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Tris(hydrogensulfato) boron as a solid heterogeneous catalyst for the rapid synthesis of α,α′-benzylidene bis(4-hydroxycoumarin) derivatives

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Abstract

α,α′-Benzylidene bis(4-hydroxycoumarin) derivatives were readily prepared in a few minutes with good yields through the reaction of an aromatic aldehyde and 4-hydroxycoumarin in aqueous media in the presence of catalytic tris(hydrogensulfato) boron [$B(HSO_4)_3$].

Keywords: Biscoumarin; 4-Hydroxycoumarin; Tris(hydrogensulfato)boron; Heterogeneous catalyst

Due to special reactivity of 4-hydroxycoumarin, the synthesis of new coumarin derivatives of dimer and tetramer type has been carried out. Coumarins and their derivatives exhibit pharmacological properties such as antibacterial, antifungal, pharmacological, anti-cancer and anticoagulant activity [1–5]. Biscoumarins derivatives are effective urease inhibitors [6]. Also, a number of coumarin derivatives were shown HIV inhibitory activity [1].

The most direct procedure for the preparation of bis-coumarins includes condensation of an aldehyde with 4-hydroxycoumarin in the presence of hazardous catalysts, such as glacial acetic acid and acetic anhydride [7], ethylenediammonium diacetate [8], and piperidine [6]. However, some of these protocols require long reaction times, harsh reaction conditions and expensive reagents [9–11]. Thus, the introduction of milder, faster and more eco-friendly methods is still in great demand.

From the environmental acceptability, recently inorganic acidic salts have widely used in organic synthesis because of minimized wastes, simplicity in handling and decreased reactor corrosion problems [12].

In continuation of our studies on the synthesis of heterocyclic compounds [13–16], we wish to report the results that led to an extremely convenient method for the preparation α,α′-benzylidene bis(4-hydroxycoumarin) from aromatic aldehydes and 4-hydroxycoumarin in the presence of tris(hydrogensulfato)boron [$B(HSO_4))_3$] in excellent yield (Scheme 1).

Tris(hydrogensulfato) boron was easily prepared by addition of chlorosulfonic acid to boric acid at room temperature. It must be noted that the preparation method is simple, clean, and without work-up procedure, because

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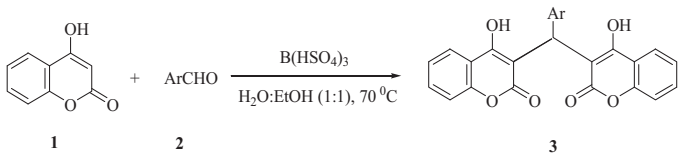


Scheme 1. Synthesis of α,α'-benzylidene bis(4-hydroxycoumarin).

HCl gas is evolved from the reaction vessel immediately (Scheme 2). This catalyst is safe and easy to handle and has been successfully applied in various organic transformations [17].

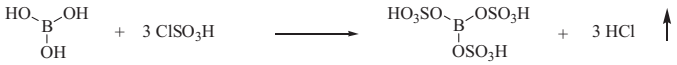
To optimize the amount of catalyst, effect of solvent and effect of temperature, reaction of benzaldehyde and 4-hydroxycoumarin was selected as the model reaction to afford 3,3′-(benzylidene)-bis-(4-hydroxycoumarin). The optimized reactant ratios were found to be 1.0 equiv. benzaldehyde and 2.0 equiv. 4-hydroxycoumarin in the presence of $B(HSO_4)_3$ (0.3 equiv.) in 5 mL aqueous ethanol (1:1, H_2O–EtOH). The expected α,α'-benzylidene bis(4-hydroxycoumarin) was produced in 86% yield after 6 min at 70 °C.

To ascertain the scope and limitation of the present reaction, several aldehydes were examined and the results of their reaction with 4-hydroxycoumarin are summarized in Table 1. Aromatic aldehydes both with activating and deactivating groups underwent smooth transformation to the corresponding bis-coumarins, without the formation of any side products, in high to excellent yields and in very short reaction times. However, the synthesis could not be achieved in the absence of the catalyst.

The reaction proceeds *via* condensation of 1 equiv. of aldehyde with 2 equiv. of 4-hydroxycoumarin to form the corresponding product as has been suggested earlier [20]. The reaction pathway is shown in Scheme 3.

As shown in Table 2, we compared results of 3-methyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate [$MIM(CH_2)_4SO_3H$] [18], sodium dodecyl sulfate (SDS) [19], phosphotungstic acid [20], $H_{14}[NaP_5W_{30}O_{110}]$–$SiO_2$ [21], piperidine [6], HBF_4 and tetrabutylammonium bromide (TBAB) [9], [bmim]BF_4 [22], in the synthesis of α,α'-benzylidene bis(4-hydroxycoumarin) derivatives with present method and demonstrated that $B(HSO_4)_3$ can act as an effective catalyst. Thus, the present work using $B(HSO_4)_3$ as a catalyst is an efficient route for production of α,α'-benzylidene bis(4-hydroxycoumarin) derivatives.

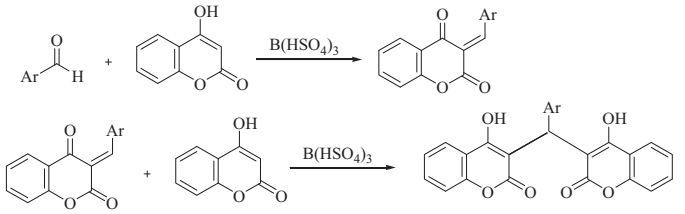
In conclusion, we have demonstrated that $B(HSO_4)_3$ is a efficient catalyst for synthesis of α,α'-benzylidene bis(4-hydroxycoumarin). The notable advantages of this method are high catalytic activity, short reaction times, good yields, simple workup, reusable catalyst, and environmental benignancy.



