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ORIGINAL PAPER

Synthesis of biscoumarin derivatives using poly(4-vinylpyridine)-supported dual acidic ionic liquid as a heterogeneous catalyst

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Abstract A supported dual acidic ionic liquid catalyst was easily prepared from its starting materials (namely poly(4-vinylpyridine) and 1,4-butanesultone) and used as a highly efficient heterogeneous catalytic system for the synthesis of biscoumarin derivatives from the reaction of 4-hydroxycoumarin with aliphatic and aromatic aldehydes. The catalyst can be easily recovered and reused without appreciable change in its efficiency.

Keywords Biscoumarins · Aldehydes · Poly(4-vinylpyridine)-supported ionic liquid · One-pot synthesis · Heterogeneous catalysis

Introduction

Brønsted acidic ionic liquids have been widely applied in many reactions as catalysts or dual catalyst–solvents. They are designed to replace traditional mineral liquid acids such as sulfuric acid and hydrochloric acid in chemical procedures [1, 2]. Among them, SO_3H-functionalized ionic liquids possessing HSO_4^- as a counteranion find a broad range of applications in organic synthesis because the existence of both SO_3H functional groups and hydrogen sulfate counteranions can enhance their catalytic acidities [3–5]. Although the catalytic ability of these ionic liquids has been demonstrated successfully in many reactions, most of them suffer from one or more of the following drawbacks such as laborious work-up procedures, difficulty of recovery and recycling, disposal of spent catalyst, difficult to handle, and corrosion problems. Thus, these shortcomings make them a prime target for heterogenization [6–9].

Coumarin is a fragrant chemical compound in the benzopyrone chemical class, and it is found in many plants [10]. There is widespread interest in the synthesis of coumarin and its derivatives owing to their diverse range of biological properties such as anti-HIV, antibiotic, antifungal, antibacterial, antioxidant, anticancer, and anticoagulant [11–15]. Also, they have been used as fluorescent brighteners, efficient laser dyes, and as additives in food and cosmetics [16–18]. Biscoumarins are one of the most important derivatives of coumarin. Among several methods reported for the synthesis of biscoumarins [16, 19–21], two-component one-pot domino Knoevenagel-type condensation/Michael reaction between aldehydes and 4-hydroxycoumarin is particularly popular. Catalysts that have been used for this conversion include piperidine [22], tetrabutylammonium bromide [23], I_2 [24], sodium dodecyl sulfate [25], ionic liquids [26–28], *p*-dodecylbenzenesulfonic acid/piperidine [29], $NaHSO_4$ [30], and $B(HSO_4)_3$ [31]. However, most of the reported methods suffer from one or more of the following drawbacks: low yields, long reaction times, harsh reaction conditions, tedious work-up leading to the generation of large amounts of toxic waste, inefficiency when aliphatic aldehydes are used in the reaction, and the use of unrecyclable, hazardous, or difficult-to-handle catalysts.

In a continuation of our work on the development of efficient and environmentally benign procedures using poly(vinylpyridine)-supported reagents and catalysts [32], we found that poly(4-vinylpyridine-*co*-1-sulfonic acid butyl-4-vinylpyridinium)hydrogen sulfate ($[P_4VPy–BuSO_3H]HSO_4$) is a good catalyst for the synthesis of 4,4′-(arylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ols) [33].

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We now wish to report that $[P_4VPy–BuSO_3H]HSO_4$ is also an efficient catalyst for the synthesis of biscoumarins by two-component one-pot domino Knoevenagel-type condensation/Michael reaction between various aliphatic and aromatic aldehydes and 4-hydroxycoumarin.

Results and discussion

$[P_4VPy–BuSO_3H]HSO_4$ was prepared from the reaction of poly(4-vinylpyridine) (P_4VPy, 2 % divinylbenzene) with 1,4-butanesultone followed by treatment with H_2SO_4. The acidic sites loading in $[P_4VPy–BuSO_3H]HSO_4$ obtained by means of acid–base titration was found to be 1.7 mmol/g (Scheme 1).

