

GRINDING TECHNIQUE FOR THE TANDEM SYNTHESIS OF BIS COUMARINYL METHANES USING [BDBDMI]Br-CAN

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ABSTRACT. 3,3-(Butane-1,4-diyl)bis(1,2-dimethyl-1*H*-imidazole-3-ium)bromide ([BDBDMI]Br) is easily used as an efficient and recyclable ionic liquid for the synthesis of bis coumarinyl methanes in the presence of a catalytic amount of ceric ammonium nitrate (CAN) under grinding. All reactions are performed in the absence of solvent in excellent yield during short reaction time. Furthermore, the ionic liquid can be reused and recovered for several times without loss of activity. This method provides several advantages such as simple work-up, environmental friendliness and shorter reaction time along with high yields. All of synthesized compounds were characterized by infrared spectroscopy, ¹H and ¹³C nuclear magnetic resonance spectroscopy and elemental analyses.

KEY WORDS: Grinding, Ionic liquid, CAN, 4-Hydroxycoumarin, Oxidation, One-pot

INTRODUCTION

Coumarin constitutes one of the major classes of naturally occurring compounds. In the well-known family of coumarin derivatives, dimeric coumarins (also called biscoumarins) occupy an interesting position. Although some types of these compounds could be isolated from plants [1], we are interested in its chemistry because of its benefits as biologically active agents. It also represents the core structure of several molecules of pharmaceutical importance. Coumarin has been reported to serve as anti-cancer [2], anti-microbial [3], anti-inflammatory [4] and anticoagulant [5]. These pharmacological properties of coumarin encouraged us to synthesize some coumarin derivatives.

The use of ionic liquids as reaction media and catalyst can offer a solution to solvent emission and catalyst recycle problems. Ionic liquid possess the advantages like negligible vapor pressure, nonflammability, no miscibility with non-polar solvents, reasonable thermal and chemical stability and recyclability [6-8]. They dissolve many organic and inorganic substrates and are tunable to specific chemical tasks [9]. Recently, ionic liquids have been successfully employed as solvents with catalytic activity for a variety of reactions [10-12].

Looking for the eco-friendly alternatives to synthesize of bis coumarinylmethanes at mild and practical protocols, we report herein the synthesis of bis coumarinylmethanes using [BDBDMI]Br-CAN under grinding as a green and novel method (Scheme 1).

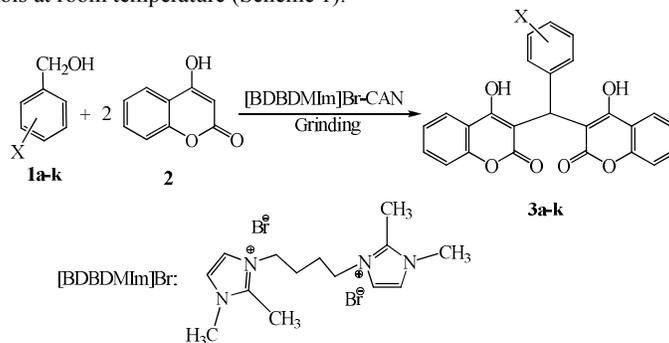
RESULTS AND DISCUSSION

As part of our interest for the development of efficient and environmentally friendly procedures for the synthesis of heterocyclic and pharmaceutical compounds [13-16], an efficient, facile and solvent free procedure was introduced for the synthesis of bis coumarinylmethane through the reaction of one equivalent of synthesized aldehyde and two equivalent of 4-hydroxycoumarin in the presence of ionic liquid [BDBDMI]Br. Although, synthesis of biscoumarins using ionic liquids such as sulfonic acid-functionalized pyridinium chloride [17], RuCl₃·nH₂O [18],

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[bmim]BF₄ [19], SO₃H-functionalized benzimidazolium cation [20], NaHSO₄/SiO₂/Indion 190 resin [21], [MIM(CH₂)₄SO₃H][HSO₄][22] and choline chloride–oxalic acid [23] was reported, however, in all of these reported methods aldehydes were used as substrate and most of these suffer from environmental pollution, expensive reagents or catalysts, long reaction time, exotic reaction conditions, unsatisfactory yields and complicated operations. In order to make this reaction simple and green, herein, we used ionic liquid [BDBDMIm]Br to the synthesis of bis coumarinylmethanes through the one-pot reaction of 4-hydroxycoumarin and various benzylalcohols at room temperature (Scheme 1).



