

K-10 Montmorillonite Catalysed Solvent Free Synthesis of Coumarins via Pechmann Condensation

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Abstract— An efficient solvent free one pot synthesis of coumarins by pechmann condensation of substituted phenols with ethyl acetoacetate using k-10 montmorillonite as a catalyst have been carried out. A plausible mechanism is proposed involving Michael addition resulting into the formation of coumarins. The reaction was refluxed at 110^oC for 3-4 hrs on water bath. This one-pot synthesis was carried out on solid clay catalyst support which provides the products in good yields. Effect of molar ratio, amount of catalyst, reaction temperature and time on the yield of 4,7-dimethyl coumarin has been discussed. All the newly synthesized compounds were established from advanced spectroscopic data. The proposed method using the environmentally friendly recyclable catalyst k-10 montmorillonite offers the unique advantages of high yields, shorter reaction times, easy and quick isolation of the products and a one-pot green synthesis.

Keywords— Solvent-free; coumarins; k-10 montmorillonite; one-pot synthesis; pechmann condensation.

I. INTRODUCTION

Coumarin and its derivatives are biologically active compounds with a wide range of specialities such as antitumor, antimicrobial, anti-HIV, anticoagulant, anti-inflammatory and antioxidant agents [1-4]. Several named reactions such as Perkin [5], Knoevenagel [6], Reformatsky [7], Wittig [8], and Pechmann [9] reactions have been taken into consideration for the synthesis of coumarins and its derivatives.

Different acid catalysts like H₂SO₄, P₂O₅, FeCl₃, POCl₃, H₃PO₄ and CF₃-COOH acid are known to catalyzed pechmann condensation reaction [10]. Conventional processes require long reaction time, corrodes reactor and creates byproducts and salt waste due to acid neutralization which are not attractive as they require catalyst in excess. The disadvantages of using these acid catalysts are toxicity, corrosiveness, hard to removal from the reaction medium, non-recoverability and environmental pollution. Application of the heterogeneous acid catalysts creates advantages like ease of operation conditions, reduced equipment corrosion and minimized contamination of the waste streams with reusability of the catalyst (11). With increasing environmental concerns it is important to design a new green method which involves the use non-hazardous and safer solvents in the synthesis of coumarins.

Montmorillonite clays have been used as efficient and green catalysts for a variety of organic reactions which can be filtered easily from reaction mixtures and may be

reused. However, syntheses of coumarins directly catalysed by montmorillonite clays have not been reported. In connection with our work on montmorillonite clays catalysis, herein we describe an environmentally important green synthesis of coumarins in high yields [12].

Therefore, a simple, efficient and green method for one-pot synthesis of coumarins under mild reaction condition is required. The method employed herein involves the condensation of phenols with β -ketoesters, in the presence of k-10 montmorillonite, which acts as a catalyst for the synthesis of coumarins. The superiority of use of k-10 montmorillonite to the current process is demonstrated in comparison with other lewis acids, Fe-salts, fluoride sources and insights into the origin of the efficiency have been discussed [17, 18].

So far, no report has been made about the use of heterogeneous catalyst for synthesis of coumarins via Pechmann condensation using k-10 montmorillonite as catalyst [19]. In this context K-10 montmorillonite acts as better catalyst which is easily available and cheaper, less toxic and can be handled under operational condition. In this study, we have analyzed the Pechmann reaction to develop a new and suitable methodology for the synthesis of coumarins. The experiments were started with the study of one-pot, two-component Pechmann condensation using K-10 montmorillonite as a catalyst under solvent-free condition (20) (Scheme 1).

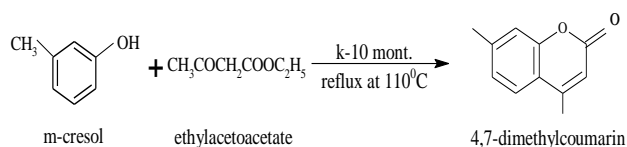


Fig.1

II. RELATED WORK

In the related work section, there is scope for K-10 montmorillonite which acts as better green catalysts which is easily available and cheaper, less toxic and can be handled under operational conditions [13, 14]. Synthesis of coumarins via pechmann condensation using inorganic ion exchangers as solid acid catalysts has been proposed by R. Joshi and U Chudasama [15]. Synthesis and Nitration of 7-Hydroxy-4-Methyl Coumarin via Pechmann Condensation Using Amberlyst-15 have been reported by Fadia Al-Haj Hussien [16].

III. METHODOLOGY

2.1 Materials: All the chemicals and reagents were purchased from Merck Chemicals, India and were used without further purification. Reactions were monitored by TLC.