In order to explore the catalytic activity of $[P_4VPy–BuSO_3H]HSO_4$, we studied the condensation reaction of aldehydes with 4-hydroxycoumarin (Table 1). Initially, to optimize the reaction conditions, we tried to convert benzaldehyde (1 mmol) to 3,3′-benzylidenebis(4-hydroxycoumarin) with 4-hydroxycoumarin (2 mmol) and $[P_4VPy–BuSO_3H]HSO_4$ in the presence of various solvents at different temperatures. It was observed that this reaction goes well at 90 °C in toluene. Afterwards, to optimize the quantity of $[P_4VPy–BuSO_3H]HSO_4$, 0.05–0.15 mmol of the catalyst was used in the this reaction. It was found that 0.1:1 mmol ratio of catalyst to benzaldehyde was sufficient to obtain 3,3′-benzylidenebis(4-hydroxycoumarin) in 93 % yield within 0.8 h. Then, under optimal conditions, a wide variety of aromatic aldehydes (containing both electron-withdrawing and electron-donating groups, entries 1–8), heteroaromatic aldehydes such as 2-furyl- and 2-thienylcarbaldehyde (entries 9, 10), and aliphatic aldehydes (entries 11, 12)

Scheme 1

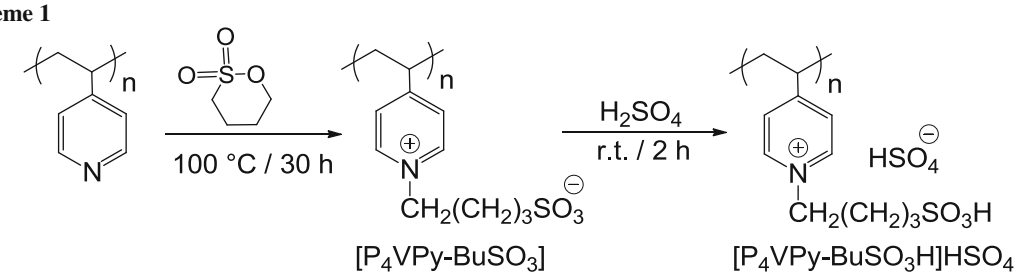
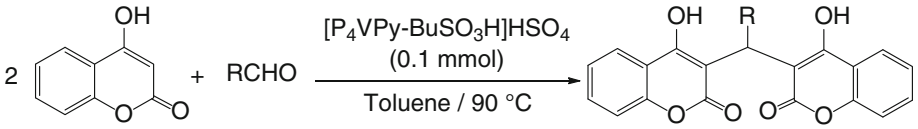


Table 1 Synthesis of biscoumarin derivatives



Entry	R	Time/h	Yield/%[a]	M.p. (Lit. m.p.)/°C
1	C_6H_5	0.8	93	232–234 (230–232 [25])
2	4-CH_3-C_6H_4	0.9	92	268–270 (266–268 [25])
3	4-OCH_3-C_6H_4	1	91	243–245 (242–244 [24])
4	4-Cl-C_6H_4	0.8	94	258–260 (256–258 [25])
5	3-Cl-C_6H_4	0.9	95	233–235 (228–230 [25])
6	4-OH-C_6H_4	1	91	223–225 (222–224 [24])
7	3-NO_2-C_6H_4	0.7	95	236–238 (235 [30])
8	4-NO_2-C_6H_4	0.6	95	233–235 (232–234 [24])
9	2-Furanyl	0.8	90	203–205 (202 [24])
10	2-Thienyl	0.9	90	206–209 (210 [24])
11	$C_6H_5CH_2CH_2$	1	91	190–193 (190 [22])
12	C_6H_5CH=CH	1	92	279–281 (278 [22])

All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples

[a] Isolated yields

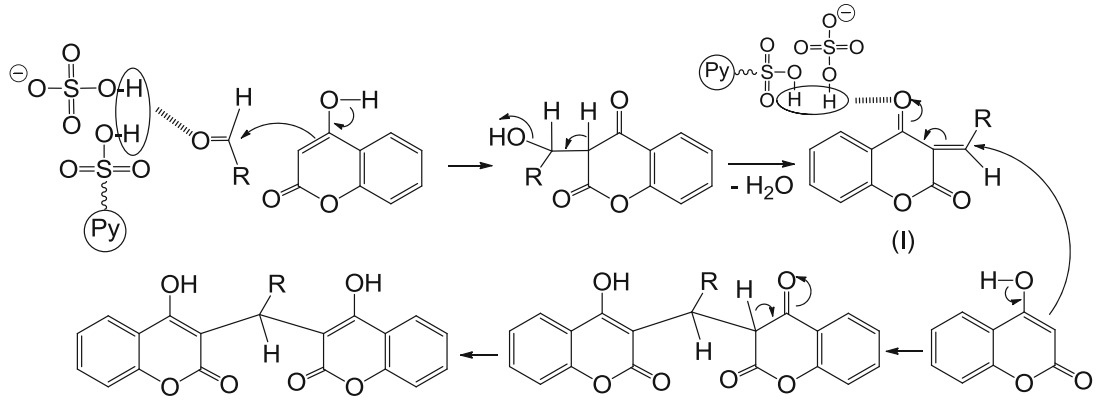
were treated with 4-hydroxycoumarin to give the corresponding biscoumarin products. As shown in Table 1, the aromatic aldehydes with electron-withdrawing groups reacted faster than the aromatic aldehydes with electron-dontaing groups. This observation can be rationalized on the basis of the mechanism in Scheme 2. The aldehyde is first activated by $[P_4VPy–BuSO_3H]HSO_4$. Nucleophilic addition of 4-hydroxycoumarin to activated aldehyde followed by loss of H_2O generates intermediate I, which is further activated by $[P_4VPy–BuSO_3H]HSO_4$. Then, 1,4-nucleophilic addition of a second molecule of 4-hydroxycoumarin to activated intermediate I, in a Michael-type addition, affords the biscoumarin product. The electron-withdrawing groups substituted on aromatic aldehyde in intermediate I increase the rate of 1,4-nucleophilic addition reaction because of the alkene LUMO is at lower energy in their presence compared with electron-donating groups [34].

