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Microwave assisted synthesis of hydroxychromenes using imidazole-functionalized silica nanoparticles as a catalyst under solvent-free conditions

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ABSTRACT

A microwave-assisted reaction of various salicylaldehydes with dialkyl acetylenedicarboxylates mediated by imidazole-functionalized silica nanoparticles is successfully and rapidly achieved to afford the corresponding hydroxychromenes in high to excellent yields under solvent-free conditions.

1. Introduction

Hydroxychromene and its derivatives are widespread in nature [1,2]. They have been widely employed as valuable intermediates in the synthesis of several complex synthetic and natural products [3]. Synthesis of butenolide derivatives from the chromenes via a three–component reaction was reported by Balalai et al. [4]. These compounds have attracted considerable attention due to their unique biological and pharmacological activities [5–7]. Many biological properties [8–11] and antifungal activities [12] were reported for the chromenes. Different synthetic strategies have been reported for the synthesis of hydroxychromenes via the reactions of ortho-hydroxy aromatic aldehydes and dialkyl acetylenedicarboxylates [13,14]. Ramazani et al. reported this reaction in the presence of silica gel under solvent-free conditions at 90 °C. They isolated and identified two products with an approximately equal ratio and identified the desired product as 4-hydroxy-4*H*-chromenes albeit as an unstable compound [15]. 4-Hydroxychromene derivatives were also prepared via the reactions of diethyl acetylenedicarboxylate with salicyl N-tosylimines or salicylaldehydes in the presence of DABCO or dimethylphenylphosphine under mild conditions in excellent yields [16]. Recently, Yoshioka et al. reported the synthesis of 2-hydroxychromenes via the reaction of salicylaldehydes with dienophiles in the presence of CsF [17].

Using conventional organic solvents especially chlorinated hydrocarbons poses a serious threat to the environment because of their toxicity and frequent volatile nature [18]. Nowadays, scientists and especially synthetic organic chemists are obliged to themselves to follow and develop green chemistry disciplines in practical organic chemistry in order the principles of sustainable chemistry in order the criteria and principles of sustainable, environmentally benign chemistry [19]. Consequently, reactions which have a chance of being conducted under solvent-free conditions can be categorized as green [20]. These reactions have

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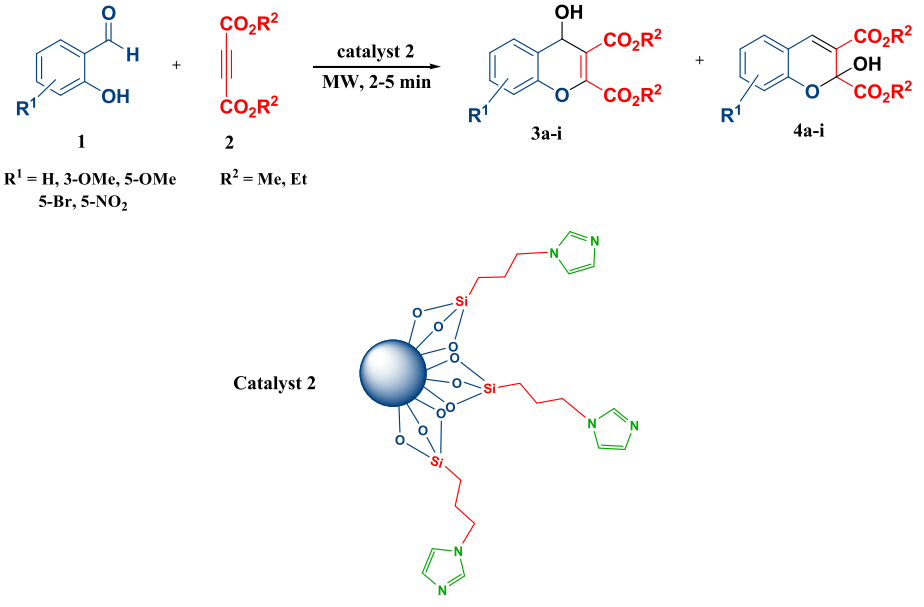
attracted tremendous attention both in academia and industry [21–24].

Heterogeneous catalysis is considered as attractive and superior in many areas of synthetic organic chemistry due to exhibiting unprecedented qualities such as ease of separation and reusability [25,26]. Heterogeneous catalysis is also important in many areas of the chemical and energy consuming industries [27]. In heterogeneous catalysis, the quality and extent of the surface area of the catalyst are vital. One of the best choices for maximizing the surface area is using silica [28]. Due to our interest in application of heterogeneous catalysts and use of MWI in organic reactions [26, 29–34], we wish to reveal here our achievements to develop the synthesis of hydroxychromenes via the reaction of salicylaldehydes and dialkyl acetylenedicarboxylates mediated by imidazole-functionalized silica nanoparticles [35] as an efficient and recyclable solid base catalyst under MWI (Scheme 1).

2. Results and discussion

The reaction between salicylaldehyde and DMAD was chosen as a model reaction. The reaction conditions were deliberately chosen being very mild initially just by refluxing the reactants in CH_2Cl_2 and purposely no catalyst was employed in order to achieve a non-catalyzed reaction. The progress of the reaction was monitored by TLC (using EtOAc/*n*-hexane 1:4 as an eluent). The reaction was preceded sluggishly and the reaction was completed in 3 h. In other trials, the reaction was examined using imidazole-functionalized silica nanoparticles [35] as a catalyst under MWI for possible synthesis of the corresponding hydroxychromenes. After a conventional work up, the purity of crude was tested by TLC (using EtOAc/*n*-hexane 1:4 as an eluent) and no trace of starting materials was detected. However, two separable spots were observed. They were separated and identified as dimethyl 4-hydroxy-4*H*-chromene-2,3-dicarboxylate (**3a**) and dimethyl 2-hydroxy-2*H*-chromene-2,3-dicarboxylate (**4a**) in 16% and 23% yields, respectively (entry 1, Table 1). Other solvents were examined in this procedure and no noticeable improvement was observed in the time of the reaction and yields of the products (entries 2–4, Table 1).

We have been engaged with the development of various organic conversions, by performing them under MWI in order to accelerate the reactions and improving their yields. Armed with these experiences, the typical reaction was examined under MWI and solvent-free conditions and found actually promising to pursue. Interestingly, the reaction was completed in very short time (2 min) in higher yields (entry 5, Table 1). To go further, we decided to perform the reaction catalytically. We decided to examine the catalytic potential of imidazole (catalyst **1**) [36,37] and freshly prepared a heterogeneous imidazole-functionalized nano-silica catalyst (catalyst **2**) [35]. Excellent yields of products were obtained in the presence of catalysts **1** and **2** under MWI solvent-free conditions (entries 7, 11, Table 1). Furthermore, it was found that catalyst **2** is more effective than catalyst **1** (Table 1). It was also found that the amount of catalyst has an appreciable effect on the yields of the product. On increasing the amount of catalyst from 0.27 to 0.72 mol% the yield increased. However, more increase in the amount of the catalyst did not show any appreciable increase in the yield of the product. Additionally, the catalytic activity of silica nanoparticles and 3-chloropropyltrimethoxysilane functionalized silica nanoparticles (CPS-nanoSiO_2) was investigated for the pilot reaction (entries 14–17, Table 1). Also, we screened the catalytic activity of various catalysts such as ZnO, MgO, K_2CO_3 and $TiCl_4$ for the pilot experiment and the results are gathered in Table 1. These results obviously showed that the catalyst **2** is the best choice for this reaction. Eventually,



Scheme 1. Microwave-assisted synthesis of chromenes using an imidazole based solid catalyst.

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