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Polyvinylpolypyrrolidone-bound boron trifluoride (PVPP-BF_3); a mild and efficient catalyst for synthesis of 4-metyl coumarins via the Pechmann reaction

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ABSTRACT

Polyvinylpolypyrrolidone-supported boron trifluoride has been studied for synthesis of 4-methyl coumarin by the Pechmann reaction. The reaction proceeded smoothly with hydroxyl phenols and ethyl acetoacetate in good yields in ethanol at reflux conditions. The polyvinylpolypyrrolidone-boron trifluoride complex is a non-corrosive and stable solid catalyst elevated Lewis acid property.

1. Introduction

Coumarins are used in the fields of biology, medicine, and polymer science. They are also present or used in perfumes and cosmetics [1–3], alcoholic beverages [4], and laser dyes [5–9]. In addition to these uses, coumarins are well documented as therapeutic agents and have been used as medicines in ancient Egypt and in aboriginal cultures [10,11]. One example, warfarin, is the most prescribed anti-coagulant on the market [12,13]. Recently, coumarin derivatives were utilized to synthesize of photoreversible polymer systems [14–16].

Coumarin derivatives were first synthesized via the Perkin reaction in 1868, and many simple coumarins are still derived from this method. In the early 1900s, the Knoevenagel reaction emerged as an important synthetic method to synthesize coumarin derivates with carboxylic acids at the three positions [17,18]. Later, researchers condensed etylcyanoacetate and various *o*-hydroxyacetophenones to synthesize 4-methylcoumarine derivatives [19,20]. In the conventional production of coumarins by the Pechmann reaction, concentrated sulfuric acid is used as the catalyst [21]. However, as an alternative to sulfuric acid, other acid catalysts such as Montmorillonite clay [22], [bmim]Cl.2$AlCl_3$ [23], $InCl_3$ [24], P_2O_5/molecular sieve 3A° [25], sulfamic acid [26], $BiCl_3$ [27], VCl_3 [28], zeolite [29], $ZrOCl_2.8H_2O$ [30], $HClO_4.SiO_2$ [31], sulfated zirconia [32], Keggin heteropoly acids [33], $SnCl_2.2H_2O$ [34] and sulfonic acid nanoreactors [35] are employed to improve the Pechmann reaction.

However, some of these methods suffer from at least one of the following disadvantages: moisture sensitivity of the majority of Lewis acids to the water produced in the Pechmann condensation renders them unsuitable for use in large scale application, strongly acidic wastes, high cost and toxicity of the reagent, tedious work-up procedures, unsatisfactory yields, and nonrecyclable reagents. Therefore, it seems that the major task of current research is to replace both homogeneous and less efficient and traditional

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heterogeneous acid catalysis procedures by more acceptable methods based on improved stable and recoverable catalysts. Substantial investigations have been made to introduce novel supported catalysts and chemical reagents. These include dispersing catalysts on inorganic supports such as metal oxide, alumina, silica, and zeolite. There are a number of advantages in using polymer-supported catalysts over the conventional catalysis. The reactions can be performed under mild condition and purification of the product is simplified because of the use of an insoluble solid support. Polymer-supported catalysts can also be recycled after use [36]. Poly (vinyl pyrrolidone) displays a strong binding affinity toward small molecules. Furthermore, its iodine complex, povidon-iodine, is widely used as an anti-infective agent in clinical treatments [37]. Recovery of boron triflouride from the reaction, however, results in the formation of large amounts of waste, which on an industrial scale is environmentally unacceptable. The use of a heterogeneous BF_3 system would offer ease of catalyst recovery and minimize the production of waste currently formed during BF_3 recovery. However, a suitable replacement supported system must also exhibit activities and selectivities comparable to the existing homogenous route. In spite of boron trifluoride etharate, polyvinylpolypyrrolidone-boron trifluoride (PVPP-BF_3) is non-corrosive and stable solid catalyst elevated Lewis acid property. Following our interest in the use of PVPP-BF_3 for amidation of benzhydrol with nitriles via Ritter reaction [38], herein, we found that PVPP-BF_3 could be used for the preparation of 4-methyl coumarins by the Pechmann reaction in good to excellent yields.

2. Experimental

Polyvinylpolypyrrolidone (PVPP) was purchased from Fluka chemical company. Other chemicals were purchased from Merck chemical company. Melting points were recorded on an electro thermal melting point apparatus. The NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a Bruker Avance DRX 400 MHz spectrometer. IR spectra were determined on a SP-1100, P-UV-Com instrument. Products were separated by simple filtration, and identified by comparison IR, and ^1H NMR spectra, with those reported for authentic samples.