Scheme 1. Synthesis of bis-coumarinylmethanes using [BDBDMIm]Br-CAN under grinding.

To investigate the efficiency of catalyst, some of other catalyst was checked in the model reaction for the synthesis of **3a**. All the reactions were carried out with catalytic amounts of catalysts. As shown in Table 1 the best results gained with 0.4 mmol (4 mmol %) of [BDBDMIm]Br (Table 1; Entry 11).

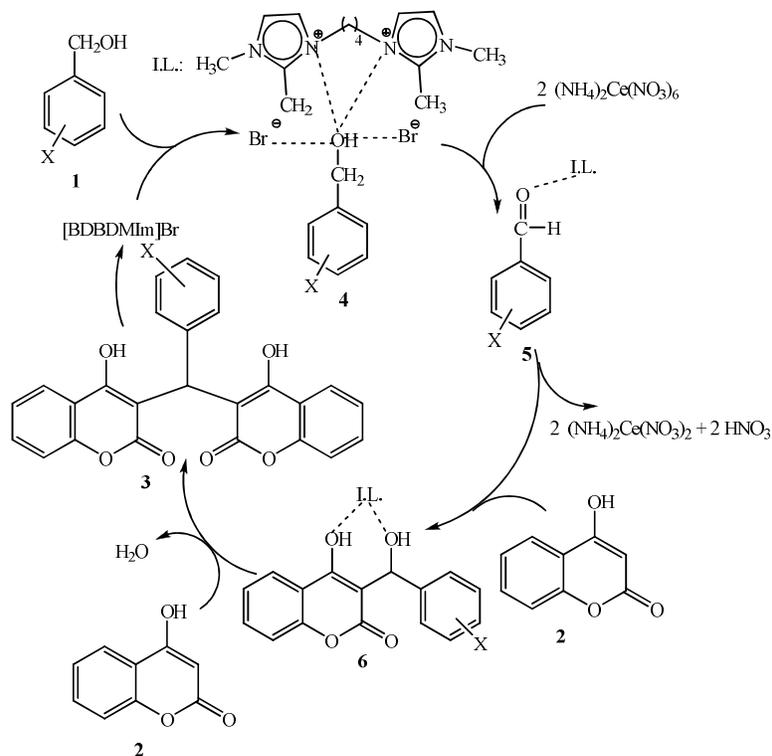
Table 1. Effect of catalyst and catalyst amount for the synthesis of **3a** using 0.55 g of CAN^a.

| Entry | Catalyst | Catalyst amount/1 mmol of aldehyde | Reaction condition | Time (min) | Yield (%) |
|-------|--------------------------------|------------------------------------|--------------------|------------|-----------|
| 1 | H ₂ SO ₄ | 4 drops | Reflux | 240 | 55 |
| 2 | I ₂ | 0.2 mmol | Reflux | 360 | 63 |
| 3 | Montmorillonite K10 | 0.2 g | Reflux | 240 | 72 |
| 4 | Montmorillonite KSF | 0.2 g | Reflux | 240 | 72 |
| 5 | Fe ₃ O ₄ | 0.2 mmol | Reflux | 180 | 78 |
| 6 | ZnCl ₂ | 0.2 mmol | Reflux | 210 | 70 |
| 7 | [BMIM]Br | 0.4 mmol | Neat, r.t. | 60 | 80 |
| 8 | [BMIM]OH | 0.4 mmol | Neat, r.t. | 60 | 76 |
| 9 | [BDBDMIm]Br | 0.2 mmol | Neat, r.t. | 30 | 85 |
| 10 | [BDBDMIm]Br | 0.4 mmol | Neat, r.t. | 20 | 94 |
| 11 | [BDBDMIm]Br | 0.6 mmol | Neat, r.t. | 20 | 98 |

^aSolvent in the entries 1-6 was water.

The reaction yields in the presence of ionic liquid were increased and the reaction times were dramatically shortened to 15-30 min. Therefore, using of ionic liquid exhibited some advantages over the classical condition by improving the reaction yields and reducing the reaction time (Scheme 2).

In the first step, we select **1a** as a model substrate and treated it with 4-hydroxycoumarin in the presence of 0.4 mmol [BDBDMIm]Br and 0.55 g of CAN under solvent free reaction. The same reaction was carried out with 0.2, 0.4 and 0.6 mmol of the ionic liquid, respectively. The best results were obtained using 0.6 mmol of the catalyst with complete conversion within 20 min and in 98% yields.



