

Recyclable Boron Sulfonic Acid as an Environmentally Benign Catalyst for the One-Pot Synthesis of Coumarin Derivatives under Solvent-Free Condition

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Abstract

A mild and green method has been developed for the preparation of coumarins derivatives through the one-pot reactions. In our study, various phenols and ethyl acetoacetate compound in which we used silica-supported boron sulfonic acid [SiO₂/B(SO₄H)₃] as a new, highly efficient and tri-functional inorganic Brønsted acid catalyst were processed under solvent-free condition and thermal. The catalysts were separated easily from reaction mixture, regenerated after a simple activation step and reused at least six times without significant loss in catalytic activity. The most significant features of this procedure are: short period of conversion and excellent yields, simple experimental procedure, environmentally benign, the elimination of corrosive liquid acids and green aspects by avoiding toxic conventional catalysts and solvents.

Keywords: Silica boron sulfonic acid; Heterogeneous catalysts; Pechmann condensation; Solvent-free; Brønsted acid and Lewis acid catalyst.

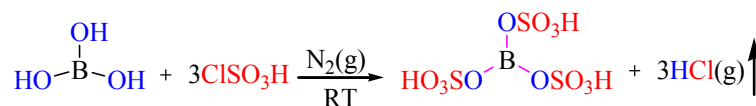
Introduction

In numerous classes of naturally occurring compounds, the coumarin ring system has got a critical and important role and they also can be regarded as important categories of heterocyclic compounds whose production has attracted the attention of several organics and medical chemists [1,2]. Coumarin derivatives are very important compounds due to the fact that they have got biological and pharmacological behaviors such as reticence of platelet aggregation [3], antibacterial characteristic [4], anticancer property [5], steroid 5-reductase inhibition [6], as well as the inhibition of HIV-1 protease [7]. These compounds are commonly being used as different food additives as well as perfumes, and also as chemicals used in agriculture,

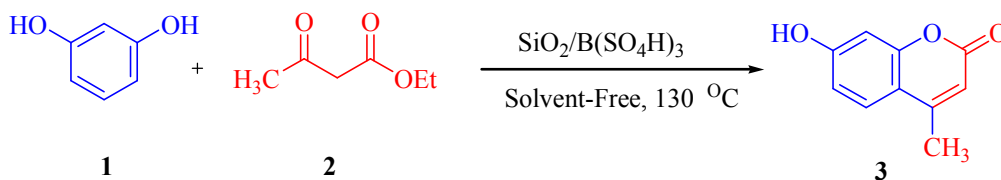
cosmetics, and pharmaceutical products [8]. Moreover, they also can be applied in the preparation of the insecticides, dispersed fluorescent, tunable dye lasers and optical brightening agents, [9]. Coumarins can be used as intermediates for manufacturing fluorocoumarins, chromenes, coumarones, and 2-acylresorcinols [10]. There are several methods for the production of coumarins, some of them include Pechmann [11], Knoevenagel [12-14], Perkin [15] and Wittig reactions [16].

Moreover, the Pechmann method is the most common one among others. Diversities of catalysts were examined for this reaction including SBA-15 [17], Bi(NO₃)₃.5H₂O [18], ZrCl₄ [19], nanocrystalline sulfated zirconia-microwave [20], HClO₄-SiO₂ [21],

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Scheme 1. Preparation of BSA

Scheme 2. Synthesis of coumarins derivatives using $\text{SiO}_2/\text{B}(\text{SO}_4\text{H})_3$, under solvent-free conditions.

NH_4VO_3 [22], TiCl_4 [23], polyaniline supported acid catalyst [24], Wells-Dawson heteropolyacid [25], ALSBA-1 molecular [26], Poly (4-vinylpyridine)-supported copper iodide [27], CMK-5 supported sulfonic acid [28], and iodine [29].

