



Application of Non-Corrosive Acids in Three-Component, One-Pot Synthesis of Commercial Coumarin Dye

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ABSTRACT

The efficiency of HZSM-5 Zeolite, tungestophosphoric acid $(H_3PW_{12}O_{40})$ and tungestosililic acid $(H_4O_{40}SiW_{12})$ were investigated in threecomponent, one-pot synthesis of coumarin dyes. These green and noncorrosive acids were highly efficient in synthesis of some coumarin dyes in excellent yield during concurrent formation of coumarin and benzimidazole or benzoxazole heterocycles (e.g. C. I. disperse yellow 232 as a commercial fluorescence dye was synthesized using tungestophosphoric acid in 45 minutes and %90 yield). Evaluations of the yields of products were studied in organic solvent (n-pentanol) and aqueous media and under solvent-free conditions considering the reaction times were studied as well. The results demonstrated that n-pentanol as an organic solvent was the best media for these preparations. Prog. Color Colorants Coat. 3(2010), 102-109. © Institute for Color Science and Technology.

1. Introduction

Among coumarin dyes, 7-aminocoumarins are widely used as blue laser dyes as well as florescence probes in many chemical and physicochemical studies. Synthesis of laser dyes, fluorescent brightener, and organic nonlinear optical materials are also some examples of their importance industry [1-14]. As a result of growing demand, the improvement in the synthetic efficiency of coumarin derivatives has been perceived recently [10, 15-23]. They are also useful as fluorescent textile dyes [24–30]. For example, Color Index (C. I.) disperse yellow 232 [3-(5'-chloro-2'-benzoxazolyl)-7-diethylamino-2H-1-benzopyran-2-one] (4a) is known as a commercial fluorescence textile dye. Previously, this dye was produced within 30 h through a six-step procedure or at 180°C [31] and recently in improved conditions through 10 to 12 h reflux in n-pentanol with %65 yield [32]. In order to produce oxazole or imidazole ring in these procedures acids are affective (Figure 1).

The activity, selectivity, and reusability of acid zeolites and heteropoly acids (HPAs) are known. These acids are also known as more active catalysts than conventional inorganic and organic acids for various reactions in solution. HPAs have gained industrial importance due to easy work-up procedures, minimization of waste generation, noncorrosive and environmentally benign, as they can be recycled [33-37]. Therefore, in the direction of our investigation on efficient synthesis of coumarin dyes [23], this study was sought to evaluate the efficiency of green solid acid catalysts such as HZSM-5 zeolite and heteropoly acids $H_3PW_{12}O_{40}$ and $H_4O_{40}SiW_{12}$ to find the optimized conditions for obtaining the most efficient, i.e. >90%, one-pot three-component synthesize of coumarin dyes 4a-d within a short time was investigated as well.

2. Experimental

Chemicals were purchased from Merck and were used without further purification. Melting points were measured on a BUCHI melting point B-545 apparatus. ¹H and ¹³C spectra were measured at 500 and 125.7 MHz, respectively, using Bruker DRX-500-AVANCE with DMSO-d₆ and CDCl₃ as solvent. IR spectra were measured on a Perkin Elmer Spectrum One BX FT-IR spectrophotometer. UV/Vis spectra were recorded by means of an UV/Vis spectrophotometer, CECIL CE 9200.

2.1. General procedure for the synthesis of compounds 4a-e.

2.1.1. Procedure for synthesis of coumarin dyes in solvent

A mixture of 1 (0.193 g, 1 mmol), 2 (0.11 mL, 1 mmol), and 3 (1 mmol) containing HZSM-5 (0.1 g) was refluxed in n-pentanol. The reaction was monitored by thin-layer chromatography (TLC). Afterward, the contents were cooled down to room temperature. Zeolite was recovered by filtration of the reaction mixture and solvent was evaporated under vacuum pressure. The products **4a-e** were afforded by crystallization in DMF.

For synthesis of coumarin dyes using HPAs, HPAs

was replaced by HZSM-5 and the mentioned procedures were done identically. For synthesis of coumarin dyes in H_2O , the overall procedure was the same except that n-pentanol was replaced by water.

2.1.2. Procedure for synthesis of coumarin dyes under solvent-free conditions

A well-mixed mixture of 1 (0.193 g, 1 mmol), 2 (0.11 mL, 1 mmol), and 3 (1 mmol) containing solid acid was prepared at room temperature. Progress of the reactions and their endpoints were monitored by TLC. The crude solid products were suspended in DMF, insoluble solid acid was recovered by filtration, and pure products 4a-e were afforded by recrystallization in DMF.

