$AlCl_3$ supported on nano silica as an efficient catalyst for the preparation of coumarin

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Abstract- The Pechmann condensation has been used as a simple and efficient method for the preparation of coumarin derivatives, which phenols and ethyl acetoacetate were reacted in the presence of $AlCl_3$ supported on nano silica as an efficient catalyst at 110 ^oC under solvent free condition to form products with good to excellent yield (55 -90%), which are identified by spectroscopic method (FT-IR, NMR) and melting points and compared with reference samples.

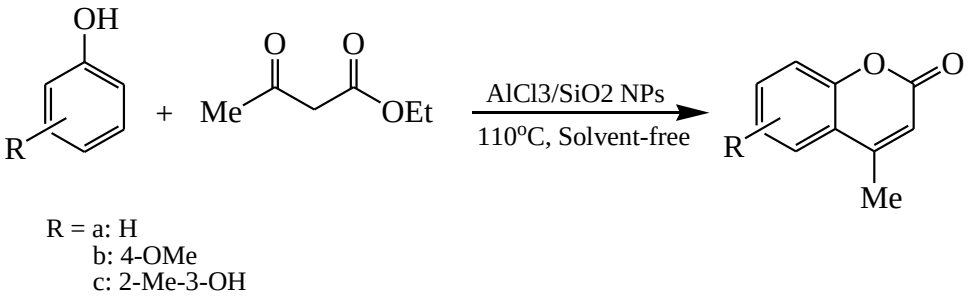
Keywords:Pechmann condensation, $AlCl_3/SiO_2$NPs, coumarin, phenols

Introduction

Coumarin derivatives are important class of heterocyclic compounds and have many application in perfumes, cosmetics, agriculture and livestock industries and also in medicine as anticoagulant.[1]. To prepare these compounds several methods such as, pechmann[2],wittig[3], knoenenaggel[4] and perkin[5] are provided each with its advantages and disadvantages. Among these the pechmann reaction is the most widely applied method to synthesis coumarins as it involves the condensation of phenols with β-ketonic esters in the presence of a variety of acidic condensing agents and gives good yields of 4-substituted coumarins. In recent years heterogeneous catalysts are gaining more importance due to enviro-economic factor. Herein, we report the condensation of the substituted phenols and ethyl acetoacetate in the presence of heterogeneous catalyst (aluminum chloride supported on silica nanoparticles) at 110^oC under solvent-free conditions to produce the coumarins in excellent yields.

Results and discussion

Initially we started with Pechmann condensation of 2,6-dihydroxytoluene and ethyl acetoacetate that had already been used vastly by other chemists in different conditions in the presence of catalytic amount of $AlCl_3/SiO_2$NPs afforded the corresponding coumarin derivatives (Scheme 1).



R = a: H
b: 4-OMe
c: 2-Me-3-OH

Scheme 1

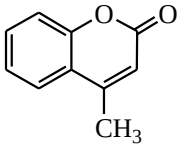
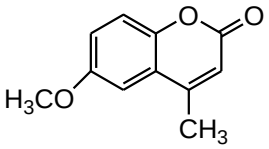
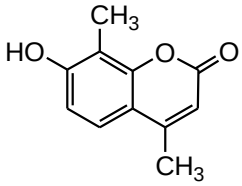
The reactions were clean and affording exclusively coumarins in high yields in a relatively short times. To study the limitation of catalyst amounts we explored some reaction conditions in solvent-free conditions which results are summarized in Table 1**.**

Table 1: Optimization of the amount of $AlCl_3/SiO_2$NPs,2,6-dihydroxytoluene(1 mmol) with ethyl acetoacetate (1/2mmol) in solvent-free conditions at 110^oC.

Entry	Amount catalyst (mg)	Yield (%)
1	0/02	70
2	0/03	90
3	0/04	85
4	0/05	85

Our results showed that by increasing the catalytic load of $AlCl_3/SiO_2$NPs from 0.02 g to 0.03 g it improved the yield from 70% to90% (Table 1, entries 1 and 2). this showed that the catalyst concentration plays a major role in this reaction. But more increasing in the catalyst amount is not appropriate and the yield diminished (conditions for Table 1, entries 3 and 4). Several coumarins were successfully synthesized in high yields by following the above method(Table 2). The reaction mixture was stirred at 110 ^oC in a preheated oil-bath. The present catalyst can easily be prepared. The experimental procedure with this catalyst is very simple and the catalyst can be removed easily by filtration. All the products were identified by comparison of analytical data (IR, NMR and MP) of those reported for authentic samples.

Table 2: $AlCl_3/SiO_2$NPs catalyzed synthesis of coumarins

Entry	Product	Time	Yield (%)
a		70	55
b		30	91
c		5	90

Experimental

General procedure

A mixture of a phenol (1 mmol), ethyl acetoacetate (1.2 mmol) and $AlCl_3/SiO_2$NPs (30 mg) was added and the reaction mixturewas stirred at 110 ˚C in a pre-heated oil-bath.

The reaction was monitored by TLC. After completion of the reaction, the residue was dissolved in hot ethanol (2 mL) and filtered to separate the catalyst. The mother liquid was concentrated to 1 mL and cooled in ice bath. the crystalline product was collected by filtration under suction. the pure 4-methylcoumarin as colorless prisms was obtained.

7-Hidroxy-4,8-dimethylcoumarin(c): 1HNMR(250 MHz, $CDCl_3$), δ (ppm): 10.45(s, 1H), 7.46 (d, 1H, *J* = 8.75), 6.86(d, 1H, *J* = 8.5), 6.14 (s, 1H), 2.36 (s, 3H), 2.15 (s, 3H) ; IR (KBr, cm^{-1}): 3218 (OH), 1683 (C=O), 1606, 1575 (C=C), 1385, 1366 (CH_3), 1091, 1031 (C-O); mp: 259°C; yield: 90%

Conclusion

In summary, a convenient method has been developed for the Pechmann reaction of phenols and ethyl acetoacetate catalyzed by $AlCl_3/SiO_2$NPs Use of inexpensive and reusable catalyst, solvent-free condition, short reaction time, high yield and ease of purification of the product are the key features of this elegant protocol.

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