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A Convenient Synthesis of Some Coumarin Derivatives Using $SnCl_2 \cdot 2H_2O$ as Catalyst

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Abstract Some substituted coumarins have been synthesized by von-Pechmann condensation using $SnCl_2 \cdot 2H_2O$ (10 mol %) as catalyst in ethanolic medium. The reactions are simple, easy in handling and environmentally benign.

Keywords Coumarin · von-Pechmann condensation · $SnCl_2 \cdot 2H_2O$

1 Introduction

Coumarins constitute an important class of compound due to their presence as an important constituent of natural products [1] as well as their variety of medicinal applications such as anti-inflammatory [2], anti-convulsant [3], anti-viral [4], anticoagulent [5], antioxidant [6], antibacterial [7], antifungal [8], anti-HIV [9], anti-carcinogenic material [10] and as antihistamine [11]. Besides the wide spectrum biological applications of coumarin and its derivatives the chemical literature also embodies their some applications from the material view point such as cosmetics [12], optical brightening agents [13], and laser dyes [14]. A recent literature report has revealed the anion sensing ability of some coumarin derivatives [15]. There are several well established protocols for the synthesis of coumarin and its derivatives [16–23]. For the last several years there has been an upsurge in the field of synthesis of coumarins through the catalysis of von Pechmann reaction by a variety of Lewis acids [24–34].

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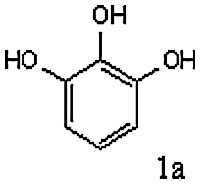
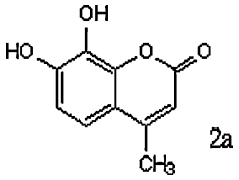
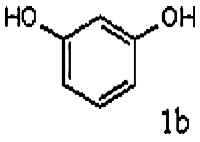
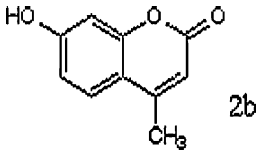
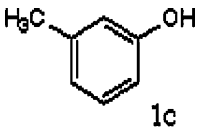
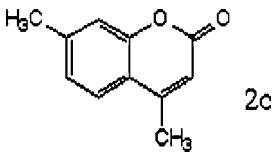
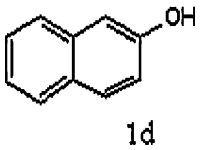
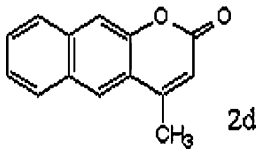
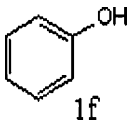
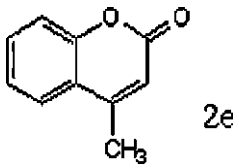
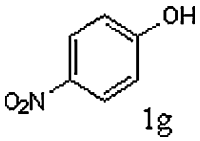
$SnCl_2 \cdot 2H_2O$ has been used as a catalyst for the synthesis of heterocycles [35–38] for the last few years but this has not been used to catalyze von Pechmann reaction leading to the synthesis of coumarins so far. Our earlier and current research interests in the synthesis of biologically important molecules [39–40] prompted us to synthesize some coumarin derivatives through catalysis of the von Pechmann reaction with a hitherto unused Lewis acid catalyst $SnCl_2 \cdot 2H_2O$ for this purpose.

The experimental procedure followed in the present communication is simple, easy to handle, and involves Sn^{2+} which is benign towards our ecosystem. Thin layer chromatography (TLC) was used to monitor the completion of reactions. The yield of the products formed, ranged from 60–34% (Table 1). The IR and ^1H NMR spectral data of the resulting products matched well with their structures and are in excellent accordance with their earlier reports.

