

Synthesis of 7-Hydroxy-4-methylcoumarin Using Polyaniline/Montmorillonite K10 Composite as Catalyst

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The polyaniline/montmorillonite K10 composite consisting of conducting polyaniline and montmorillonite K10 was synthesized by the intercalation. The insertion of polyaniline between the interlayer of the clay was observed by means of IR spectroscopy. The composite was used as catalyst in Pechmann reaction. The advantages of the composite are ease of preparation, recovery and simple work-up.

Key Words: Pechmann reaction, Solid acid catalyst, Polyaniline/montmorillonite K10 composite, Coumarin derivative.

INTRODUCTION

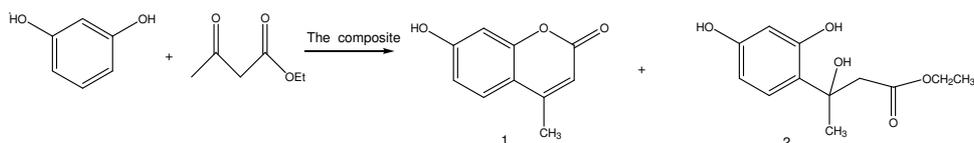
Coumarin and its derivatives form an elite class of compounds, occupying a special place in the realm of natural products and synthetic organic chemistry. The compounds which contain the subunit of coumarin display a broad range of applications, as fragrances, pharmaceuticals, additives to food, cosmetics, agrochemicals, optical brightening agents, tunable dye lasers, biological activities like hypnotic, insecticidal and anticoagulant properties¹. Coumarins can be synthesized by several routes including Pechmann², Perkin³, Knoevenagel⁴ and Reformatsky⁵ reactions. The Pechmann reaction which starts with simple compounds such as phenols and ethyl acetoacetate gives good yields of coumarins and is a valuable method to synthesize them. Coumarins by the Pechmann reaction can be prepared by using homogeneous acid catalysts such as sulfuric acid², hydrochloric acid⁶, phosphoric acid⁷ and trifluoroacetic acid⁸ and Lewis acids such as zinc chloride⁹, phosphoryl chloride¹⁰, bismuth(III) nitrate pentahydrate¹ and aluminium chloride¹¹. The disadvantages of using these acid catalysts are (i) toxicity, (ii) corrosiveness, (iii) hard to removal from the reaction medium, (iv) high amounts of usage (v) non-recoverability and (vi) environmental pollution.

Usage of the heterogeneous acid catalysts assumes advantages like ease of operation conditions, reduced equipment corrosion and minimized contamination of the waste streams combined with reusability of the catalyst. Nafion resin/silica nanocomposite¹², polyaniline (Pani)^{13,14}, montmorillonite (MMT)^{15,16}, amberlyst ion-exchange resin¹⁷ have been used as heterogeneous catalysts for this purpose.

Recently, the composite materials derived from polymers associated with layered inorganic materials have received considerable attention, both in industry and in

academia, because of the exhibiting remarkable improvement in the properties of materials when compared with virgin polymer or conventional micro and macro-composites. The intercalation of organic guest species into inorganic materials is a way to construct an ordered organic-inorganic assembly. The encapsulated polymers in the interlayer spaces of layered materials may provide different characteristics, which cannot be attained from a pristine polymer. Among the many layered materials, clay minerals (*e.g.*, MMT) have been extensively investigated because they are inexpensive, nontoxic, abundant powders which can be filtered easily from reaction mixtures and may be reused. Furthermore, they provide attractive features, such as a large surface area and ion-exchange properties. Conducting polymers such as polyaniline¹⁸ or polypyrrole¹⁹ can be combined with clays. Polyaniline is the most promising polymer due to its simple synthesis, excellent electrical properties and good environmental stability. Polyaniline/clay composites are usually prepared from the mixtures of aniline and clays in an aqueous solution¹⁸.

A new eco-friendly catalyst, polyaniline/MMT K10, is used as a replacement of conventional ones to synthesize 7-hydroxy-4-methyl coumarin with Pechman reaction (**Scheme-I**).



Scheme-I

EXPERIMENTAL

Aniline (reagent-grade) from E. Merck was distilled prior to use. Reagent-grade ammonium persulfate (APS), ethyl acetoacetate, resorcinol, HCl and NaOH from E. Merck were used without further purification. MMT K-10 clay was purchased from Fluka. The IR spectra were obtained by the KBr method using a Mattson 1000 Fourier transform (FTIR) spectrometer. For each spectrum, 100 scans were obtained with a resolution of 16 cm^{-1} . ^1H NMR spectra were obtained on a Varian nuclear magnetic resonance spectrometer (Model Mercury Plus 300) using deuterated solvents.