Almost all of the mentioned procedures are associated with some kinds of disadvantages such as using expensive catalysts and organic solvents, low regioselectivity, tedious workup, long reaction time and low selectivity. Boron sulfonic acid $\text{B}(\text{SO}_4\text{H})_3$, as a new solid acid catalyst, was first introduced by *Kiasat* and *Mehrjardi* for the regioselective conversion of epoxides to thiocyanohydrins under solvent-free reaction conditions (Scheme 1) [30]. In continuation of our research using $[\text{SiO}_2/\text{B}(\text{SO}_4\text{H})_3]$ for organic transformations, we prepared the catalyst according to the known procedure and applied it for synthesis of coumarin derivatives [31-37].

We report, herein, for the first time, the syntheses of coumarins via Pechmann condensations of ethyl acetoacetate and various phenols in the presence of Brønsted acid and Lewis acidic SBSA under solvent-free conditions at $130\text{ }^\circ\text{C}$ (Scheme 2).

Materials and Methods

General

All reagents were purchased from commercial sources and used without further purification. All products are known and their structures were identified by comparing their IR and ^1H NMR data and also their melting points with those reported in the literatures. The progress of reaction was followed by thin-layer chromatography (TLC) using silica gel SILG/UV 254 and 365 plate. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 on 300 MHz using TMS as internal

standard. IR spectra of the compounds were obtained on a Perkin Elmer spectrometer version 10.03.06 using a KBr disk. Melting Points were taken on an electrothermal capillary melting point apparatus without any further correction.

Preparation of boron sulfonic acid

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 hour at room temperature. HCl was evolved immediately. After completion of the addition, the mixture was shaken for 1 h while the residual HCl was eliminated by suction. The mixture was washed by diethyl ether to remove unreacted chlorosulfonic acid, then 14.4 g SiO_2 was added to it and then mixed together. Finally, the mixture was dried and a grayish solid material was obtained in 95.6 % yield [30].

General procedure for the preparation of coumarin derivatives

A mixture of resorcinol (5 mmol) and ethyl acetoacetate (5 mmol) in the presence of SBSA (5 mol %, 0.05 g) was heated with stirring at $130\text{ }^\circ\text{C}$ for an appropriate period of time. The progress of the reaction was monitored by TLC (thin layer chromatography). Upon completion, the mixture was allowed to cool, ethyl acetate (5 mL) was added and the catalyst was recovered by filtration, then it was washed with ethyl acetate (5 mL), dried and reused according to the procedure mentioned above. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol afforded the requested coumarins in

high yields. All the products were identified by comparing the analytical data (melting point, IR, NMR) with those reported in the literatures. The results are summarized in Table 4. Compounds 3b, 3d, 3e, 3f, 3g and 3h are known [50].

Selected spectral data of the products

7-Hydroxy-4-methyl-2H-chromen-2-one (compound 3a): IR (KBr): 1118, 1265, 1625, 1720, 3016 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): 2.40 (s, CH_3), 6.07 (s, 1H), 6.67 (CH), 6.75 (d, $^3J = 8.0\text{Hz}$, CH), 7.30 (d, $^3J = 7.9\text{Hz}$, CH), 10.5 (s, OH) ppm. ^{13}C NMR (75 MHz, CDCl_3): 18.48, 102.6, 110.7, 112.4, 113.2, 126.9, 153.8, 155.2, 160.7, 161.6 ppm.

4-Methyl-2H-benzo[h]chromen-2-one (compound 3c): IR (KBr): 1021, 1248, 1581, 1735, 3021 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): 2.48 (s, CH_3), 6.48 (s, CH), 7.65-8.35 (m, 6 CH) ppm. ^{13}C NMR (75 MHz, CDCl_3): 19.1, 114.3, 115.5, 121.7, 122.0, 122.6, 124.4, 127.8, 128.4, 129.1, 134.8, 152.6, 154.6, 160.1 ppm.

7-Amino-4-methyl-2H-chromen-2-one (compound 3k): IR (KBr): 1081, 1271, 1550, 1659, 3012, 3412, 3421 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): 2.30 (s, CH_3), 5.91 (s, 1H), 6.12 (s, NH_2), 6.42 (s, CH), 6.60 (d, $^3J = 7.6\text{Hz}$, CH), 7.40 (d, $^3J = 8.0\text{Hz}$, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3): 18.4, 99.0, 107.9, 109.3, 111.6, 126.6, 153.5, 154.2, 155.9, 161.2 ppm.