Scheme 2. A possible mechanism for the synthesis of bis coumarinylmethanes.

To investigation of generality of this method some benzyl alcohols bearing electron withdrawing or electron releasing substituents were checked. The results were presented in Table 2.

Table 2. Synthesis of bis coumarinylmethane **3a-k** using [BDBDMIm]Br at room temperature.^a

| Compound | X | Time (min) | Yield (%) ^b | Mp (°C) | | Ref |
|-----------|-------------------|------------|------------------------|---------|----------|------|
| | | | | Found | Reported | |
| 3a | 4-NO ₂ | 20 | 98 | 231-233 | 232-234 | [24] |
| 3b | 3-NO ₂ | 20 | 98 | 233-235 | 234-236 | [25] |
| 3c | 2-NO ₂ | 45 | 89 | 201-203 | 202 | [24] |
| 3d | 4-Br | 25 | 92 | 265-267 | 267 | [25] |
| 3e | 3-Br | 60 | 90 | 286-288 | 287 | [24] |
| 3f | 4-Cl | 30 | 92 | 255-256 | 256-258 | [24] |
| 3g | 3-Cl | 45 | 90 | 254-256 | - | - |
| 3h | 2-Cl | 60 | 87 | 223-224 | 224 | [21] |
| 3i | 4-F | 20 | 92 | 212-214 | 214 | [25] |
| 3j | 4-OH | 45 | 90 | 223-225 | 22-224 | [21] |
| 3k | 3-OH | 45 | 90 | 218-220 | - | - |
| 3l | 2-OH | 60 | 82 | 253-255 | 254-256 | [24] |
| 3m | H | 60 | 90 | 254-255 | 256-258 | [24] |

^aAll products were characterized by their physical constant, comparison with authentic samples, IR and NMR spectroscopy. ^bYields based upon starting aldehyde.

In order to investigate the reusability of [BDBDMIm]Br, a recycling experiment was conducted. The catalyst could be recycled up to five times without significant loss of activity (Table 3).

Table 3. Evaluation of reusability of [BDBDMIm]Br for the synthesis of **3a**.

| Run | 1 | 2 | 3 | 4 | 5 | 6 |
|------------|----|----|----|----|----|----|
| Time (min) | 20 | 20 | 20 | 21 | 20 | 25 |
| Yield (%) | 98 | 98 | 96 | 98 | 97 | 86 |

A possible mechanism for the synthesis of bis coumarinylmethane derivatives (Scheme 2) is proposed. It is assumed that the reaction may proceed initially through full activation by polarization of benzyl alcohols with [BDBDMIm]Br to form intermediate **4**. Next, benzyl alcohols convert to benzaldehydes **5** by oxidation with CAN ((NH₄)₂Ce(NO₃)₆). In fact oxidation state of Ce(IV) changes to oxidation state in (NH₄)₂Ce(NO₃)₅ (Ce(III)) and nitric acid [26, 27]. Then nucleophilic addition of 4-hydroxycoumarin to intermediate **5** affords **6**. Finally, nucleophilic attack of second 4-hydroxycoumarin to compound **6** and dehydration lead to compound **3**.

CONCLUSIONS

In conclusion, we have investigated the ionic liquid [BDBIM]Br as a mild and efficient catalyst for the synthesis of substituted biscoumarin compounds. The remarkable advantages offered by this method are: catalyst is inexpensive, non-toxic, easy handling and reusable, simple work-up procedure, short reaction time, high yields of product with better purity and green aspect by avoiding toxic catalyst and hazardous solvent. To the best of our knowledge this is the first report on synthesis of biscoumarin compounds using ionic liquid [BDBDMIm]Br.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Chemicals were purchased from Merck and Fluka and used as purchased. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker DRX 500 Avance spectrometer in CDCl₃ and DMSO-d₆ as solvent and with TMS as internal standard. FT-IR spectra were recorded on a Shimadzu FT-IR-8400S spectrometer. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyzer.