Scheme 2. Synthesis of tris(hydrogensulfato) boron.

Table 1
Synthesis of α,α'-benzylidene bis(4-hydroxycoumarin).

Entry	Aldehyde	Product	Time (min)	Yield (%)	m.p. (°C)	
					Found	Reported [9,19,20,23]
1	Benzaldehyde	**3a**	6	86	230–232	233–234
2	4-Nitrobenzaldehyde	**3b**	4	98	232–234	238–239
3	3-Nitrobenzaldehyde	**3c**	5	82	229–231	234–236
4	4-Cyanobenzaldehyde	**3d**	4	86	242–244	240–242
5	4-Fluorobenzaldehyde	**3e**	3	88	211–212	213–215
6	4-Chlorobenzaldehyde	**3f**	4	92	256–258	258–259
7	3-Methoxybenzaldehyde	**3g**	4	81	238–240	238
8	4-Methoxybenzaldehyde	**3h**	5	83	246–248	249–250
9	4-Bromobenzaldehyde	**3i**	4	95	264–266	265–267
10	4-Methylbenzaldehyde	**3j**	5	87	266–268	269–270
11	4-Choloro-3-nitrobenzaldehyde	**3k**	4	88	269–270	–



Scheme 3. Proposed mechanism.

1. Experimental

1.1. Preparation of tris(hydrogensulfato)boron ($B(HSO_4)_3$)

A 50 mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Boric acid (1.55 g, 25 mmol) was charged in the flask and chlorosulfonic acid (8.74 g, *ca.* 5 mL, 75 mmol) was added dropwise over a period of 1 h at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 1 h, while the residual HCl was eliminated by suction. Then the mixture was washed with diethyl ether to remove the unreacted chlorosulfonic acid. Finally, a grayish solid material was obtained in 93% yield (7.0 g) and then, in a mortar mixed with silica gel (1:4).

1.2. Representative procedure for synthesis of α,α′-benzylidene bis(4-hydroxycoumarin) derivatives

A solution of aromatic aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), and $B(HSO_4)_3$ (0.018 g) in 5.0 mL aqueous ethanol (50%) was stirred at 70 °C for the appropriate times (Table 1). Upon completion of the reaction, monitored by TLC, the reaction mixture was allowed to cool to room temperature. The solid was filtered off and washed with water (2 × 20 mL) and purified by recrystalization from ethanol. The structures of all products **3a**–**k** were confirmed by IR, ^{1}HNMR, ^{13}CNMR, and elemental analysis.

3,3′-(3-Nitrobenzylidene)-bis-(4-hydroxycoumarin)(entry 3): IR(KBr): 3424, 2925, 1655, 1616, 1564, 1494, 1450, 1347, 762 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.39 (s, 1H, CH), 7.28–8.04 (m, 12H, ArH), 8.04–9.52 (m, 2H, OH).

3,3′-(4-Cholorobenzylidene)-bis-(4-hydroxycoumarin)(entry 6): IR(KBr): 3420, 2923, 1668, 1606, 1563, 1490, 1451, 1351, 765 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.63 (s, 1H, CH), 7.16–7.90 (m, 12H, ArH), 7.90–9 (m, 2H, OH).

3,3′-(4-Methoxybenzylidene)-bis-(4-hydroxycoumarin)(entry 8): IR(KBr): 3443, 2926, 1668, 1606, 1563, 1510, 1452, 1352, 767 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.71 (s, 3H, CH_3O), 6.31 (s, 1H, CH), 6.80–7.93 (m, 12H, ArH), 8.16–8.78 (m, 2H, OH).

Table 2
Comparison results of $B(HSO_4)_3$ with other catalysts reported in the literature.

Entry	Conditions	Catalyst	Time (min)	Yield (%)
1	Solvent-free, 80 °C	[MIM$(CH_2)_4SO_3H$] (20 mol%)	25–30	86–96
2	H_2O, 60 °C	SDS (20 mol%)	2.5–3 h	80–96
3	H_2O, 80 °C	Phosphotungstic acid (15 mol%)	14–25	90–98
4	EtOH, 25 °C	$H_{14}[NaP_5W_{30}O_{110}]$–$SiO_2$ (0.3 mol%)	20–30	90–98
5	EtOH, r.t.	Piperidine	4 h	89–97
6	H_2O, 25 °C	HBF_4 (10 mol%)	10–12 h	55–70
7	H_2O, reflux	TBAB (10 mol %)	25–40	82–95
8	Solvent-free, 60–70 °C	[bmim]BF_4 (4 mmol)	2–3 h	77–91
9	H_2O:EtOH (1:1), 70 °C	$B(HSO_4)_3$ (0.3 mmol)	3–6	81–98

3,3′-(4-Choloro-3-nitrobenzylidene)-bis-(4-hydroxycoumarin)(entry 11): IR(KBr): 3423, 2920, 1665, 1613, 1558, 1536, 1450, 1348, 765 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 6.28 (s, 1H, CH), 7.26–7.85 (m, 11H, ArH), 8.15–8.56 (m, 2H, OH); ^{13}C NMR (DMSO-d_6): δ 36.42, 103.23, 116.24, 119.31, 121.99, 123.81, 124.03, 124.51, 131.39, 132.07, 132.89, 143.87, 147.94, 152.90, 164.70, 167.34. Anal. Calcd. for $C_{25}H_{14}ClNO_8$: C, 60.80; H, 3.27; N, 2.84; Found: C, 60.89; H, 3.25; N, 2.90.

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