

Montmorillonite K-10: An efficient and reusable catalyst for the synthesis of quinoxaline derivatives in water

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Abstract

Montmorillonite K-10 is an efficient, cost-effective and recyclable catalyst for a one-pot synthesis of quinoxaline derivatives in water at ambient temperature. This procedure presented is operationally simple, practical and green.

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1. Introduction

Reactions that are performed in water have gained increased interest in synthetic chemistry over the past decade not only for the advantages accorded by avoiding extensive drying of reactants, catalysts and solvents, but also for the development of environmentally friendly processes [1]. Moreover when a heterogeneous catalyst is used, the insoluble catalyst can be separated by simple filtration and the catalyst can be recycled. Therefore, the development of a heterogeneous catalyst in water seems highly desirable.

Commercially available montmorillonite K-10 (Mont K-10) clay is one such material that can fulfill these requirements. Mont K-10 are environmentally benign and economically feasible solid catalysts that offer several advantages, such as ease of handling, non-corrosiveness, low cost and regeneration. Mont K-10 is a solid acid of moderate acid strength. Its Hammett constant is $H_0 = -8$, which is similar to that of concentrated HNO_3 . Its high surface area ($250 \text{ m}^2/\text{g}$) to make it a useful and active catalyst. Both its structural features [2] and synthetic potential [3] have been extensively studied. Mont K-10 is a layered aluminosilicate with a dioctahedral layer sandwiched between two tetrahe-

dral layers. Clays function as efficient catalysts for various organic transformations due to their Brønsted and Lewis acidities in both their natural and ion-exchanged forms [4]. Due to strong catalytic activity as Brønsted acid, Mont K-10 clay has been used extensively as a catalyst in: Diels-Alder reaction [3a], Friedel-Crafts reaction [3b], Nicholas reaction [3c], esterification [3d] and condensation [3e].

Quinoxalines are very important compounds due to their wide spectrum of biological activities behaving as anticancer [5], antiviral [6], antibacterial [7], and activity as kinase inhibitors [8]. In addition to medicinal applications, quinoxaline derivatives have been found applications as dyes [9] and building blocks in the synthesis of organic semiconductors [10]. Considering the significant applications in the fields of medicinal, industrial and synthetic organic chemistry, there has been tremendous interest in developing efficient methods for the synthesis of quinoxalines. Consequently, various methods have been developed for the synthesis of quinoxaline derivatives. The most common method is the condensation of an aryl-1,2-diamine with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid [11]. Improved methods have been reported for the synthesis of quinoxaline derivatives including the Bi-catalyzed oxidative coupling [12], a solid-phase synthesis [13], microwave [14], and the use of $\text{RuCl}_2\text{-(PPh}_3)_3\text{-TEMPO}$ [15], MnO_2 [16], POCl_3 [17], zeolites [18], iodine

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[19], cerium ammonium nitrate [20], $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [21] and SA/MeOH [22] as catalyst or promoter. However, many of these processes suffer from one or other limitations such as drastic reaction conditions, low product yields, tedious work-up procedures, the use of toxic metal salts as catalysts, and relatively expensive reagents. Moreover, this reaction is usually carried out in polar solvents such as acetonitrile and DMSO leading to tedious work-up procedures. The main disadvantage of almost all existing methods is that the catalysts are destroyed in the work-up procedure and cannot be recovered or reused.

There is increasing interest in developing environmentally benign reactions and atom-economic catalytic processes that employ 1,2-diamine and 1,2-dicarbonyl compounds for synthesis of quinoxaline in recent years. In continuation of the studies on the new variants, of a one-pot synthesis of quinoxaline derivatives and our ongoing green organic chemistry program that uses water as a reaction medium, herein we describe a green and efficient method for the synthesis of quinoxaline derivatives in good to high yields by the condensation 1,2-diamine with 1,2-dicarbonyl compounds catalyzed by Mont K-10 in water (Scheme 1).

