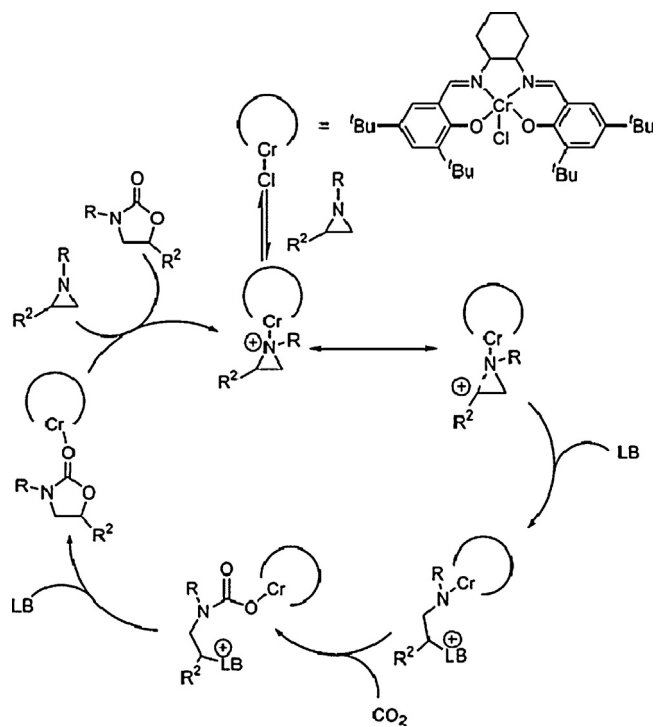


Fig. 3. A proposed mechanism for the coupling of CO<sub>2</sub> and aziridines by the (salen)chromium(III)/DMAP catalyst system. Reprinted with permission from Miller and Nguyen (2004). Copyright (2004) American Chemical Society.

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