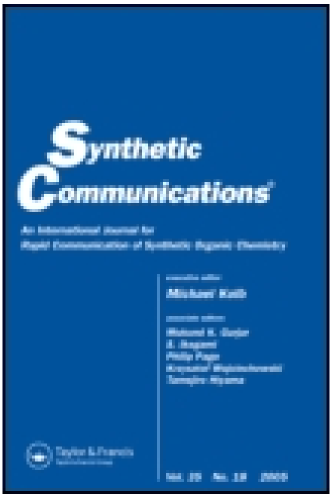

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EFFICIENT SYNTHESIS OF BIS-COUMARINS USING SILICA-SUPPORTED PREYSSLER NANOPARTICLES

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Reaction of aldehydes and 4-hydroxycoumarin in the presence of catalytic amount of silica-supported Preyssler nanoparticles led to synthesis of bis-coumarins in excellent yields.

Keywords: Bis-coumarin; heteropolyacids; recyclable catalyst

INTRODUCTION

Coumarin derivatives form an important class of compounds. These compounds possess several types of pharmacological properties such as anticancer, anti-HIV, anticoagulant, spasmolytic, and antibacterial activity.[1] A large number of structurally novel coumarin derivatives have been reported to show substantial cytotoxic activity in vitro and in vivo.

Development of methods using heteropolyacids (HPAs) as catalysts for organic synthetic processes related to fine chemicals, such as flavors and pharmaceuticals,[2] have received attention in the past decade. The catalysts based on HPAs have many advantages over liquid acid catalysts. They are not corrosive but are environmentally benign, presenting fewer disposal problems. Solid HPAs have attracted much attention in organic synthesis because of their easy workup procedures, easy filtration, and minimal cost and waste generation due to reuse and recycling of the catalysts.[3]

Over the past decade, because of the unique properties of nanoparticles along with their potential applications in different fields,[4] synthesis and characterization of catalysts with lower dimension have became the most interesting topic of research. As the particle size decreases, the relative number of surface atoms increases and thus activity increases. Moreover, because of quantum size effects, nanometer-sized particles may exhibit unique properties for a wide range of applications.[5]

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Recently, these considerations raised the interest in synthesis of Keggin nanocatalysts,[6] but the synthesis and catalytic activity of Preyssler nanocatalyst have been largely overlooked.

In our attempt to use HPAs as catalysts in organic reactions, we recently reported that the Preyssler type, $H_{14}[NaP_5W_{30}O_{110}]$, shows strong catalytic characterization.[7] Because of the unique properties of nanoparticles along with their novel properties and potential applications in different fields,[4] we decided to immobilize $H_{14}[NaP_5W_{30}O_{110}]$ into the SiO_2 nanoparticles and investigate the catalytic behavior of this new catalyst.

Herein we report a mild, efficient, and environmentally benign procedure for the synthesis of bis-coumarins from reaction of aldehydes and 4-hydroxycoumarin in the presence of silica-supported Preyssler nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ as an efficient catalyst (Scheme 1).

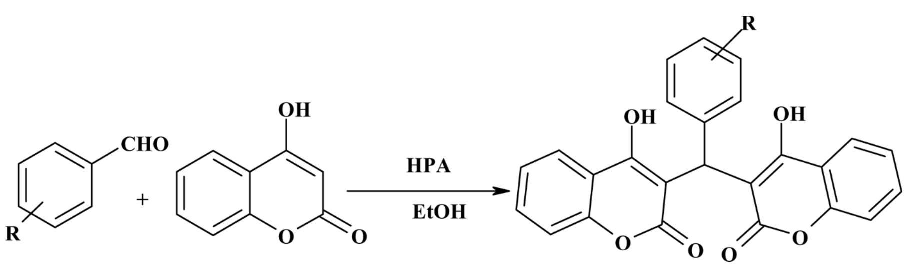
Various reaction conditions, such as different amount of catalysts, were examined to obtain the optimum reaction condition. The results of synthesis of bis-coumarin derivatives in the presence of a catalytic amount of silica-supported Preyssler nanoparticles are summarized in Table 1.