2.1.3. Procedure for recycling of HZSM-5

In order to salvage HZSM-5 from the reaction mixtures, it was suspended in DMF, stirred for 5 min at 40°C, and separated *via* filtration. After that, HZSM-5 was reactivated with 0.1 M HCl (in the solid to liquid ratio 1:10; 20 mL, 0.01 M HCl for 1 g zeolite) for a period of 24 h. Finally, it was filtrated again, and chloride ions were removed by several washing steps with distilled water and the product was air-dried in an oven at 70°C for 3 h.

3. Results and discussion

The reaction of 4-diethylamino-2-hydroxybenzaldehyde **1** with ethyl cyanoacetate **2** and ortho-phenylenediamine or ortho-phenylenehydroxyamine derivatives **3** in the presence of solid acids leads to the corresponding 3-(5'substituted-2'-benzoxazolyl)-7-diethylamino-coumarine **4a-d** and 3-benzimidazolyl-7-diethylamino-coumarine **4e** (Figure 1).



Figure 1: Synthesis of 4 from 1,2, and 3 in one pot.

Compound	HZSM-5 (g)	Time(h)	Lit. ^a Time (h)	Temp (C)	Lit. Temp([°] C)	Yield (%)	Lit. Yield
4 a	0.1	4.5	10-12 ^c , 24 ^b	100	138 ^c ,180 ^b	80	65 ^c ,70 ^b
4b	0.1	5	10-12 ^c	100	138 ^c	90	78 ^c
4c	0.1	5	10-12 ^c	100	138 ^c	90	68 ^c
4d	0.1	6	-	100	-	75	-

Table 1: Reaction conditions for the preparation of compounds 4a-e using HZSM-5.

^a The reported times and temperature were compared with literature (Lit) reported.

^b reported in reference no. 31

^c reported in reference no. 32



Figure 2: The XRD patterns of ZSM-5 samples.

The mechanism of the reaction has been reported previously [23]. HZSM-5 zeolite as a solid acid was activated from NaZSM-5 zeolite [38] and used in synthesis of **4a-e** in superior yield (85-98%) within 4-5 h (Figure 2). The highest yields were obtained using 0.1 g HZSM-5 zeolite as an optimum amount (Table 1).

The synthesis of coumarin dyes in the presence of HZSM-5 zeolite as a catalyst in n-pentanol was successful, but other efforts using H_2O or solvent-free conditions failed.

XRF patterns of the initial NaZSM-5 zeolite showed

hydrogen 1.7, sodium 0.6, aluminum 2.3, silicate 93.7, oxide 192, and the characteristic diffraction peaks of ZSM-5 samples appeared in the XRD patterns at 20 of 7.9°, 8.8°, 23.1°, 23.9°, and 24.4°,24.4°, indicating an exclusive structure of the zeolite topology [39] (Figure 2).

Reusability of the zeolite as an important advantage of the catalytic processes, particularly in industry, was proved by IR spectra of catalyst before (a) and after (b) reaction (Figure 3).



Figure 3: IR spectrum of catalyst before (a) and after (b) the catalytic reaction.

Table 2: Reaction condition	ons for the preparat	tion of compounds 4	a-e usina tunaes	tophosphoric acid

	$H_3PW_{12}O_{40}$				Tomn	I it ^a Time	Lit Tomp	Lit Viold
Compound	0.05 g		0.1 g		remp.	Lit. Time	Litt. Temp.	
	Time (min)	Yield (%)	Time (min)	Yield (%)	(°C)	(h)	(°C)	(%)
4a	70	70	45	90	100	10-12 ^c , 24 ^b	138 ^c , 180 ^b	65°,70 ^b
4b	75	75	50	75	100	10-12 ^c	138 ^c	78 ^c
4c	60	75	40	85	100	10-12 ^c	138 ^c	68 ^c
4d	80	50	60	75	100	-	-	-
4e	70	40	45	55	100	-	-	-

^a The reported times and temperature were compared with literature (Lit) reported.

^b reported in reference no. 31.

^c reported in reference no. 32.

Subsequently, due to the unique properties of HPAs such as Bronsted acidity, the later reactions in n-pentanol, aqueous media (H₂O), and under solvent-free conditions, were carried out in the presence of a catalytic amount of different types of HPAs, including tungestophosphoric acid (H₃PW₁₂O₄₀) and tungestosililic acid (H₄O₄₀SiW₁₂).

0.05, 0.1, and 0.15 g of solid acids were added per 1

mmol of each reactant, and the best results were obtained with 0.1 g solid acid.

