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Short Communication

Poly(4-vinylpyridinium)hydrogen sulfate: A novel and efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes under conventional heating and ultrasound irradiation

Nader Ghaffari Khaligh *

Department of Chemistry, College of Science, University of Guilan, Rasht, P.O. Box 41335-19141, Iran

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A B S T R A C T

A simple and convenient procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes is described through a one-pot condensation of 2-naphthol with aryl aldehydes in the presence of poly(4-vinylpyridinium)hydrogen sulfate as an efficient, cheap, readily synthesized and eco-friendly catalyst in a solvent free media using conventional heating and ultrasound irradiation.

1. Introduction

Solid acids have many advantages over liquid acids in organic catalysis. They do less harm to environment and have no corrosion or disposal of effluent problems. They are reusable and easy to be separated from liquid products. As economically and ecologically benign catalysts, their research and application have attracted much attention in chemistry and industry. There are more than 100 industrial processes using over 103 solid acids as catalysts at the end of last century [1]. The replacement of traditional homogeneous catalysts with solid acids is becoming an inevitable trend. Solid acid can be mainly divided into eight categories: oxides (Al_2O_3, SiO_2, etc.), sulfides (CdS, ZnS, etc.), metal salts ($AlPO_4$, $CuSO_4$, etc.), zeolites (HZSM-5, HY, H-β, etc.), heteropolyacids ($H_3PW_{12}O_{40}$, etc.), natural clays (kaolin, montmorillonite K10 and KSF, etc.), supported solid acids (BF_3/Al_2O_3, SO_4^{2-}/ZrO_2, etc.) and cationic ion-exchange resins (Amberlyst-15, Nafion NR 50, etc.).

The synthesis of xanthenes, especially benzoxanthenes, has emerged as a powerful tool in organic synthesis due to their wide range of biological and therapeutic properties such as antibacterial [2], antiviral [3] and anti-inflammatory activities [4] as well as in photodynamic therapy [5] and for antagonism of the paralyzing action of zoxazolamine [6]. Furthermore, due to their useful spectroscopic properties, they are used as dyes [7], in laser technologies [8], and in fluorescent materials for visualization of biomolecules [9]. Many procedures describe the synthesis of xanthenes and benzoxanthenes including cyclodehydrations [10], alkylations γ to the heteroatoms [11], trapping of benzynes by phenols [12], cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone [13], the reaction of 2-naphthol with aldehydes or acetals under acidic conditions and intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones [14]. In addition, 14*H*-dibenzo[*a*,*j*]xanthenes and related products are prepared by reaction of β-naphthol with formamide [15], 2-naphthol-1-methanol [16], carbon monoxide [17] and sulfomic acid [18].

Even though various procedures are reported, disadvantages including low yields, prolonged reaction times, use of an excess of reagents/catalysts and use of toxic organic solvents necessitate the development of an alternative route for the synthesis of xanthene derivatives.

Ultrasonic-assisted organic synthesis (UAOS) as a green synthetic approach is a powerful technique that is being used more and more to accelerate organic reactions [19,20]. UAOS can be extremely efficient and it is applicable to a broad range of practical syntheses. The notable features of the ultrasound approach are enhanced reaction rates, formation of purer products in high yields, easier manipulation and considered a processing aid in terms of energy conservation and waste minimization which compared with traditional methods, this technique is more convenient taking green chemistry concepts into account [21–23]. However, the use of ultrasound in heterocyclic system is not fully explored [24–37]. In order to expand the application of ultrasound in the synthesis of heterocyclic compound, we wish to report a general, efficient and eco-friendly method for the synthesis of aryl-14-*H*-dibenzo[*a*,*j*]xanthenes.

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* Tel.: +98 21 66431738; fax: +98 21 66934046.
E-mail addresses: ngkhaligh@gmail.com, ngkhaligh@guilan.ac.ir

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In this paper, we investigated the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes in the presence of poly(4-vinylpyridinium)hydrogen sulfate under normal heating and sonication conditions. The reported route is an efficient, convenient and novel method for condensation of aldehydes with 2-naphthol in the presence of poly(4-vinylpyridinium)hydrogen sulfate as solid acid (Scheme 1).

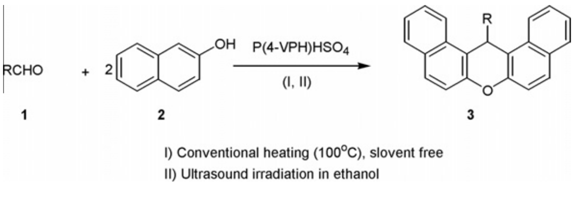
2. Results and discussion

In an initial study, in order to examine the catalytic activity of catalyst and the amount of catalyst in this condensation reaction, benzaldehyde was first reacted with 2-naphthol in solvent free conditions at 100 °C and in ethanol under ultrasound irradiation in the presence 0, 5, 10, 15 and 20 mg catalyst separately. The best results were obtained using 10 mg of P(4-VPH)HSO_4. Using lower amounts of catalyst resulted in lower yields, while higher amounts of catalyst did not affect the reaction times and yields and in the absence of catalyst, nearly no product could be detected (Table 1).

