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Review Article

Chemical fixation of CO2 with aniline derivatives: A new avenue to the synthesis of functionalized azole compounds (A review)

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ABSTRACT

The use of carbon dioxide (CO_2) as a C1 feedstock in organic synthesis has attracted increasing attention since it may provide access to value-added chemicals from an economical, non-toxic, abundant, renewable and environmental friendly resource. Among these procedures, cyclization of aniline derivatives with CO_2 to corresponding functionalized azoles represents one of the most attractive and straightforward protocols. This mini review survey research works on the preparation of benzene-fused azole compounds (benzimidazoles, benzothiazoles, and benzimidazolones) from the reaction of anilines with CO_2. The review will be helpful for synthetic organic chemists to further investigations of this novel and interesting methodology and encourage them to the synthesis of important natural and biologically active azole derivatives employing this valuable synthetic strategy.

1. Introduction

Needless to say, carbon dioxide (CO_2) is the major greenhouse gas responsible for global warming, ocean acidification, and many environmental issues. CO_2 emissions from human activities are now higher than at any point in our history. In fact, fossil-fuel use by human emit approximately 38000 million tons of CO_2 per year in earth's atmosphere. Consequently, in the last decades considerable efforts have been devoted into developing versatile processes to this greenhouse gas capture, storage, and utilization [1]. On the other hand, CO_2 is actually an economical, non-toxic, abundant, renewable and environmental friendly C1 feedstock providing a wide variety of value-added chemicals, such as cyclic carbonates, carbamates, carboxylic acids, esters, aldehydes, alcohols, and azole compounds [2–10].

Azole compounds (five-membered aromatic rings with at least two heteroatoms that at least one of them is a nitrogen atom) are one of the most important classes of heterocyclic compounds that have attracted a lot of attention due to the fact that they are key structural units for a wide range of natural products [11–13] and currently marketed drugs (Fig. 1) [14–18]. Therefore, the development of practical, environmentally friendly, and convenient synthetic procedures that benefit from inexpensive, easily available, and simple starting materials for the construction of these valuable nitrogen-containing heterocycles is highly desirable [19–22]. As a part of our continual review papers [23–25], we herein highlight the advances in the synthesis of benzene-fused azoles though chemical fixation of CO_2 to aniline derivatives which will be helpful in the development of improved methods for the synthesis of these important N-heterocycles with sustainable chemistry and Green Chemistry perspectives. The review is divided into three major sections. The first section focuses exclusively on the synthesis of benzimidazoles from *ortho*-phenylenediamines and CO_2. The second section will discuss construction of benzothiazole derivatives through chemical fixation of CO_2 to 2-aminothiophenols. The third will cover carbonylation of *ortho*-phenylenediamines with CO_2 to functionalized 2-benzimidazolones.

2. Benzimidazoles

It is well known that *ortho*-phenylenediamines can readily undergo cyclization by CO_2 to generate a wide variety of benzimidazoles under relatively mild conditions. The first report of the synthesis of functionalized benzimidazoles by such a cyclization appeared in 2013 when *o*-phenylenediamines **1** were cyclized in the presence of H_2 to the corresponding benzimidazole derivatives **2** using $RuCl_2(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)-ethane) as a catalyst under solvent free-conditions. In the optimization study, Liu and co-workers