2.2 Synthesis:

m-cresol (1.08 g) was dissolved completely in ethyl acetoacetate (1.35 g) in a 50 ml dry round bottom flask. K-10 montmorillonite clay (1.5 g) was added to this

homogeneous mixture and mixed thoroughly using a glass rod. The reaction mixture finally appeared as a paste. It was placed on hot water bath and heated gently for 3-4 h. After completion of the reaction mixture was cooled to room temperature and 4,7-dimethyl coumarin was extracted with ether by vigorous shaking. The clay was separated by filtration through whatmann filter paper. Separation with ether was repeated for twice. Finally the filtrate was evaporated and the product is obtained as a white solid.

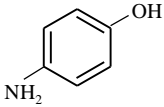
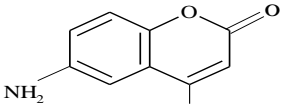
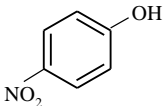
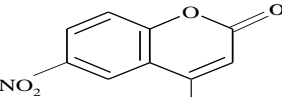
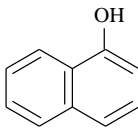
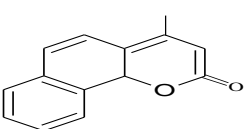
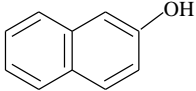
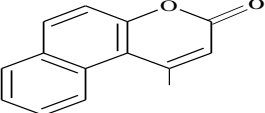
Synthesis was also carried out by using p-cresol, o-chlorophenol, p-chlorophenol, p-aminophenol, p-nitrophenol, α -naphthol and β -naphthol. The corresponding results are summarized in Table 1. As can be seen from the results, k-10 montmorillonite acts as an effective catalyst, significantly increasing the reaction rate; moreover, it can be easily separated.

2.3 Spectral studies:

Infrared spectrum was recorded using KBr pellet in nujol mull on Perkin-Elmer RX-I spectrophotometer in the range of 4000-500 cm^{-1} . Nuclear Magnetic Resonance ($^1\text{H-NMR}$) spectrum of newly synthesized products has been scanned on FT-NMR-Cryo magnet spectrum 400 MHz (Bruker) spectrometer. Also $^{13}\text{C-NMR}$ has been carried out at 75 MHz spectrometer. Mass spectra were determined on a Varion-Saturn 2000 gas chromatograph-mass spectrometer (MS). Melting points were determined with an electro thermal melting point apparatus and were approximate.

Table 1: Synthesis of coumarin derivatives.

Entry	Phenolic compounds	Product	Yield (%)	M.P. ($^{\circ}\text{C}$)
1(a)			85	110
1(b)			84	72
1(c)			79	91
1(d)			80	94

1(e)			80	132
1(f)			64	139
1(g)			83	139
1(h)			80	140

IV. RESULTS AND DISCUSSION

Coumarins are simple heterocyclic compounds that can be obtained from natural sources, especially green plants. They are used in food additives, perfumes, cigarettes, pharmaceuticals, cosmetics, light-activated compounds and fluorescent laser dyes. Herein, we report an efficient method for the preparation of coumarin derivatives using k-10 montmorillonite as a catalyst in the Pechmann reaction. The mechanistic details of the reaction involving Michael addition are given as follows:

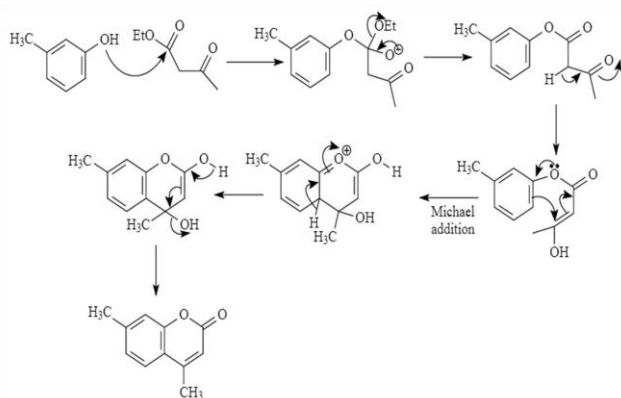


Fig. 2

Initially, for the optimization of the reaction conditions, a mixture of m-cresol and ethylacetoacetate was set as a model and its behavior was studied under a variety of experimental conditions such as temperature, time of reaction and amount of catalyst. The best result was achieved by carrying out the reaction of m-cresol and ethylacetoacetate (with 1:1 mol ratio) in the presence of (0.2g, 10% mol) of k-10 montmorillonite at 110°C for 3-4 hrs on water bath. As Pechmann reaction is an acid catalysed reaction so k-10 montmorillonite provides acidic conditions. With respect to green context, strong and

corrosive H₂SO₄ is avoided. A solid and green catalyst k-10 montmorillonite is employed. Reaction is carried out in solid state avoiding use of solvent. Catalyst can be recycled and reused. Reaction occurs in short time. An ice bath condition during addition is avoided.