To optimize the amount of catalyst, the yields of two derivatives of bis-coumarin using various amounts of catalysts (0.2, 0.3, and 0.5 mol%) were obtained. The results for synthesis of bis-coumarin derivatives using different amounts of silica-supported Preyssler nanoparticles are shown in Table 2. It is clear from this table that the yields of reactions with very small amounts of catalyst are very high, and the optimum amount of catalyst was selected as 0.3 mol% for all derivatives.

To investigate the effect of solvent on this reaction, the syntheses of two derivatives of bis-coumarin have been carried out in three solvents including water, the 1:1 mixture of water/EtOH, and EtOH. The results are summarized in Table 3.

The effect of temperature on this reaction has been studied by carrying out the synthesis of two derivatives of bis-coumarin at various temperatures (room temperature, 50°C, and refluxing temperature). The results showed that increasing the reaction temperature has no significant effect on the yields of reactions, and only in refluxing temperature is a slight reduction in reaction time, 5 min, observed. The optimum temperature was thus room temperature (Table 4).

To compare the efficiency of silica-supported Preyssler nanoparticles with Preyssler-type HPAs, the reactions have been carried out in the presence of both catalysts in the same reaction conditions. The results are summarized in Table 5.



Scheme 1. Synthesis of bis-coumarins in the presence of silica-supported Preyssler nanoparticles.

Table 1. Synthesis of bis-coumarins in the presence of silica-supported Preyssler nanoparticles as catalyst

Entry	R	Time (min)	Yield (%)[a]	Mp (°C)	
				Found	Reported[9,10]
1	H	30	92	228	228–230
2	4-OCH_3	25	90	242	242–244
3	4-CH_3	30	90	266	265–267
4	4-Cl	20	98	252	252–254
5	3-NO_2	20	96	240	240–242
6	4-NO_2	20	94	233	232–234
7	2-OH	20	96	231	230–232

[a]Yields of isolated products.

Table 2. Results of using various amount of silica-supported Preyssler nanoparticles in synthesis of two derivatives of bis-coumarin

Entry	R	Time (min)	Catalyst amount (mol%)	Yield (%)[a]
1	4-Cl	30	0.2	93
2	4-Cl	20	0.3	98
3	4-Cl	20	0.5	98
4	4-NO_2	30	0.2	90
5	4-NO_2	20	0.3	94
6	4-NO_2	20	0.5	94

[a]Yields refer to isolated products.

Table 3. Effect of using various solvents on the synthesis of two derivatives of bis-coumarin

Entry	R	Time (min)	Solvent	Yield (%)[a]
1	4-Cl	35	Water	88
2	4-Cl	30	Water/EtOH	93
3	4-Cl	20	EtOH	98
4	4-NO_2	30	Water	85
5	4-NO_2	25	Water/EtOH	89
6	4-NO_2	20	EtOH	94

[a]Yields refer to isolated products.

Table 4. Effect of various temperatures on the synthesis of two derivatives of bis-coumarin

Entry	R	Time (min)	Temperature (°C)	Yield (%)[a]
1	4-Cl	20	25	99
2	4-Cl	20	50	99
3	4-Cl	15	80	99
4	4-NO_2	20	25	94
5	4-NO_2	20	50	94.2
6	4-NO_2	15	80	94.5

[a]Yields refer to isolated products.

Table 5. Comparison of efficiency of silica-supported Preyssler nanoparticles and Preyssler in the synthesis of bis-coumarins

Entry	R	Time (min)	Catalyst	Yield (%)[a]
1	H	30	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$	92
2	H	40	$H_{14}[NaP_5W_{30}O_{110}]$	88
3	4-OCH_3	25	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$	90
4	4-OCH_3	40	$H_{14}[NaP_5W_{30}O_{110}]$	82
5	4-CH_3	30	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$	90
6	4-CH_3	35	$H_{14}[NaP_5W_{30}O_{110}]$	85
7	4-Cl	20	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$	98
8	4-Cl	35	$H_{14}[NaP_5W_{30}O_{110}]$	90
9	3-NO_2	20	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$	96
10	3-NO_2	40	$H_{14}[NaP_5W_{30}O_{110}]$	90
11	4-NO_2	20	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$	94
12	4-NO_2	35	$H_{14}[NaP_5W_{30}O_{110}]$	88
13	2-OH	20	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$	96
14	2-OH	40	$H_{14}[NaP_5W_{30}O_{110}]$	89

[a]Yields refer to isolated products.