2. Results and discussion

Initially, following the report by Darabi et al. [22], we attempted the condensation of *o*-phenylenediamine and benzil (PhCOCOPh) using sulfamic acid ($\text{H}_2\text{NSO}_3\text{H}$, SA) in water, in place of MeOH, at room temperature for the synthesis of quinoxaline, resulting in the formation of a condensation product after 12 h (70%, Yield). Thus, using sulfamic acid as catalyst in an aqueous media, the reaction was slow with unsatisfactory yields. While using Mont K-10 as catalyst with similar substrates in water, to our surprise, the reaction proceeded smoothly within 2–4 h and afforded the products in quantitative yield.

Encouraged by the remarkable results obtained with the above reaction conditions, and in order to show the generality and scope of this new protocol, we used various 1,2-diamine and 1,2-dicarbonyl compounds in the presence of Mont K-10 and the results obtained are summarized in Table 1. Most of the reactions proceed very cleanly at room temperature and no undesirable side-reactions were observed, although the yields were highly dependent on the substrate used. For instance, substrate bearing a strong electron withdrawing group gave lower yield even after longer reaction times (Table 1, entry 3). To check the versatility of this method, we have also studied compounds such as furil and 1-phenyl-1,2-propanedione, and obtained

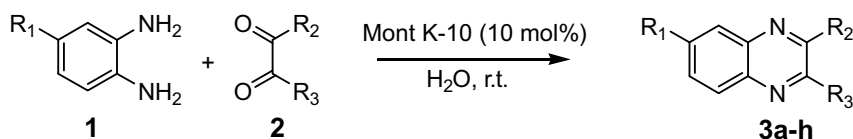
the products in excellent yields (Table 1, entries 5 and 6). The generality of this system was also confirmed by the use of other dicarbonyls, i.e. diacetyl ($\text{CH}_3\text{COCOCH}_3$) and other diamine, i.e. 1,2-ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), as shown in Table 1 (entries 7 and 8).

The possibility of recycling the catalyst was examined. For this reason, the reaction of *o*-phenylenediamine and benzil in water at room temperature in the presence of Mont K-10 was studied. When the reaction was complete, ethyl acetate was added and organic materials were extracted and the aqueous solution was saved for the next reaction. The recycled catalyst could be directly reused four times without any treatment and, no observation of appreciable loss in its catalytic activities (Table 2).

Mont K-10 have long been used as acidic catalysts and existence of both Lewis and Bronsted acid sites [23] is well established. The condensation reaction of 1,2-diamine with 1,2-dicarbonyl compounds follows the regular mechanism of acid-catalyzed condensation reactions [24], we assumed that the mechanism of the condensation reaction probably involve the complexation of Mont K-10 with the diketone by acting as an acid and also playing a complex role in promoting the dehydration to give a carbocationic intermediate as shown in Scheme 2: (i) coordination of a 1,2-dicarbonyl onto acid sites from Mont K-10, followed by (ii) the nucleophilic attack on the carbonyl C providing I intermediate, (iii) dehydration to give a carbocation intermediate and (iv) elimination of a proton to give quinoxaline products. Yao et al. [20] and Heravi et al. [21] also reported that CAN and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ play a complex role in accelerating the dehydration steps, and thus promotes the formation of quinoxaline products. Using sulfamic acid as catalyst in an aqueous media, the reaction was slow with unsatisfactory yields. The result suggest that Mont K-10 provide a suitable strength of the Brønsted acid sites which required for the efficient condensation reaction of 1,2-diamine with 1,2-dicarbonyl compounds, and prevents the neutralization by the basic diamine, when compared with sulfamic acid acids. Furthermore, the two-dimensional silicate sheets of Mont K-10 provide wide spaces for the catalytic reaction, and effectively act as the macro counter anions to decrease their anion coordination ability toward the H^+ site [25], leading to high activity for generation of carbocation intermediate.

3. Experimental

General experimental procedure: A mixture of 1,2-diketone **1** (1 mmol), 1,2-diamine **2** (1 mmol) and montmorillonite K-10 (10 mol%) in water (3 mL) was stirred at room



Scheme 1.

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