Results and Discussion

The use of solvent-free procedures and silica-

supported catalysts for organic transformations have been well documented, because of their simplicity of purifications and releasing lower wastes into environment. Besides, they also have been used in various organic transformations [38-39].

Boron sulfonic acid was easily prepared. This reaction includes the addition of chlorosulfonic acid to boric acid under N_2 atmosphere at room temperature. This reaction was clean and easy, because HCl gases were evolved from the reaction vessel immediately (Scheme 1).

First of all, the catalytic effect of SBSA on the condensation reaction of resorcinol and ethyl acetoacetate under solvent-free conditions is described earlier. While under catalyst free conditions only 5% yield was obtained within 24 hours (Entry 1, Table 1), in the presence of SBSA catalyst, the reaction time was decreased and a mixture of various coumarins was produced. As can be seen from Table 1, the best result were obtained at 0.05 g of the SBSA under solvent-free conditions and gave 7-Hydroxy-4-methyl-2H-chromen-2-one in 91% yield and 15 min (Entry 4, Table 1). No further increase in the yield was observed on increasing the amount of catalyst under the same condition (Entry 5, Table 1). The use of 0.1 g of SBSA caused the reaction to take longer time and lower yield (Entry 6, Table 1).

Performing the reaction in organic solvents such as ethanol, water-ethanol, and acetonitrile at room temperature gave no improvement in yields, albeit in longer reaction times (2-5 hours) (Table 2). The optimized conditions for this reaction was examined

Table 1. Optimization of the amount of catalyst in the preparation of 7-hydroxy-4-methyl-2H-chromen-2-one^a

Entry	Catalyst (g)	Time (min)	Yield ^b (%)
1	0.00	24 hr	5
2	0.01	180	30
3	0.03	50	67
4	0.05	15	91
5	0.07	40	83
6	0.1	90	77

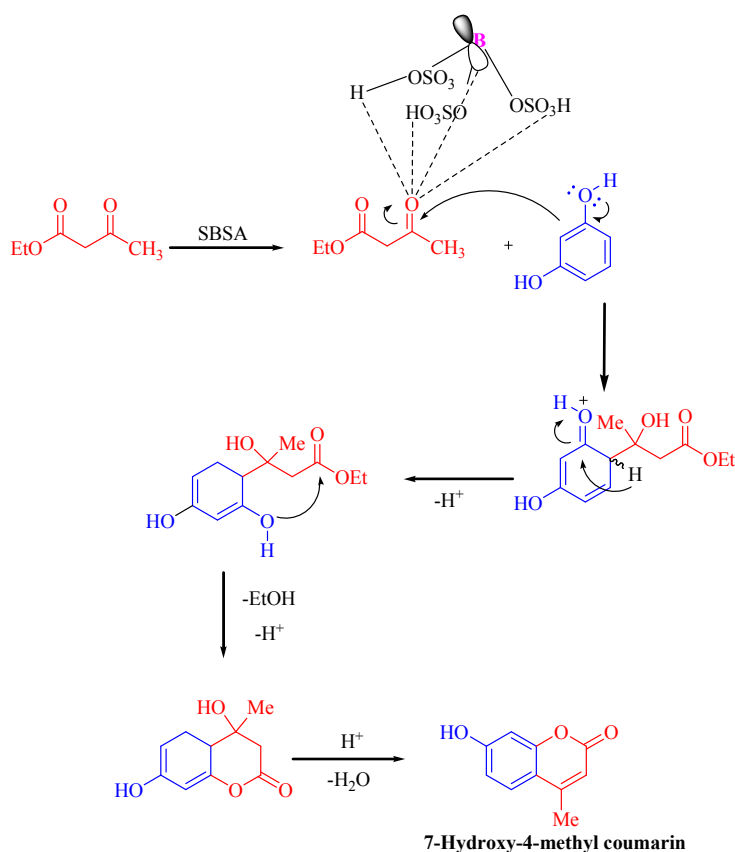
^aReaction condition: resorcinol (5 mmol) and ethyl acetoacetate (5 mmol) in the presence of SBSA at room temperature. ^bYield of isolated products