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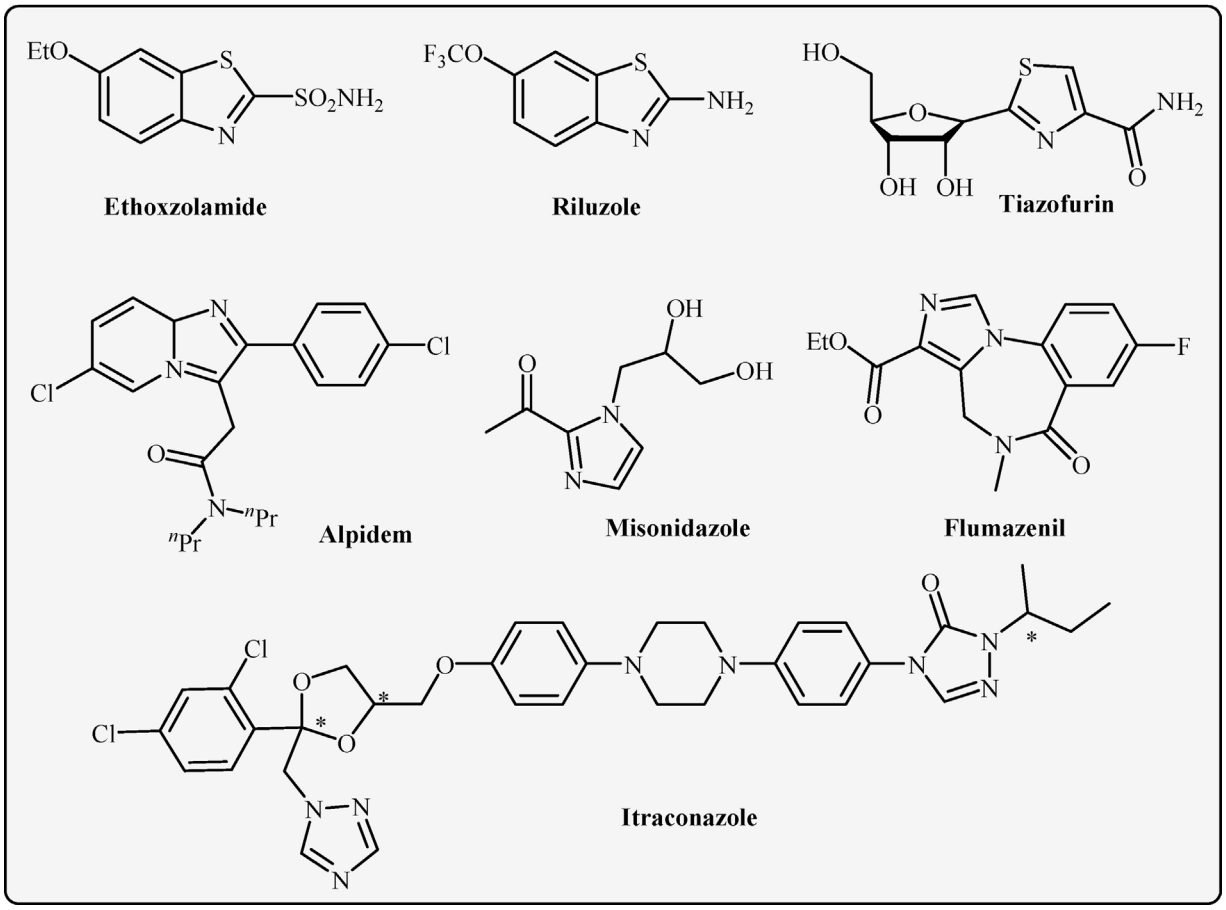
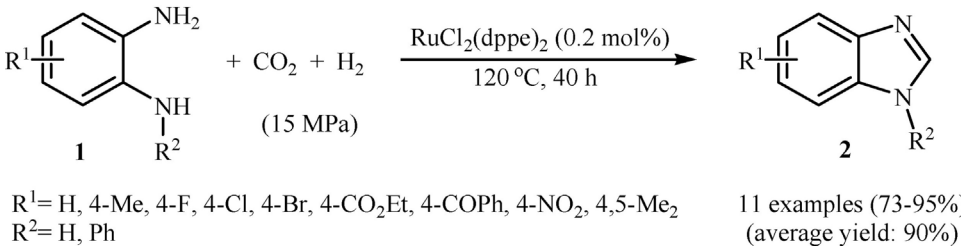
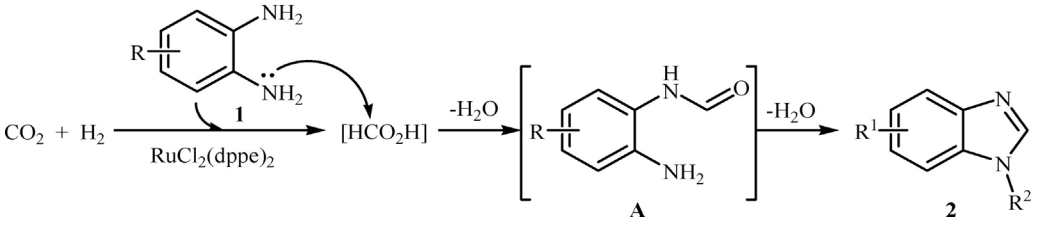


Fig. 1. Selected examples of some clinically used azole-based compounds.



Scheme 1. Ru-catalyzed synthesis of benzimidazoles **2** through cyclization of *ortho*-phenylenediamines **1** with CO_2 in the presence of H_2.



Scheme 2. Mechanistic proposal for the reaction in Scheme 1.

found that $RuCl_2(PPh_3)_3$ also promoted the reaction; however in lower yields. It should be noted that no cyclization occurred in the absence of the catalyst. The authors also found that the conversion of *ortho*-phenylenediamines increased remarkably with pressure. Under optimized conditions ($RuCl_2(dppe)_2$ (0.2 mol%), 120 °C, 15 MPa) the reaction tolerated both primary and secondary anilines, affording the products in good to excellent yields (Scheme 1). Important functionalities such as halides (F, Cl, Br) as well as sensitive nitro, ester, and ketone functionalities that would allow further elaboration of the products were well tolerated under the reaction conditions. The mechanism shown in Scheme 2 was proposed for this cyclization. It consists of the following key steps: (1) initial formation of formic acid *via* hydrogenation of CO_2 promoted by *o*-phenylenediamine **1** as a base; (2) nucleophilic addition of aniline **1** to carbonyl group of formic acid to afford the formamide intermediate **A**; and (3) quick intramolecular cyclization of intermediate **A** to give the final benzimidazoles 2 [26].

In the same year, the Cantat group studied the cyclization of a variety of aromatic and heteroaromatic *ortho*-diamines by CO_2 in the presence of hydrosilanes. They showed that the treatment of 1,2-diamines **3** with 3 equiv. of PMHS poly(methylhydrosiloxane) in the