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Catalysis Communications 9 (2008) 470–474

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The synthesis of coumarin-3-carboxylic acids and 3-acetyl-coumarin derivatives using heteropolyacids as heterogeneous and recyclable catalysts

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Received 5 May 2007; received in revised form 19 June 2007; accepted 2 July 2007
Available online 10 July 2007

Abstract

Coumarin-3-carboxylic acids and 3-acetyl-coumarins were obtained in high yields with excellent purity from *ortho*-hydroxybenzaldehydes and 1-ethylacetoacetate or malonic acid after a 2 h reflux in ethanol in the presence of a catalytic amount of different heteropolyacids (HPAs). The less reactive 1-(2-hydroxy-phenyl)-ethanone was first reacted with alcoholic ammonia to form ketimines, which were then condensed with 1-ethylacetoacetate or malonic acid to generate 4-methyl coumarin-3-carboxylic acids and 4-methyl 3-acetyl-coumarins in moderate yields.

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Keywords: Coumarin-3-carboxylic acids; 3-Acetyl-coumarins; Recyclable catalysts; Heteropolyacids

1. Introduction

The synthesis of coumarins and their derivatives has attracted considerable attention from organic and medicinal chemists for many years as a large number of natural products contain this heterocyclic nucleus. They are widely used as additives in food, perfumes, cosmetics [1], pharmaceuticals and optical brighteners [2] and dispersed fluorescent and laser dyes [3]. Thus the synthesis of this heterocyclic nucleus is of much interest.

The application of heteropolyacids, HPAs, as catalytic materials is growing continuously in the catalytic field. These compounds possess unique properties such as: well-defined structure, Brönsted acidity, possibility to modify their acid–base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and release electrons, high proton mobility, being environmentally benign and presenting fewer disposal problems [4]. Because of their stronger acidity, they generally exhibit higher catalytic activity than conventional catalysts such as mineral acids, ion exchange resins, mixed oxides, zeolites, etc. [5]. They are used as industrial catalysts for several liquid phase reactions [6], such as alcohol dehydration [7], alkylation [8] and esterification [9].

Herein we report the synthesis of coumarin-3-carboxylic acids and 3-acetyl-coumarins by cyclization of 2-hydroxylbenzaldehyde derivatives and 1-ethylacetoacetate or malonic acid in the presence of a catalytic amount of different type of HPAs including, $H_{14}[NaP_5W_{30}O_{110}]$, $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$ and $H_6[P_3W_{18}O_{62}]$ (Scheme 1).

The less reactive 1-(2-hydroxy-phenyl)-ethanone was first reacted with alcoholic ammonia to form ketimines, which were then condensed with 1-ethylacetoacetate or malonic acid to generate 4-methyl coumarin-3-carboxylic

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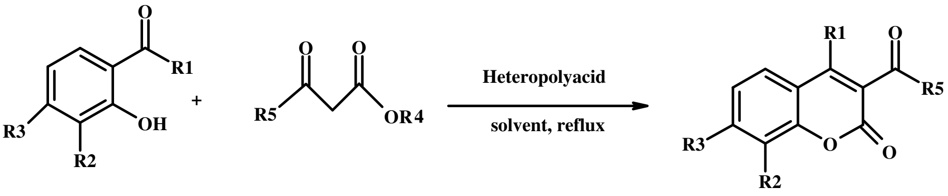
doi:10.1016/j.catcom.2007.07.005



Scheme 1.

acids and 4-methyl 3-acetyl-coumarins in moderate yields (Scheme 2).

2. Experimental

2.1. Chemicals and apparatus

All the chemicals were obtained from Merck Company and used as received. $H_{14}[NaP_5W_{30}O_{110}]$ was prepared according to earlier works [10]. $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ were prepared according to the literatures [11]. The Wells–Dawson $H_6[P_2W_{18}O_{62}]$ was prepared as described elsewhere [12] from an aqueous solution of α/β $K_6P_2W_{18}O_{62} \cdot 10H_2O$ salt, which was treated with ether and concentrated (37%) HCl solution.

2.2. General procedure

2.2.1. Synthesis of coumarin-3-carboxylic acids and 3-acetyl-coumarins

A mixture of 2-hydroxyl-benzaldehyde derivatives (10 mmol) and 1-ethylacetoacetate or malonic acid (10 mmol) and heteropolyacid (1 mmol) in an appropriate solvent (10 mL) was refluxed for 2 h. The progress of the reaction was monitored by TLC using EtOAc: hexane (1:2) as eluents. Because of insolubility of these catalysts in ethanol [13–15], after completion of the reaction, the catalyst was filtered and the solvent was evaporated. The pure products were obtained by column chromatography. All products were identified by comparison of their physical and spectroscopic data with those reported for authentic samples.

2.2.2. Synthesis of 4-methyl coumarin-3-carboxylic acids and 4-methyl 3-acetyl-coumarins

1-(2-Hydroxy-phenyl)-ethanone (20 mmol) was mixed with 7 M ammonia solution in methanol (15 mL) overnight at room temperature. Some crystals were formed the next day. The solvent and excess ammonia were removed. Residue was refluxed with 1-ethylacetoacetate or malonic acid (20 mmol) and catalytic amount of heteropolyacids (2 mmol) in ethanol for 2 h, and then allowed to cool to room temperature. After complete precipitation, the product was filtered and recrystallized from aqueous acetone. The solvent was removed after the reaction. The residue was proportioned between 5% aqueous sodium carbonate solution (20 mL) and ethyl acetate (10 mL). The aqueous phase was acidified with 1 M HCl to pH 2, followed by extraction with ethyl acetate (10 mL × 3). The organic phase was combined, washed with water, dried over anhydrous Na_2SO_4. The residue was recrystallized from aqueous acetone.

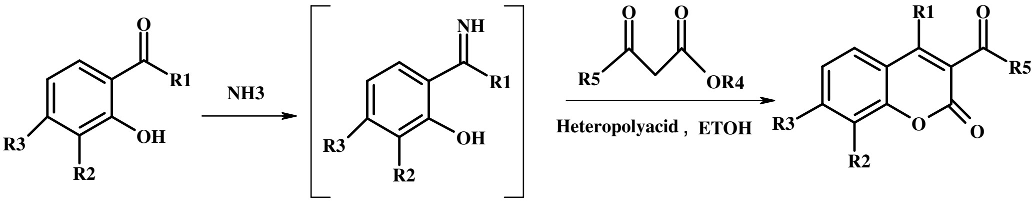
2.3. Reusability of catalyst

At the end of the reaction, the catalyst could be recovered by a simple filtration. The recycled catalyst could be washed with dichloromethane and subjected to a second run of the reaction process. To assure that catalysts were not dissolved in ethanol, the catalysts were weighted after filteration and before using and reusing for the next reaction. The results show that these catalysts are not soluble in ethanol. In Table 1, the comparison of efficiency of $H_{14}[NaP_5W_{30}O_{110}]$ in synthesis of coumarin derivatives after five times is reported. As it is shown in Table 1 the yields of reactions after using $H_{14}[NaP_5W_{30}O_{110}]$ for five times showed only slight decrease.

3. Results and discussion

Due to the ever-mounting environmental concern in the field of chemistry, it is advisable to use easily recovered and recycled catalyst especially expensive or toxic metallic ones for the next use [16]. In this respect, only few of the aforementioned, catalysts meet this criterion of green chemistry.

In connection with our program of using heteropoly acid in organic reactions [15] we wish to report the result of a study on the use of three type of HPAs including



Scheme 2.

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