Preparation of polyaniline/montmorillonite K10 composite: 5 g of clay were dispersed into 250 mL of water. After 24 h stirring, 0.93 g of aniline (10 mmol) and 1.96 g of H_2SO_4 (20 mmol), respectively was added dropwise to the clay suspension. The resulting mixture was stirred for another 24 h at room temperature. 2.28 g of ammonium persulfate (10 mmol) in 10 mL deionized water was added dropwise to the above mixture with magnetic stirring in the ice-bath ($0\text{-}5\text{ }^\circ\text{C}$) for 0.5 h. The reaction mixture was left by stirring at room temperature for 4 h. The precipitated Pani/MMT K10 composite was filtered using the Buchner-type funnel and then washed with distilled water, methanol and acetone until the washing liquid was colourless. Finally, the product was dried in vacuum overnight at room temperature.

Experimental procedure for Pechmann reaction: In a typical experiment, 0.5 g of resorcinol (4.5 mmol) was taken in 10 mL round bottomed flask and added 1.18 g of ethyl acetoacetate (9 mmol) followed by 100 mg of Pani/MMT K10 catalyst (20 wt % with respect to resorcinol). The reaction mixture was heated at 150 °C for 6 h. At the end of the reaction, the reaction mixture was poured into water and maintained overnight for crystallization of product, then filtered. The collected solid was dried in the air, dissolved in acetone and filtered. The catalyst was removed by filtration and the acetone was removed on a rotary evaporator. The residue was purified by dissolving in 1 N NaOH solution and then regenerated with 1 N HCl solution. The precipitated product was filtered, washed with water and dried in the air. The product (**1**) was characterized by melting point and ¹H NMR spectrum. Insoluble product in aqueous NaOH solution was obtained as crystalline material (**2**), m.p. 145 °C and also characterized. (**2**); ¹H NMR (300MHz, CDCl₃): δ 1.34 (3H, quartet, *J* = 7.03 Hz), 1.50 (3H, s), 2.09 (2H, s), 4.25 (2H, t, *J* = 7.03 Hz), 4.70 (1H, s), 6.38 (1H, sd, *J* = 1.47 Hz), 6.55 (1H, dd, *J* = 7.32, 1.47 Hz), 7.15 (1H, d, *J* = 7.32 Hz). IR (KBr, ν_{max} , cm⁻¹): 3412, 3004, 1676, 1600, 1523, 1446, 1395, 1319, 1191, 1114, 1012, 859, 655.

RESULTS AND DISCUSSION

Preparation of 7-hydroxy-4-methyl coumarin was carried out with resorcinol and ethyl acetoacetate by varying molar ratio, amount of catalyst (Pani/MMT K10 composite), the reaction time and temperature of the reaction and the yield of the product is reported in Table-1. The preparation of 7-hydroxy-4-methyl coumarin was carried out by using different molar ratios of resorcinol:ethyl acetoacetate (1:1.0, 1:1.5 and 1:2.0). The yield increased as 39, 55 and 70 % (entries 6, 7 and 1) with increasing the amount of ethyl acetoacetate and maximum yield was obtained with the use of two equivalent of ethyl acetoacetate. The amount of catalyst was varied as 10, 20 and 30 wt % with respect to resorcinol. 70 and 59 % yield (entries 1 and 3) was obtained with the use of 20 and 30 % catalyst, respectively while 61 % yield (entry 2) was obtained with the use of 10 % catalyst. The reaction was carried out by varying the reaction time between 4, 6 and 8 h and maximum yield (78 %) was obtained around 8 h (entry 5). The yield increased from 33-71 % with increasing the temperature from 130-170 °C (entries 8 and 9). Based on the above results, the entry 5 is best for preparation of 7-hydroxy-4-methyl coumarin. The results are fairly close to those obtained by using Pani (H₂SO₄) as catalyst¹³.