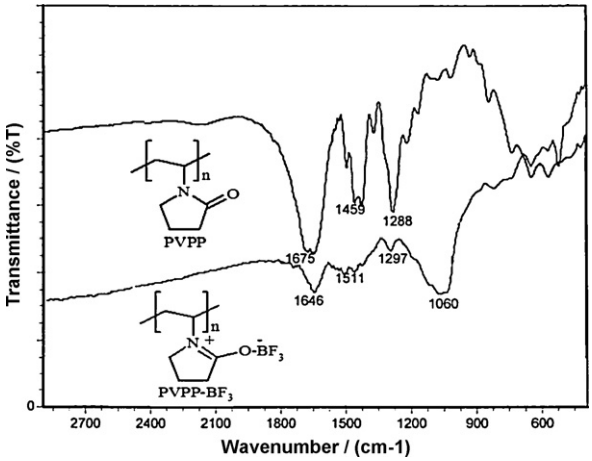


Fig. 1. The FT-IR spectrum of polyvinylpolypyrrolidone (PVPP) and (PVPP-BF_3) complex.

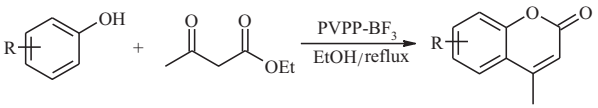
2.1. Catalyst preparation

In this method, boron trifluoride etherate was immobilized on PVPP to give a stable polymeric Lewis acid reagent according to our previous article [38]. To a suspension of 3 g PVPP in 25 ml CH_2Cl_2, a solution of 5 ml $BF_3.Et_2O$ in 15 ml CH_2Cl_2 was added dropwise and the mixture stirred for 1 h at room temperature. The resulting resin was filtered and washed with 2×10 ml CH_2Cl_2 and dried in a vacuum desiccator to give a stable and non-hygroscopic powder.

2.2. Synthesis of 4-meyl coumarins: general procedure

A solution of 3 mmol phenol and 3.1 mmol ethyl acetoacetate in 5 ml ethanol was prepared. 1 mmol (0.1 g) PVPP-BF_3 was added to the solution and the

Table 1
Synthesis of coumarins via Pechmann condensations of phenols with ethyl acetoacetate by PVPP-BF_3.[a]



Entry	R	Time (h)	Yield (%)[b]
1	3-OH	2	91
2	4-OH	2	89
3	3,5-$(OH)_2$	2	96
4	3-Me-5-OH	2	95
5	2-Me-3-OH	2	90
6	2,3-$(OH)_2$	2.5	88
7	3,5-$(Me)_2$	2.5	85
8	3-MeO	3	78
9	2-COOH-4-OH	2	82
10	1-naphtol	3	76

[a] All entries were carried on phenols (3 mmol), ethyl acetoacetate (3.1 mmol) and PVPP-BF_3 (1 mmol) in ethanol (5 ml) under reflux conditions.
[b] All yields refer to isolated products.

reaction mixture was stirred for 2–3 h under reflux conditions until TLC analysis showed that no phenol remained. The reaction mixture was filtered, and the solvent was evaporated on a rotatory evaporator under diminished pressure. The solid residue was recrystalized from water/ethanol to afford pure crystals of the proper coumarins in 72–96% yields. The products were characterized by FT-IR, ^{1}HNMR and physical constants.

3. Results and discussion

Characterizing of the Lewis acid sites presented on the polymer was performed by recording the FT-IR spectrum of PVPP-BF_3, which shows a strong broad absorption at 1000–1060 cm^{-1} for the B-F bonds and a moderate absorption at 1646 cm^{-1} corresponds to the imine group on the backbone (Fig. 1). Loading capacity of the reagent was determined by titration and found to be 10 mmol/g, whereas its silica-supported analogue has a loading capacity of less than 4 mmol/g [39,40].

A variety of coumarins was prepared from phenols and ethyl acetoacetate in the presence of PVPP-BF_3 in good to excellent yields (Table 1, entries 1–10). It is worth mentioning that the corresponding coumarin was isolated by simple filtration of the catalyst followed by crystallization from the crude filtrate. In some cases, the products were further purified by column chromatography. Interestingly, this reagent gives not only good yields of the products but also regenerates easily. Furthermore, the PVPP-BF_3 can be reused and retained its activity after several months of storage.

4. Conclusion

We have developed a simple and efficient method for the Pechmann reaction using PVPP-BF_3 complex as a high loading of Lewis acid, which is stable, easy to prepare and handle, and represents effective activity for the Pechmann reaction. This method provides an easy access to a variety of 4-methyl coumarins.

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