As shown in this table, the yields of reactions, catalyzed by silica-supported Preyssler nanoparticles are better than by Preyssler nanoparticles alone.

To show the merit of this method for synthesis of bis-coumarins, the comparison of our result for reactions of 4-nitro-benzaldehyde and 4-hydroxycoumarin using silica-supported Preyssler nanoparticles as catalyst with those reported in previous works has been carried out (Table 6).

As shown in this table, the synthesis of bis-coumarins in the absence of catalyst led to long reaction times and poor yields. Using I_2 as catalyst gave bis-coumarin in good yield (95%) and short reaction time (28 min). Although I_2 is an efficient catalyst for this reaction, its required amount is 10 mol%, and there is no report based on its reusability. Only 0.3 mol% of $(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$ can catalyze the reaction, and its reusability is another advantage.

In summary, bis-coumarin derivatives were obtained from reaction of aldehydes and 4-hydroxycoumarin in the presence of a catalytic amount of silica-supported Preyssler nanoparticles. Using this catalyst offers advantages including

Table 6. Comparison of synthesis of one bis-coumarin derivative in various conditions

Entry	R	Condition	Catalyst	Time (min)	Yield (%)[a]
1	4-NO_2	Stir in EtOH at room temperature	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$ (0.3 mol%)	20	94
2	4-NO_2	Stir in EtOH at room temperature	$H_{14}[NaP_5W_{30}O_{110}]$ (0.3 mol%)	30	88
3	4-NO_2	Stir in water at 100 °C	I_2 (10 mol%)	28	95[11]
4	4-NO_2	Reflux in EtOH	—	240	79[12]
5	4-NO_2	Reflux in EtOH or glacial acetic acid	—	360	76[10]

[a]Yields of isolated products.

simplicity of operation, easy workup, good yields of products, and the recyclability of the catalyst.

EXPERIMENTAL

All the chemicals were purchased from Merck Company. Melting points were measured using Barnstead Electrothermal instrument. Gas chromatographic (GC)/ mass analysis was performed using an Agilent 6890 GC system, Hp-5 capillary (30 m × 530μm × 1.5μm nominal). Silica-supported Preyssler nanoparticles were prepared according the literature.[8] All compounds were known, and their physical data were compared with those of authentic compounds and found to be identical.[9,10]

Synthesis of Silica-Supported Preyssler Nanoparticles

A solution of Preyssler acid in a specified amount of water was added to a solution of sodium bis(2-ethylhexyl)sulfosuccinate in cyclohexane (0.2 M). The molar ratio of water to surfactant was selected as 3, 5 and 7. Then, tetraethoxysilan was added into the microemulsion phase. After mixing for various times (8, 12, 18, 25, and 30 h) at room temperature, dispersed Preyssler acid/SiO_2 nanostructures were centrifuged (1500 rpm), and the particles were rinsed with acetone (four times) and dried in a vacuum oven.

Synthesis of α-Aminonitrile Derivatives: General Procedure

A catalytic amount of silica-supported Preyssler nanoparticles (0.3 mol%) was added to a mixture of aldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol). The mixture was stirred vigorously in EtOH at room temperature for the appropriate reaction time. The reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the precipated product was separated through filteration and washed with ethanol to give the pure product.

Table 7. Comparison of efficiency of silica-supported Preyssler nanoparticles in synthesis of bis-coumarins after three times

		Yield (%)[a]		
Entry	R	First run	Second run	Third run
1	H	92	90	90
2	4-OCH_3	90	88	87
3	4-CH_3	90	89	88
4	4-Cl	98	96	94.5
5	3-NO_2	96	95	95
6	4-NO_2	94	93	92
7	2-OH	96	95	95

[a]Yields refer to isolated products.

Recycling of the Catalyst

After filtration of the products, the catalyst could be recycled by evaporation of the residue solution and washing with diethyl ether in each case. The recovered catalyst could be dried and reused for the next reaction with only a slight loss in activity. The catalyst was recovered and reused for three times in these reactions. The obtained results are summarized in Table 7.

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