3.1 Effect of catalyst amount

The specific impact of different molar amount of catalyst on the yield did not notice when the amount of catalyst was increased (Table 2). Using of large quantities of k-10 montmorillonite, did not affect to the preparation of 1(a), so from an economic perspective, it is preferred using the least possible quantity of catalyst.

The yields were increased initially with increase in the catalyst amount. This shows that both the strength of the acid sites and their concentration play a crucial role in this reaction (Table 2). When 30 mole % of the catalyst was used, the yield of 4,7-dimethyl coumarin decreased. Generally montmorillonite catalysed reactions involve adsorption and diffusion of reactants through the pores and interlayers [21]. The diffusion of the reactants to the active sites can become a limiting process in such porous solid acid catalysts [22]. The product 4,7-dimethyl coumarin remains adsorbed within the active sites of the catalyst and may restrict diffusion for the fresh reactants if excess catalyst is used. Hence, decreased yield of 4,7-dimethyl coumarin was observed due to unavailability of active sites to the reactants when excess catalyst was used.

3.2 Effect of temperature

To study the effect of temperature, synthesis of 1(a) was carried out at the temperature range of 40°C – 240°C. As indicated in Table 2, it is clear that by increasing the temperature until 110°C the yield improved from 18% to 85%, but by increasing the temperature more than 110°C, the yield was decreased until 55% at 150°C, that is probably due to the formation of side products such as

chromones, the self-condensation of ethyl acetoacetate and isomerization.

3.3 Effect of reaction time

The condensation reaction has been studied at five different intervals of time. The time of reaction was optimized 240 min where the reaction was completely finished with the highest yield (monitored by TLC), but by

increasing the time up to 300 min the yield was decreased, it is probably due to increasing the side products. This can be attributed to decomposition of unreacted reactants and product formed due to prolonged heating. A similar effect had been reported over modified metal oxides in the preparation of 7-hydroxy-4-methylcoumarin by D'Souza and Nagaraju [23].

Table 2: Effect of k-10 montmorillonite percentage, temperature, time and molar ratio in the synthesis of 4,7-dimethyl coumarin.

Entry	Amount of catalyst (mol.%)	Yield (%)	Temperature (°C)	Yield (%)	Time (min.)	Yield (%)	Molar ratio (m-cresol:ethyl acetoacetate)	Yield (%)
1.	-	Traces	40	18	30	20	1:1	50
2.	10	78	80	65	80	45	1:2	56
3.	20	85	110	85	110	72	1:1.5	66
4.	30	81	130	78	240	85	1:1.7	59
5.	40	71	150	55	300	72	1:2	56

3.4 Effect of molar ratio

The condensation was carried out using equimolar ratio of the reactants, wherein the 4,7-dimethyl coumarin yield was 50%. When the molar ratio of m-cresol to ethyl acetoacetate was increased from 1:1 to 1:1.5, higher quantities of the 4,7-dimethyl coumarin were formed. This shows that the reaction equilibrium shifts towards the formation of 4,7-dimethyl coumarin when ethyl acetoacetate concentration was increased. However, the percentage yield of 4,7-dimethyl coumarin was reduced when the m-cresol to ethyl acetoacetate ratio was 1:1.7 and 1:2 after 6 h. Higher concentration of ethyl acetoacetate thus inhibited the 4,7-dimethyl coumarin formation. Therefore, for further studies, the m-cresol to ethyl acetoacetate ratio of 1:1 was selected (Table 2).

3.5 Reusability

The used catalyst was dried at 110°C for 2 h, ground to a fine powder and reused to study its activity for the reaction. Upon recycling, k-10 montmorillonite showed a reduced activity towards formation of 4,7-dimethyl coumarin from 66 to 41% after a single run. The loss in activity is due to leaching of k-10 montmorillonite from the support into the reaction mixture and also into acetone during separation of catalyst from reaction mixture. However, it is important to note that we report a procedure for Pechmann condensation, under catalytic conditions, avoiding use of high temperature, more amount of one of the reactants and the catalyst amount used by us is more reduced than that of the reports available in the literature [24-30].