General procedure for preparation of compounds **3a-k**

A mixture containing benzyl alcohol (1 mmol), 4-hydroxycoumarin (2 mmol) and 4 mmol% of [BDBDMIm]Br [16] and 0.55 g of CAN was stirred at room temperature for the required reaction times. The progress of the reaction was monitored by TLC (EtOAc : petroleum ether 1:2). Having completed the reaction, we extracted the product with CHCl₃/H₂O. After separation of phases and evaporation of the organic phase and recrystallization of the residue, the pure product was obtained. The aqueous phase was concentrated under reduced pressure, washed with Et₂O, and evaporated under reduced pressure to recover the ionic liquid for subsequent use.

Selected spectral data

4-Hydroxy-3-((4-hydroxy-2-oxo-2H-chromen-3-yl)(4-nitrophenyl)methyl)-2H-chromen-2-one (3a). Yellow solid, IR (KBr) (ν_{\max} , cm⁻¹): 3433, 1662, 1561, 1608, 1520, 1348, 1103; ¹H NMR

(400 MHz, DMSO- d_6) δ : 6.40 (s, 1H), 6.84 (s, br., 2H), 7.30-7.42 (m, 6H), 7.58 (s, br., 2H), 7.88 (d, $J = 6.7$ Hz, 2H), 8.08 (d, $J = 6.7$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO- d_6 , δ / ppm): 36.8, 103.4, 116.0, 118.5, 123.3, 123.7, 124.1, 128.2, 131.9, 145.6, 150.1, 152.5, 164.5, 166.4. Anal. calc. for $\text{C}_{25}\text{H}_{15}\text{NO}_8$: C, 65.65; H, 3.31; N, 3.06. Found: C, 65.63; H, 3.29; N, 3.08.

4-Hydroxy-3-((4-hydroxy-2-oxo-2H-chromen-3-yl)(3-nitrophenyl)methyl)-2H-chromen-2-one (**3b**). Cream solid, IR (KBr) (ν_{max} , cm^{-1}): 3428, 3079, 1658, 1611, 1564, 1528, 1347, 1102, 1058. ^1H NMR (400 MHz, DMSO- d_6) δ : 6.39 (s, 1H), 7.27-7.35 (m, 4H), 7.50-7.57 (m, 4H), 7.86 (d, 1H, $J = 8.0$ Hz), 7.92 (s, 1H), 8.03 (d, 1H, $J = 8.0$ Hz).

4-Hydroxy-3-((4-hydroxy-2-oxo-2H-chromen-3-yl)(2-nitrophenyl)methyl)-2H-chromen-2-one (**3c**). Cream solid, IR (KBr) (ν_{max} , cm^{-1}): 3429, 3075, 2930, 1656, 1609, 1562, 1354, 1522, 1069; ^1H NMR (400 MHz, DMSO- d_6) δ : 5.14 (s, 1H), 7.26-7.33 (m, 4H), 7.40 (d, 2H, $J = 7.6$ Hz), 7.42-7.58 (m, 3H), 7.66 (d, 1H, $J = 7.6$ Hz), 7.84 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, DMSO- d_6): 34.4, 103.6, 116.1, 117.7, 123.7, 123.8, 124.1, 127.2, 130.0, 131.9, 132.2, 134.7, 149.5, 152.3, 163.4, 165.0.

3-((4-Fluorophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-4-hydroxy-2H-chromen-2-one (**3i**). Cream solid, IR (KBr) (ν_{max} , cm^{-1}): 3424, 1670, 1610, 1561, 1099; ^1H NMR (400 MHz, DMSO- d_6) δ : 6.36 (s, 1H), 7.05 (t, 2H, $J = 8.0$ Hz), 7.19-7.29 (m, 2H), 7.31 (t, 2H, $J = 8.8$ Hz), 7.37 (d, 2H, $J = 8.0$ Hz), 7.59 (td, 2H, $J = 8.4, 2.0$ Hz), 7.91 (dd, 2H, $J = 8.0, 2.0$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO- d_6): 35.5, 104.3, 115.0, 116.1, 117.7, 124.0, 128.8, 132.2, 132.8, 135.7, 152.3, 159.5, 161.9, 165.1.

3-((4-Bromophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-4-hydroxy-2H-chromen-2-one (**3d**). Cream solid, IR (KBr) (ν_{max} , cm^{-1}): 3421, 3071, 2938, 1669, 1610, 1561, 1488, 1096, 765. ^1H NMR (400 MHz, DMSO- d_6) δ : 6.33 (s, 1H), 7.12 (d, 2H, $J = 8.0$ Hz), 7.34-7.42 (m, 4H), 7.59 (t, 4H, $J = 7.6$ Hz), 7.90 (d, 2H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, DMSO- d_6): 35.8, 104.0, 116.1, 117.9, 118.7, 123.9, 124.0, 129.2, 131.0, 132.1, 139.7, 152.3, 164.8, 165.4.