The IR spectrum of the composite was shown in Fig. 1. The band at 3648 cm⁻¹ is ascribed to the -OH stretching vibrations of structural OH groups coordinated to the cations in octahedral arrangement²⁰. The peak 1651 cm⁻¹ is assigned to bending vibrations of -OH group of water molecules²¹. The band due to the Si-O-Si stretching mode is observed at 1063 cm⁻¹. The spectra exhibit the Si-O bending vibrations at 553 and 476 cm⁻¹ due to Si-O-Al and Si-O-Si, respectively²². These peaks are the characteristic vibrations of MMT. The band at 1523 cm⁻¹ is assigned to the C=N

stretching mode. The peak 1319 cm^{-1} is associated with the C-N stretching mode²³. These peaks are ascribed to the formation of polyaniline.

TABLE-1
YIELD OF 7-HYDROXY-4-METHYL COUMARIN CARRIED
OUT AT DIFFERENT REACTION TIME, MOLAR RATIO,
CATALYST CONCENTRATION AND TEMPERATURES

Entry	Catalyst (mg)	Molar ratio ^a	Time (h)	Temperature (°C)	Yield (%)
1	100	1:2	6	150	70
2	50	1:2	6	150	61
3	150	1:2	6	150	59
4	100	1:2	4	150	49
5	100	1:2	8	150	78
6	100	1:1	6	150	39
7	100	1:1.5	6	150	55
8	100	1:2	6	130	33
9	100	1:2	6	170	71

a: Molar ratio of resorcinol:ethyl acetoacetate.

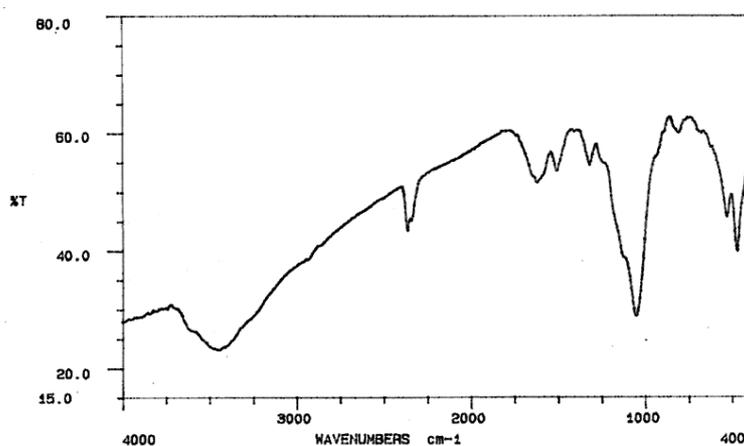


Fig. 1. IR spectrum of the composite

The Pani/MMT K10 composite serve as catalysts for the synthesis of 7-hydroxy-4-methyl coumarin with good yield. This method has some advantages such as easy preparation, simple work-up procedure, recovery and eco-friendly of the catalyst.

The preparation of coumarin was also carried out with different catalysts to establish activation effect (resorcinol:ethyl acetoacetate; 1:2, time: 6 h, catalyst: 20 wt % with respect to resorcinol, temperature: 150 °C). Pani (H_2SO_4) and montmorillonite used without activation and activated Pani (H_2SO_4)¹³ gave 68, 38 and 70 % yield, respectively, whereas unactivated composite which was used in our all experiments afforded 65-70 % yield. These similar results show that the yield of the products do not depend on the activation process. It is interesting that the composite

gave 53 and 67 % yield, respectively after activation process at 150 and 300 °C for 2 h. This suggest that the activation process might affect only montmorillonite which has both Bronsted and Lewis acidities.

In typical Pechmann reaction, a product (**2**) (undissolved in NaOH) in addition to the coumarin (**1**) was obtained. This product was characterized by its ¹H NMR and IR spectrum. IR Spectrum of compound contain band at 1676 cm⁻¹ which is characteristic of the stretching vibration of the ester carbonyl group. The OH band was observed at 3412 cm⁻¹. The typical ethyl ester peaks were also showed at 1191 and 1012 cm⁻¹. The ¹H NMR spectrum showed resonances for the aromatic protons at δ 7.15 (d), 6.55 (dd) and 6.38 (sd), the hydroxyl group at δ 4.7 (s), two oxymethylene and three methyl protons of ethyl alkyl group of the ether-type oxygen of the ester group at δ 4.25 (quartet) and δ 1.34 (t), respectively, a methylene protons adjacent to the ester carbonyl group at δ 2.09 (s) and three methyl protons on β- carbon atom adjacent to the ester carbonyl group at δ 1.5 (s).

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