3.6 Characterization [31-36]:

1 (a): 4,7-dimethyl-2H-chromen-2-one:-

FT-IR (KBr): 3454.20, 3233.39, 2778.05, 2638.68, 2482.73, 2230.30, 2130.82, 1596.10, 1511.51, 1344.98, 833.34, 798.30 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 7.79 (s, 1H, Ar-H), δ = 7.08 (s, 1H, Ar-H), δ = 7.10 ((s, 1H, Ar-H), δ = 2.28 (s,

3H, -CH₃), δ = 2.40 (s, 3H, -CH₃), δ = 6.23 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 160.8, 154.6, 116.6, 152.7, 143.1, 117.4, 125.6, 112.5, 125.7, 19.4, 21.3.

LC-MS (m/z): 174.07 (M + 1).

Elemental Analysis for C₁₁H₁₀O₂; Theoretically calculated C = 75.84%, H = 5.79%, O = 18.37%; experimentally found C = 75.16%, H = 5.20%, O = 18.20%.

1 (b): 4,6-dimethyl-2H-chromen-2-one,

FT-IR (KBr): 3394.67, 2929.63, 2332.68, 2130.25, 2021.27, 1864.10, 1707.04, 1597.47, 1512.08, 1437.81, 797.54, 687.18 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 7.52 (s, 1H, Ar-H), δ = 7.33 (d, 1H, Ar-H), δ = 7.31 (d, 1H, Ar-H), δ = 2.42 (s, 3H, -CH₃), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 160.8, 150.5, 120.9, 152.7, 135.1, 116.9, 127.0, 112.5, 132.0, 19.4, 21.7.

LC-MS (m/z): 174.07 (M + 1).

Elemental Analysis for C₁₁H₁₀O₂; Theoretically calculated C = 75.84%, H = 5.79%, O = 18.37%; experimentally found C = 74.24%, H = 5.75%, O = 19.01%.

1 (c): 8-chloro-4-methyl-2H-chromen-2-one,

FT-IR (KBr): 3379.31, 2985.95, 2727.33, 2326.39, 2094.56, 1996.44, 1730.54, 1667.77, 1598.17, 1514.65, 1433.54, 830.47, 797.34 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 7.72 (d, 1H, Ar-H), δ = 7.46 (d, 1H, Ar-H), δ = 7.36 (dd, 1H, Ar-H), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 129.8, 160.8, 145.2, 122.4, 152.7, 126.7, 112.5, 130.8, 126.8, 19.4.

LC-MS (m/z): 194.01 (M + 1).

Elemental Analysis for C₁₀H₇ClO₂; Theoretically calculated C = 61.72%, H = 3.63%, O = 16.44%; experimentally found C = 60.16%, H = 3.20%, O = 16.20%.

1 (d): 6-chloro-4-methyl-2H-chromen-2-one,

FT-IR (KBr): 3407.19, 2294.06, 2123.18, 1999.35, 1866.65, 1730.50, 1599.16, 1515.39, 1432.39, 1373.40, 797.12 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 8.02 (s, 1H, Ar-H), δ = 7.46 (d, 1H, Ar-H), δ = 7.30 (d, 1H, Ar-H), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 131.0, 160.8, 151.6, 122.4, 152.7, 129.5, 122.9, 126.8, 112.5, 19.4.

LC-MS (m/z): 194.01 (M + 1).

Elemental Analysis for C₁₀H₇ClO₂; Theoretically calculated C = 61.72%, H = 3.63%, O = 16.44%; experimentally found C = 60.88%, H = 3.92%, O = 16.38%.

1 (e): 6-amino-4-methyl-2H-chromen-2-one,

FT-IR (KBr): 3285.87, 2983.30, 2679.62, 2351.40, 2116.94, 199.17, 1879.14, 1654.99, 1600.51, 1513.77, 1447.38, 1374.40, 832.14, 792.94 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 7.03 (s, 1H, Ar-H), δ = 6.96 (d, 1H, Ar-H), δ = 7.21 (d, 1H, Ar-H), δ = 5.28 (s, 2H, -NH₂), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 160.8, 143.5, 145.1, 121.8, 152.7, 117.5, 120.5, 111.1, 112.5, 19.4.

LC-MS (m/z): 175.06 (M + 1).

Elemental Analysis for C₁₀H₉NO₂; Theoretically calculated C = 68.56%, H = 5.18%, O = 18.27%; experimentally found 67.96%, H = 5.85%, O = 18.77%

1 (f): 6-nitro-4-methyl-2H-chromen-2-one,

FT-IR (KBr): 3385.21, 2756.02, 2311.19, 2107.55, 1998.96, 1911.05, 1668.68, 1597.21, 1514.81, 1459.90, 1340.49, 831.30, 796.49 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 8.56 (s, 1H, Ar-H), δ = 8.38 (d, 1H, Ar-H), δ = 7.62 (d, 1H, Ar-H), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 160.8, 159.6, 144.6, 121.9, 152.7, 118.4, 124.5, 120.4, 112.5, 19.4

LC-MS (m/z): 205.04 (M + 1).