Using the optimum concentration of tungestophosphoric acid $(H_3PW_{12}O_{40})$, **4a-d** were obtained with 75% to 90 % yield within 45 to 60 min. Using this approach, much more products are obtained in shorter times. However, in the case of benzimidazole derivative of coumarin dye **(4e)**, the expected yield was

not obtained (Table 2).

Under the same optimum concentration (0.1 g) of $H_4O_{40}SiW_{12}$, quite better yields of **4b-e** were obtained in comparison with $H_3PW_{12}O_{40}$ and HZSM-5 (Table 3). Unlike tungestophosphoric acid, tungestosililic acid was found to be an extraordinary agent that efficiently catalyzes the synthesis of known commercial benzimidazole-based coumarin dye **(4e)**, disperse yellow

C.I. 184, with 98% yield.

Reactions with the mentioned heteropoly acids in H_2O as a green solvent gave the result of up to only 30% to 40% yield after 2.5 to 4.5 h (Table 4).

 $H_3PW_{12}O_{40}$ -mediated solvent-free synthesis of **4b** and **4e** was done more efficiently than $H_4O_{40}SiW_{12}$, while the latter showed higher efficiency for the synthesis of **4c** and **4e** (Table 5).

Table 3: Reaction conditions for the preparation of compounds 4a-e using tungestosilicic acid.

	$H_4O_{40}SiW_{12}$				Tomn	L it ^a Timo	Lit Tomp	Lit Viold
Compound	0.0	0.05 g		0.1 g				
	Time (h)	Yield (%)	Time (min.)	Yield (%)	<u>(°C)</u>	(h)	(°C)	(%)
4a	3	50	70	70	100	10-12 ^c , 24 ^b	138 ^c , 180 ^b	65 ^c ,70 ^b
4b	2.5	45	90	98	100	10-12 ^c	138 ^b	78 ^c
4c	2.5	50	60	80	100	10-12 ^c	138 ^c	68 ^c
4d	3	40	95	85	100	-	-	-
4e	2	45	98	98	100	-	-	-

^a The reported times and temperature were compared with literature (Lit) reported.

^b reported in reference no. 31

^c reported in reference no. 32

Table 4: Reaction conditions for the preparation of compounds 4a-e using HPAs in H₂O.

Compound	H_3PW_{12}	O ₄₀ 0.1 g	H ₄ O ₄₀ SiW ₁₂ 0.1 g		
Compound	Time (h)	Yield (%)	Time (h)	Yield (%)	
4a	3	35	3.5	35	
4b	3	35	3	30	
4c	2.5	40	3	30	
4d	4.5	35	5	30	
4e	2.5	40	3	40	

Table 5: Reaction conditions for the preparation of compounds 4a-e using HPAs under solvent free conditions.

Compound	H_3PW_{12}	O ₄₀ 0.1 g	H ₄ O ₄₀ SiW ₁₂ 0.1 g		
Compound	Time (h)	Yield (%)	Time (h)	Yield (%)	
4 a	2.5	55	1.5	50	
4b	2.5	96	3	60	
4c	1.5	60	2	85	
4d	3	40	3.5	40	
4e	2.5	90	3	70	

The structures of compounds **4a-e** were deduced from ¹H, and ¹³C NMR spectroscopic data. All results of the melting points, and IR and NMR spectroscopic data were in clear accordance with the previous report [23] which confirms the formation of **4a-e**.

For example, the ¹H NMR spectrum of **4a** exhibits a singlet for the CH groups aroused from coumarin moiety at 8.61 ppm. In ¹³C NMR, carbons of coumarin moiety on **4a** appear at 96.9 (CH), 108.5 (C), 110.9 (CH), 112.7 (CH), 132.3 (CH), 149.5 (C), 153.5 (C), 158.3 (C), and 162.4 (C).

The color shades of these products were brilliant yellow with green fluorescence. Reasonably, high extinction coefficients were found for the **4a-e** products. The emission peaks of the products appeared in the same area at 510-513 nm, and similar emission intensities were found for **4b-e**, which were greater than for **4a**[23].