To find out whether the reaction takes place in the solid matrix of $[P_4VPy–BuSO_3H]HSO_4$ or whether the acidic sites simply released in the reaction medium are responsible for the catalytic properties, $[P_4VPy–BuSO_3H]HSO_4$ was added to toluene and the mixture was stirred at 90 °C for 2 h. Then, the catalyst was filtered off and the filtrate was analyzed for its acid content, which showed a negligible release of the acidic sites. The filtrate was found to be inactive in the condensation of 4-hydroxycoumarin with aldehydes. These observations indicate that $[P_4VPy–BuSO_3H]HSO_4$ is stable under the reaction conditions, and there is no leaching of acid moieties during reactions.

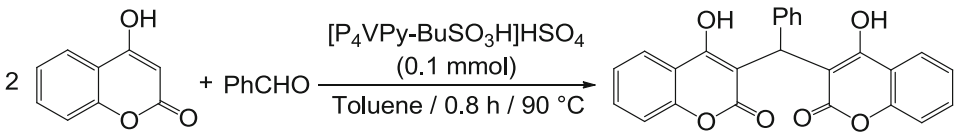
The recovered $[P_4VPy–BuSO_3H]HSO_4$ can be washed with toluene and used again at least five times without any noticeable loss of catalytic activity (Scheme 3).

In conclusion, $[P_4VPy–BuSO_3H]HSO_4$ is an efficient heterogeneous acid catalyst for the synthesis of biscoumarin derivatives under modest conditions. The significant advantages of this methodology are high yields, short reaction times, simple work-up procedure, easy preparation and handling of the catalyst, and minimization of cost and waste generation owing to reuse and recycling of the catalyst.

Scheme 2



Scheme 3



Run No.	1	2	3	4	5
Yield /%	93	93	92	90	90

Experimental

Chemicals were either prepared in our laboratory or purchased from Merck and Fluka. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica-gel Polygram SILG/UV_{254} plates. Gas chromatography was recorded on Shimadzu GC 14-A. IR spectra were measured by a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer. A Leco sulfur analyzer was used for the measurement of sulfur in the catalyst. Melting points were determined on a Fisher–Jones melting point apparatus.

Synthesis of [P_4VPy–$BuSO_3H$]HSO_4

In a round-bottomed flask (50 cm^3) equipped with a reflux condenser, 1 g of P_4VPy was added to 1.5 cm^3 1,4-butanesultone and the mixture was stirred at 100 °C for 30 h, filtered, washed with 20 cm^3 distilled water, and dried at 80 °C overnight. Afterwards, 5 cm^3 H_2SO_4 (3 M) was added to the obtained resin and the mixture was stirred at room temperature for 2 h, filtered, washed with 20 cm^3 distilled water, and dried at 80 °C overnight to give [P_4VPy–$BuSO_3H$]HSO_4.

Titration of acidic site loading

Dry [P_4VPy–$BuSO_3H$]HSO_4 (1 g) was added to 10 cm^3 aqueous solution of NaCl (2 M) and the resulting mixture was stirred for 24 h and then titrated potentiometrically with aqueous solution of NaOH (0.01 mol/dm^3) as titrant and phenolphthalein as an indicator.

Typical procedure for synthesis of biscoumarins

To a solution of benzaldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), and 3 cm^3 toluene was added [P_4VPy–$BuSO_3H$]HSO_4 (0.1 mmol) and the resulting mixture was magnetically stirred at 90 °C. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was filtered off and washed with toluene (2×5 cm^3) and the filtrate was concentrated on a rotary evaporator under reduced pressure. The crude product was recrystallized from ethanol to give 3,3′-benzylidenebis(4-hydroxycoumarin).

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