Table 2. Optimised solvent conditions

Entry	Solvent ^a	Time (h)	Yield ^b (%)
1	Dichloromethane	3	65
2	Ethanol	3.5	71
3	EtOH:H ₂ O ^c	4	45
4	Water	4	35
5	Acetonitrile	5	55
6	Ethyl Acetate	2	52
7	Chloroform	3	49
8	Tetrahydrofuran	2.5	36

^aReaction was carried out in 10 mL of solvents at room temperature. ^bYield of isolated products

^cRatio 1:1



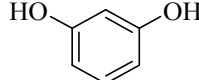
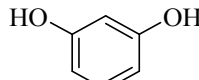
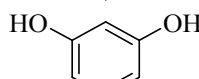
Scheme 3. Proposed reaction mechanism for the Pechmann condensation using SBSA as catalyst.

using an equimolar of the starting materials and heating the mixture at 130 °C for 15 min in the presence of 0.05 g of the catalyst under solvent-free conditions. Having optimized conditions in hand, the generality of the reaction was investigated using various phenols and ethyl acetoacetate compound. The results are summarized in Table 4. Diversities of phenols and naphthols were applied in this procedure to give high to excellent yields of products. Both electron-donating and -withdrawing groups on the phenol rings are tolerated well in this procedur, albeit at different reaction

times. All the reactions were completed within 10-60 minutes with high yields (75–98 %). The SBSA may play a dual role as a Brønsted acid and as a Lewis acid catalyst, and can be simply removed from the reaction mixture by simple filtration. The Lewis acidic property can cause a better link with reagents; resulted in an easy handling and a better effect.

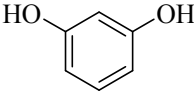
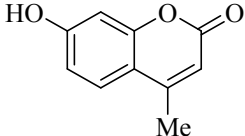
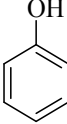
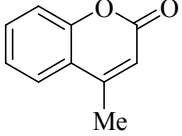
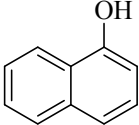
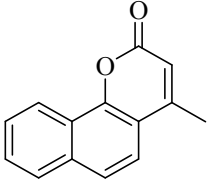
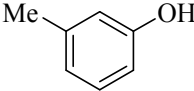
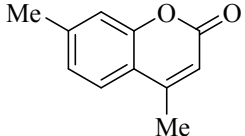
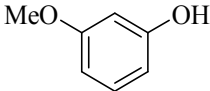
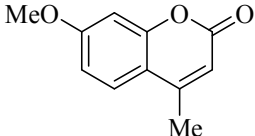
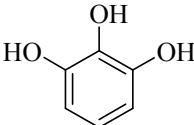
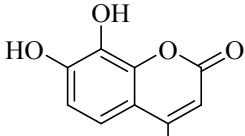
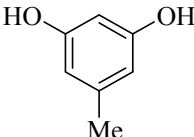
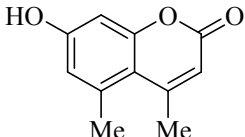
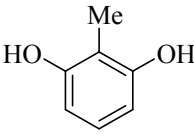
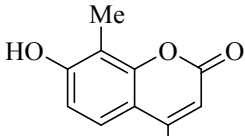
Based on the above discussion, a probable mechanism for the formation of 7-Hydroxy-4-methyl coumarin using SBSA was proposed and presented in Scheme 3. It seems that on proton transfer to a keto

Table 3. Optimization of temperature in the presence of SBSA (0.05 g)

Entry	Substrate	Catalyst (g)	Temperature (°C)	Time (min)	Yield ^a (%)
1		0.05	25	24 hr	91
2		0.05	90	180	25
3		0.05	130	15	98