3-(5-Chloro-2-benzoxazolyl)-7-(diethylamino)-2H-1benzopyran-2-one 4a. Yellow powder; mp 194-196 °C; IR (KBr) $(v_{max}=cm^{-1})$: 2970, 2926, 1729, 1620, 1589, 1529. 1H NMR (500 MHz, CDCl₃): δ_H 1.26 (6H, t, ${}^{3}J_{\text{HH}}$ 7.2 Hz, 2 CH₃), 3.47 (4H, q, ³J_{HH} 7.2 Hz, 2 CH₂), 6.54 $({}^{1}\text{H}, \text{d}, {}^{4}J_{\text{HH}} 2.3 \text{ Hz}, \text{CH}), 6.66 ({}^{1}\text{H}, \text{dd}, {}^{3}J_{\text{HH}} 8.9 \text{ Hz}, {}^{4}J_{\text{HH}}$ 2.3 Hz, CH), 7.29 (¹H, dd, ³J_{HH} 8.3 Hz, ⁴J_{HH} 1.9 Hz, CH), 7.42 (¹H, d, ${}^{3}J_{\text{HH}}$ 8.9 Hz, CH), 7.50 (1H, d, ${}^{3}J_{\text{HH}}$ 8.3 Hz, CH), 7.75 (¹H, d, ⁴J_{HH} 1.9 Hz, CH), 8.61 (¹H, s, CH); ¹³C NMR (125.7 MHz, DMSO-d₆): δ_C 13.2 (2CH₃), 45.3 (2CH₂), 96.9 (CH), 104.9 (CH), 108.5 (C), 110.9 (CH), 112.7 (CH), 119.7 (CH), 125.7 (CH), 129.7 (C), 132.3 (CH), 143.6 (C), 147.3 (C), 149.5 (C), 153.5 (C), 157.5 (C), 158.3 (C), 162.4 (C). Anal. calcd. for C₂₀H₁₇N₂O₃Cl (368.5): C, 65.13; H, 4.61; N, 7.60%. Found: C, 65.16; H, 4.64; N, 7.58%.

3-(5-Methyl-2-benzoxazolyl)-7-(diethylamino)-2H-1benzopyran-2-one 4b. Yellow powder; mp 208-210 °C; IR (KBr) $(v_{max}=cm^{-1})$: 2969, 2924, 1739, 1615, 1583, 1549. ¹H NMR (500 MHz, CDCl₃): δ_H 1.25 (6H, t, ${}^{3}J_{\rm HH}$ 7.2 Hz, 2 CH₃), 2.47 (3H, s, CH₃), 3.46 (4H, q, ³J_{HH} 7.2 Hz, 2 CH₂), 6.54 (¹H, d, ⁴J_{HH} 2.0 Hz, CH), 6.64 (¹H, dd, ³*J*_{HH} 8.9 Hz, ⁴*J*_{HH} 2.0 Hz, CH), 7.13 (¹H, d, ³*J*_{HH} 8.2 Hz, CH), 7.41 (¹H, d, ${}^{3}J_{HH}$ 8.9 Hz, CH), 7.45 (1H, d, ${}^{3}J_{HH}$ 8.2 Hz, CH), 7.57 (1H, s, CH), 8.60 (1H, s, CH); ¹³C NMR (125.7 MHz, DMSO-d₆): δ_C 13.2 (2 CH₃), 21.9 (CH₃), 45.2 (2 CH₂), 96.9 (CH), 105.8 (CH), 108.5 (C), 110.8 (CH), 111.3 (CH), 120.0 (CH), 126.9 (CH), 132.1 (CH), 134.8 (C), 142.5 (C), 146.8 (C), 149.2 (C), 153.2 (C), 157.8 (C), 158.2 (C), 160.8 (C). Anal. calcd. for C₂₁H₂₀N₂O₃ (348): C, 72.41; H, 5.75; N, 8.04%. Found: C, 72.44; H, 5.73; N, 8.07%.

3-(2-Benzoxazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one **4c**. Yellow powder; mp 184-186 °C; IR (KBr) (v_{max} =cm⁻¹): 2971, 2927, 1738, 1609, 1588, 1550. ¹H NMR (500 MHz, DMSO-d₆): δ_H 1.11 (6H, t, ${}^3J_{HH}$ 7.0 Hz, 2 CH₃), 3.45 (4H, q, ${}^3J_{HH}$ 7.0 Hz, 2 CH₂), 6.55 (1H, d, ${}^4J_{HH}$ 1.7 Hz, CH), 6.76 (1H, dd, ${}^3J_{HH}$ 8.9 Hz, ${}^4J_{HH}$ 1.7 Hz, CH), 7.35 (2H, m, 2 CH), 7.64 (1H, d, ${}^3J_{HH}$ 8.9 Hz, CH), 7.70 (2H, m, 2 CH), 8.74 (1H, s, CH); 13 C NMR (125.7 MHz, DMSO-d₆): δ_C 13.2 (2 CH₃), 45.2 (2 CH₂), 96.9 (CH), 105.6 (CH), 108.5 (C), 110.8 (CH), 111.4 (CH), 120.2 (CH), 125.5 (CH), 125.9 (CH), 132.2 (CH), 142.3 (C), 147.0 (C), 150.7 (C), 153.5 (C), 157.7 (C), 158.3 (C), 160.8 (C). Anal. calcd. for C₂₀H₁₈N₂O₃ (334): C, 71.85; H, 5.39; N, 8.38%. Found: C, 71.87; H, 5.36; N, 8.40%.