3-((3-Bromophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-4-hydroxy-2H-chromen-2-one (**3e**). Pink solid, IR (KBr) (ν_{max} , cm^{-1}): 3421, 3074, 1664, 1609, 1561, 1498, 1095, 765. ^1H NMR (400 MHz, DMSO- d_6) δ : 6.35 (s, 1H), 7.10 (s, br, 3H), 7.31-7.36 (m, 7H), 7.58 (t, 2H, $J = 7.2$ Hz), 7.90 (d, 2H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, DMSO- d_6): 36.1, 103.7, 116.0, 118.1, 121.7, 123.8, 124.0, 126.1, 128.6, 129.4, 130.3, 132.0, 143.6, 152.3, 164.7, 165.7).

3-((4-Chlorophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-4-hydroxy-2H-chromen-2-one (**3f**). Cream solid, 300 °C, IR (KBr) (ν_{max} , cm^{-1}): 3434, 1668, 1613, 1562, 1495, 1093, 767. ^1H NMR (400 MHz, DMSO- d_6) δ : 6.28 (s, 1H), 7.14 (d, 2H, $J = 8.0$ Hz), 7.24-7.35 (m, 6H), 7.57 (t, 2H, $J = 8.0$ Hz), 7.88 (d, 2H, $J = 8.0$ Hz).

3-((3-Chlorophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-4-hydroxy-2H-chromen-2-one (**3g**). Pink solid, IR (KBr) (ν_{max} , cm^{-1}): 3398, 3074, 1665, 1610, 1562, 1489, 1098, 764. ^1H NMR (400 MHz, DMSO- d_6) δ : 6.34 (s, 1H), 7.12-7.37 (m, 1H), 7.59 (t, 2H, $J = 7.2$ Hz), 7.92 (d, 2H, $J = 8.0$ Hz).

3-((2-Chlorophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-4-hydroxy-2H-chromen-2-one (**3h**). Yellow solid, IR (KBr) (ν_{max} , cm^{-1}): 3429, 1658, 1612, 1562, 1495, 1053, 759. ^1H NMR (400 MHz, DMSO- d_6) δ : 6.16 (s, 1H), 7.16-7.23 (m, 2H), 7.27-7.37 (m, 6H), 7.56 (t, 1H, $J = 7.6$ Hz), 7.89 (d, 1H, $J = 8.0$ Hz).

4-Hydroxy-3-((4-hydroxy-2-oxo-2H-chromen-3-yl)(3-hydroxyphenyl)methyl)-2H-chromen-2-one (3k). Brown solid, IR (KBr) (ν_{\max} , cm^{-1}): 3397, 1655, 1612, 1569, 1489, 1054. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 6.28 (s, 1H), 6.52-6.58 (m, 3H), 7.0 (t, 1H, $J = 8.0$ Hz), 7.30-7.37 (m, 4H), 7.59 (t, 2H, $J = 8.0$ Hz), 7.91 (d, 2H, $J = 8.0$ Hz).

4-Hydroxy-3-((4-hydroxy-2-oxo-2H-chromen-3-yl)(2-hydroxyphenyl)methyl)-2H-chromen-2-one (3l). Cream solid, IR (KBr) (ν_{\max} , cm^{-1}): 3251, 3078, 1710, 1671, 1634, 1571, 1220. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 5.74 (s, 1H), 7.14 (t, 1H, $J = 7.8$ Hz), 7.19 (d, 1H, $J = 8.0$ Hz), 7.31-7.45 (m, 5H), 7.43 (d, 1H, $J = 8.4$ Hz), 7.48 (d, 1H, $J = 8.0$ Hz), 7.59 (t, 1H, $J = 8.0$ Hz), 7.69 (t, 1H, $J = 7.4$ Hz), 8.07 (brs, 1H), 8.08 (d, 1H, $J = 7.6$). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): 28.7, 113.8, 116.1, 116.3, 116.5, 122.7, 124.0, 124.6, 125.4, 128.7, 132.3, 132.6, 149.2, 152.0, 156.3, 160.5.

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