^aYield of isolated products

Table 4. Synthesis of Coumarin derivatives via Pechmann condensation

Entry	Phenols	Product	Time (min)	Yield ^{a,b} (%)	Melting Point (°C)
1	 3a	 Me	15	98	184-185 [40-41]
2	 3b	 Me	10	99	79-80 [42]
3	 3c	 Me	35	91	153-154 [40, 43]
4	 3d	 Me	25	87	220-222 [42]
5	 3e	 Me	25	88	163-164 [42]
6	 3f	 Me	15	95	244-246 [44]
7	 3g	 Me Me	20	89	247-249 [45]
8	 3h	 Me	25	88	135-136 [46]

group of ethyl acetoacetate from SBSA by interaction of ethyl acetoacetate with catalyst followed by the nucleophilic attack of the hydroxyl group of resorcinol,

resulting in an intermediate and ethanol. The intermediate rapidly undergoes cyclization through acid catalysed intra-molecular condensation yielding 7-

Table 4. Continued

9			20	90	240-243 [44]
10			15	87	281-282 [40, 43]
11			15	93	221-222 [47]
12			30	90	240-242 [48]
13			45	85	134-136 [41]
14			60	75	184-186 [49]
15			25	87	150-152 [49]

^aYield of isolated products, ^bAll products were characterized by spectroscopic data

hydroxy-4-methyl coumarin.

The catalyst system is a free flowing powder that can be stored at room temperature for several months without losing its catalytic potentiality and it may be considered as a very cheap source of solid supported acidic catalyst compared to other available commercially expensive solid supported acids. It was found that SBSA can be used as an inexpensive and reusable catalyst for the synthesis of coumarin derivatives under solvent-free condition. The SBSA was

separated by simple filtration and was washed by chloroform and finally was dried. Good yield was observed when SBSA was reused even after six times recycling (Table 5).

The efficiency of the present work is compared with those reported in the literature (Table 6). The present work shows satisfactory results compared to the previous ones with regard to yields and reaction times.

The ¹H NMR spectrum of 3a exhibits three singlet at $\delta = 2.40$ and 6.07 ppm for two C-H groups and one

Table 5. The catalytic activity of SBSA in six cycles

Run	1	2	3	4	5	6
Yield (%)	98	97	95	94	92	90

Table 6. Comparison of the present work with those reported in the literature

Catalyst	Reaction Conditions	Catalyst loading (mol %)	Time (min)	Yield (%) ^a
H ₃ PW ₁₂ O ₄₀	Toluene Reflux	1	20	96
Sm(NO ₃) ₃ ·6H ₂ O	solvent-free, 80 °C	10	20	98
MTSA ^b	solvent-free, 80 °C	0.05	10	94
I ₂	acetonitrile	0.025 ^d	4 ^e	75
SiO ₂ -NaHSO ₄	CH ₃ CN, reflux	10	1 ^e	95
TiCl ₄	solvent-free, r.t.	10 ^e	50	97
NH ₄ VO ₃	EtOH, r.t.	10	32	81
This work	Solvent-free, 130 °C	5	15	98

^aYield of isolated products, ^bMelamine Trisulfonic Acid, ^cIn hour, ^dIn g, ^eIn mmol

singlet at $\delta = 10.50$ ppm for hydroxyl group. Also, two doublets at $\delta = 6.75$ ($^3J=8.0$) and 7.30 ($^3J=7.9$) for C-H are visible. For **3c**, the ¹H NMR spectrum exhibits a singlet peak at $\delta = 2.48$ ppm for CH₃ group and a singlet peak for C-H group at $\delta = 6.48$ ppm, and at $\delta = 7.65$ - 8.35 ppm for the rest aromatic hydrogens.

Conclusion

In summary, we have developed an efficient method for the synthesis of coumarin derivatives through Pechmann reaction under solvent-free conditions using SBSA as a newly prepared catalyst reagent. This procedure has an excellent yield, relatively short reaction times, non-toxicity of reagent, eco-friendly, simplicity of reaction, and mild reaction conditions. This method is environmentally and economically useful because it produces lower waste compared to reported ones. The catalyst is readily available and also inexpensive and it can conveniently be handled and removed from the reaction mixture. This protocol could serve as a valuable alternative to known reaction systems.

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