3-(5-Ethylsulphonyl-2-benzoxazolyl)-7-(diethyl amino)-2H-1-benzopyran-2-one 4d. Yellow powder; mp 200-202 °C; IR (KBr) (v_{max} =cm⁻¹): 2977, 2935, 1729, 1634, 1590, 1521. ¹H NMR (500 MHz, CDCl₃): δ_H 1.23 (3H, t, ³J_{HH} 7.3 Hz, CH₃), 1.25 (6H, t, ³J_{HH} 7.1 Hz, 2 CH₃), 3.17 (2H, q, ³J_{HH} 7.3 Hz, CH₂), 3.48 (4H, q, ³J_{HH} 7.1 Hz, 2 CH₂), 6.55 (1H, d, ⁴J_{HH} 2.1 Hz, CH), 6.67 (1H, dd, ³J_{HH} 8.9 Hz, ⁴J_{HH} 2.1 Hz, CH), 7.45 (1H, d, ³J_{HH} 8.9 Hz, CH), 7.74 (1H, d, ³J_{HH} 8.5 Hz, CH), 7.90 (1H, dd, ${}^{3}J_{\rm HH}$ 8.5 Hz, ${}^{4}J_{\rm HH}$ 1.6 Hz, CH), 8.33 (1H, d, ${}^{4}J_{\rm HH}$ 1.6 Hz, CH), 8.66 (1H, s, CH); ¹³C NMR (125.7 MHz, DMSOd₆): δ_C 13.16 (CH₃), 13.23 (2 CH₃), 45.3 (CH₂), 45.4 (2 CH₂), 96.9 (CH), 104.5 (CH), 108.5 (C), 111.0 (CH), 111.2 (CH), 120.1 (CH), 125.7 (CH), 132.2 (CH), 136.0 (C), 142.7 (C), 147.8 (C), 152.8 (C), 153.7 (C), 157.6 (C), 158.3 (C), 163.2 (C). Anal. calcd. for C₂₂H₂₂N₂O₆S (442): C, 59.73; H, 4.98; N, 6.33%. Found: C, 59.75; H, 4.95; N. 6.35%.

3-(-2-Benzimidazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one 4e. Yellow powder; mp 218–220 °C; IR (KBr) (v_{max} =cm⁻¹): 3338, 2972, 2931, 1692, 1619, 1591, 1529. ¹H NMR (500 MHz, DMSO-d₆): δ_H 1.11 (6H, t, ³J_{HH} 7.0 Hz, 2CH₃), 3.43 (4H, q, ³J_{HH} 7.0 Hz, 2 CH₂), 6.61 (1H, d, ⁴J_{HH} 1.7 Hz, CH), 6.76 (1H, dd, ³J_{HH} 8.9 Hz, ⁴J_{HH} 1.7 Hz, CH), 7.12 (1H, m, 2 CH), 7.57 (2H, m, 2 CH), 7.65 (1H, d, ³J_{HH} 8.9 Hz, CH), 8.87 (1H, s, CH), 12.22 (1H, s, NH); ¹³C NMR (125.7 MHz, DMSO-d₆): δ_C 13.2 (2 CH₃), 45.2 (2 CH₂), 97.1 (CH), 108.9 (C), 110.8 (CH), 113.2 (CH), 118.7 (2 CH), 122.6 (2 CH), 131.7 (CH), 143.9 (2 C), 148.1 (C), 152.5 (C), 157.3 (C), 158.7 (C), 161.1 (C). Anal. calcd. For C₂₀H₁₉N₃O₂ (333): C, 72.07; H, 5.70; N, 12.61%. Found: C, 72.15; H, 5.68; N, 12.64%.

4. Conclusions

In summary, an improved synthesis method for some coumarin dyes using green and noncorrosive solid acids as HZSM-5 Zeolite, tungestophosphoric acid $(H_3PW_{12}O_{40})$ and tungestosililic acid $(H_4O_{40}SiW_{12})$ was

reported which leads to superior yields (more than % 90) in a short time. Considering time and yield, the procedure using heteropolyacids in n-pentanol is the best pathway to obtain the aforementioned coumarin dyes.

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