Elemental Analysis for C₁₀H₇NO₄; Theoretically calculated C = 58.54%, H = 3.44%, O = 31.19%; experimentally found 58.24%, H = 3.18%, O = 31.88%

1 (g): 4-methyl-2H-benzo[h]-chromen-2-one,

FT-IR (KBr): 3358.93, 2917.87, 2703.19, 2115.37, 1997.05, 1922.26, 1740.40, 1628.39, 1586.97, 1468.81, 1105.71, 994.86, 833.86, 747.85 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 8.53 (d, 1H, Ar-H), δ = 7.67 (dd, 1H, Ar-H), δ = 7.69 (dd, 1H, Ar-H), δ = 8.11 (d, 1H, Ar-H), δ = 7.22 (d, 1H, Ar-H), δ = 7.84 (d, 1H, Ar-H), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 160.8, 155.3, 124.8, 117.9, 134.1, 152.7, 112.5, 120.4, 121.1, 127.5, 126.8, 19.4

LC-MS (m/z): 210.07 (M + 1).

Elemental Analysis for C₁₄H₁₀O₂; Theoretically calculated C = 79.98%, H = 4.79%, O = 15.22%; experimentally found C = 79.18%, H = 4.09%, O = 15.98%

1 (g): 4-methyl-2H-benzo[h]-chromen-2-one,

FT-IR (KBr): 3358.93, 2917.87, 2703.19, 2115.37, 1997.05, 1922.26, 1740.40, 1628.39, 1586.97, 1468.81, 1105.71, 994.86, 833.86, 747.85 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 8.53 (d, 1H, Ar-H), δ = 7.67 (dd, 1H, Ar-H), δ = 7.69 (dd, 1H, Ar-H), δ = 8.11 (d, 1H, Ar-H), δ = 7.22 (d, 1H, Ar-H), δ = 7.84 (d, 1H, Ar-H), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 160.8, 155.3, 124.8, 117.9, 134.1, 152.7, 112.5, 120.4, 121.1, 127.5, 126.8, 19.4

LC-MS (m/z): 210.07 (M + 1).

Elemental Analysis for C₁₄H₁₀O₂; Theoretically calculated C = 79.98%, H = 4.79%, O = 15.22%; experimentally found C = 79.18%, H = 4.09%, O = 15.98%

1 (h): 1-methyl-3H-benzo[h]-chromen-2-one,

FT-IR (KBr): 3360.93, 2915.67, 2713.19, 2118.27, 1997.05, 1922.26, 1740.40, 1628.39, 1586.97, 1468.81, 1105.71, 994.86, 833.86, 747.85 (cm⁻¹).

¹H-NMR (400 MHz, DMSO-d₆): δ = 8.50 (d, 1H, Ar-H), δ = 7.69 (dd, 1H, Ar-H), δ = 7.65 (dd, 1H, Ar-H), δ = 8.11 (d, 1H, Ar-H), δ = 7.22 (d, 1H, Ar-H), δ = 7.84 (d, 1H, Ar-H), δ = 2.43 (s, 3H, -CH₃), δ = 6.27 (s, 1H, proton ortho to C=O).

¹³C NMR (100 MHz, DMSO-d₆): δ = 160.8, 155.3, 124.8, 117.9, 134.1, 152.7, 112.5, 120.4, 121.1, 127.5, 126.8, 19.4

LC-MS (m/z): 210.07 (M + 1).

Elemental Analysis for C₁₄H₁₀O₂; Theoretically calculated C = 79.98%, H = 4.79%, O = 15.22%; experimentally found C = 80.21%, H = 4.78%, O = 16.00% .

V. CONCLUSION AND FUTURE SCOPE

An efficient and green protocol for the synthesis of coumarins via Pechmann condensations using k-10 montmorillonite as a catalyst under solvent-free condition have been carried out. All the newly synthesized compounds were established from advanced spectroscopic data. Moreover, the low cost of the catalyst comparison with other traditional catalysts such as sulfuric acid and by reused several times, solvent-free condition, low toxicity of the catalyst, fast reaction times, simple experimental procedure, and recyclability of the catalyst and high yields of the products are the advantages of green procedure over conventional synthetic procedure.

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