2 Experimental Procedure

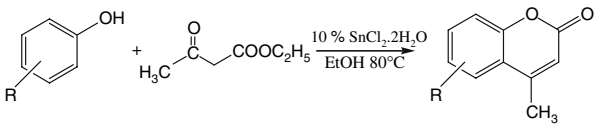
For the synthesis of coumarin derivatives a general procedure was adopted. This involved dissolution of 2 m Mol of the corresponding phenol in ethyl alcohol (2 mL) in a 25 mL round bottom flask followed by addition of 2 m Mol ($\sim$0.3 mL) of ethylacetoacetate with constant stirring and warming followed by addition of 10 mol% of $SnCl_2 \cdot 2H_2O$ in portions. The respective reaction mixtures were boiled under reflux with stirring at the temperature of 80 °C. Thin layer chromatography (TLC) was used to monitor the completion of reactions. On the completion of reactions indicated by TLC, solvents were evaporated and the solid residues were extracted with hot water for the isolation of 2a–2b and hot ethanol–water

Table 1 Synthesis of coumarins via von Pechmann condensation of phenols with ethylacetoacetate catalyzed by $SnCl_2 \cdot 2H_2O$

Entry	Substrate	Reaction product	Reaction temperature	Reaction time (Min)	Yield[a] %
1	 1a	 2a	80	75	60
2	 1b	 2b	80	150	52
3	 1c	 2c	80	135	48
4	 1d	 2d	80	210	40
5	 1f	 2e	80	300	34
6	 1g	No reaction	75	360	–

[a] Recrystallised yield

mixture (50%v/v) for the isolation of 2c–2e. Under the same reaction conditions TLC did not indicate a similar reaction between *p*-Nitrophenol and ethylacetoacetate. A probable reason may be the total use of $SnCl_2 \cdot 2H_2O$ for the conversion of nitro phenol into amino phenol [41] leading to nonavailibility of the catalyst ($SnCl_2 \cdot 2H_2O$) for the expected von Pechmann reaction. The corresponding extracts were cooled and resulting microcrystalline products were filtered, washed with cold water and dried under vacuum separately followed by their characterization through ^1H NMR and IR spectroscopic methods. The corresponding spectroscopic data matched very well with the earlier reports for these compounds. The entire course of reaction described above may be given schematically as follows; Scheme 1



Scheme 1

3 Selected Spectroscopic Data

3.1 7,8-Dihydroxy-4-methyl-chromen-2-one

Compound 2a: (^1H NMR, 300 MHz, ($CDCl_3$): 2.41(s, 3H, Me), 6.13(s, 1H, C=CH), 6.90–7.25(m, 2H, ArH), ArOH peak not observed. IR KBr (cm^{-1}) 3419, 3240, 2925, 1652, 1596, 1512, 1440, 1388, 1335, 1306, 1186, 1062, 1006, 804, 722, 629, 542, 468, 430.

3.2 7-Hydroxy-4-methyl-chromen-2-one

Compound 2b: (^{1}H NMR, 300 MHZ, DMSO-d_6): 2.36 (s, 3H, Me), 6.13(s, 1H, C=CH), 6.7–7.6(m, 3H, ArH), 10.52(s, 1H, ArOH). IR KBr (cm^{-1}) 3498, 3115, 2952, 2819, 2635, 1670, 1606, 1453, 1392, 1275, 1212, 1136, 1072, 986, 901, 846, 805, 748, 583, 535, 476, 443.

3.3 7,4-Dimethyl-chromen-2-one

Compound 2c: (^{1}H NMR, 300 MHZ, DMSO-d_6): 2.31 (s, 3H, Me), 2.10(s, 3H, Me) 4.17(s, 1H, C=CH), 6.71–7.29 (m, 3H, ArH) IR KBr (cm^{-1}) 2970, 2920, 1704, 1636, 1579, 1442, 1378, 1248, 1212, 1146, 1070, 560.

3.4 4-Methyl-benzo[g]chromen-2-one

Compound 2d: (^{1}H NMR, 300 MHZ, DMSO-d_6)- 2.48 (s, 3H, Me), 7.10–8.30 m, (1H, C=CH + 6H, ArH). IR KBr (cm^{-1}) 3056, 1702, 1622, 1595, 1512, 1461, 1381, 1344, 1272, 1213, 1173, 1144, 1078, 957, 847, 816, 784, 749, 664.

3.5 4-Methyl-chromen-2-one

Compound 2e: (^{1}H NMR, 300 MHZ, DMSO-d_6): 1.63 (s, 3H, Me), 6.63–7.43, m (1H, C=CH + 4 ArH) IR KBr (cm^{-1}) 2975, 1705, 1602, 1570, 1444, 1375, 1238, 1185, 941, 835, 667, 559.

The chemical shift values given above are all in δ ppm.

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