The condensation of 2-naphthol and aryl aldehydes (carrying both electron-withdrawing and electron-donating groups), in the presence of P(4-VPH)HSO_4 0.010 g as a solid acid catalyst in a solvent free media using conventional heating at 100 °C (method A) and ultrasound irradiation with a frequency of 35 kHz and a nominal power 200 W (method B) yielded desired 14*H*-dibenzo[*a*,*j*]xanthenes in high purity with excellent yields. The reactions required 45–78 min with conventional heating at 100 °C, and 20 min with ultrasound irradiation with a frequency of 35 kHz. We initially investigated the catalytic activity of P(4-VPH)HSO_4, which promotes the condensation reaction between 1:2 ratio of benzaldehyde and 2-naphthol in the presence of P(4-VPH)HSO_4 0.010 g catalyst in a solvent free media using conventional heating at 100 °C and ultrasound irradiation with a frequency of 35 kHz. We found that under the best reaction conditions in the presence of 0.010 g of P(4-VPH)HSO_4 full conversion into the 14-(phenyl)-14*H*-dibenzo[*a*,*j*]xanthene occurred in 55 min and 20 min. P(4-VPH)HSO_4 in excess of 20 mg did not help to increase the yield to any greater extent (Table 1, entry 5). The nature of the functional group on the aromatic ring of the aldehyde exerted a strong influence on the reaction time. An increase of the reaction rate was observed with arylaldehyde bearing electron-withdrawing (such as $-NO_2$) group in the para-position (Table 2, entry 7), in comparison to the unsubstituted arylaldehyde. The presence of a electron-donating (such as $-OCH_3$) group (Table 2, entry 10) decreased both the rate and the yield.

Table 3, compares our results (time, yield, reaction conditions) with results obtained by other groups. As can be seen, our method is simpler, more efficient, and uses no toxic solvents.

Compared with traditional solvents and catalysts, it is easy for this catalyst to be reused, which is prior to the conventional solvents and catalysts [28]. Hence, we decided to study the catalytic activity of recycled solid acid P(4-VPH)HSO_4 for the synthesis of 14-(Phenyl)-14*H*-dibenzo[*a*,*j*]xanthene (Table 4). After the separation of product, the catalyst was washed with dichloromethane and vacuumed to remove CH_2Cl_2 and the resulting catalyst was reused directly for the next run. As shown in Table 3, the solid acid P(4-VPH)HSO_4 can be recycled at least five times without significant decrease in catalytic activity, the yields ranged from 97% to 92%.



Scheme 1. Synthesis of 14-aryl-14H-dibenzo[*a*,*j*]xanthenes in the presence of poly(4-vinylpyridinium) hydrogen sulfate under normal heating and sonication conditions.

3. Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. Products were identified by comparison of their melting points, IR and ^1H NMR data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The reaction conversions were measured by GC on a Shimadzu model GC-16A instrument using a 25 m CBPI-S25 (0.32 mm ID, 0.5 μm coating) capillary column. The ^1H NMR (250 or 300 MHz) and ^{13}C NMR (62.5 or 75 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Microanalyses were performed on a Perkin–Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-540 B.V.CHI apparatus in open capillary tubes. BANDELIN Sonorex (with a frequency of 35 kHz and a nominal power 200 W) ultrasonic bath was used for ultrasonic irradiation. Built-in heating, 30–80 °C thermostatically adjustable. The reaction vessel placed in side the ultrasonic bath containing water.

3.1. Catalyst synthesis

H_2SO_4 (0.3 mL, 5.3 mmol, as a 96% standard solution) was added to the suspension of powdered poly(4-vinyl pyridine) (1.0 g) in 10 mL dry methanol. The mixture was stirred at room temperature for 8 h then methanol was removed under reduced pressure to form P(4-VPH)HSO_4 catalyst. The excessive sulfuric acid were washed by deionized water until the sulfate anions were absent in the liquid (checked by reaction with $BaCl_2$). The solid powder was dried under vacuum at 65 °C for 48 h to afford P(4-VPH)HSO_4 (0.5 mmol g^{-1}) as a pale yellow powder. The catalyst is washed with solvent and dried then reused for subsequent reactions.

3.2. General procedure for the synthesis of aryl-14H-dibenzo[a, j]xanthenes

3.2.1. Conventional heating method (method A)

A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol) and P(4-VPH)HSO_4 (0.010 g) was heated at 100 °C. The progress of the reaction was followed by TLC. After completion of the reaction, the reaction mixture was diluted with ethanol (10 mL) and stirred for 10 min in 80 °C. The solid (catalyst) were collected by filtration and the residue was kept at room temperature and the resulting crystalline product was collected by filtration. The product was found to be pure and no further purification was necessary.

3.2.2. Ultrasound irradiation method (method B)

In a two-necked flask, a mixture of 2-naphthol (2 mmol), aldehyde (1 mmol), P(4-VPH)HSO_4 (0.010 g) and ethanol (10 mL) was irradiated in an BANDELIN Sonopuls HD 3200 ultrasonic apparatus at 40 °C for 20 min. The mixture was filtered to recover the catalyst and the residue was crystallized. The pure products were obtained in 87–95% yields.

3.3. Representative spectral data

3.3.1. 14-(Phenyl)-14H-dibenzo[a, j]xanthene (Table 1, entry 1)

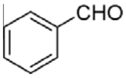
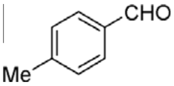
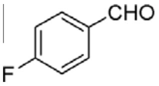
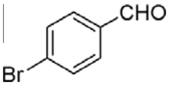
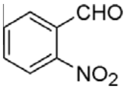
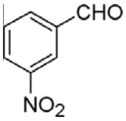
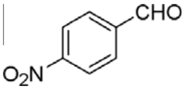
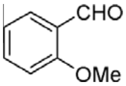
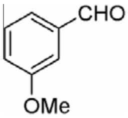
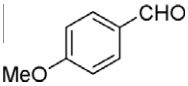
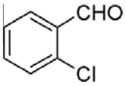
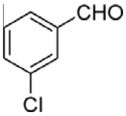
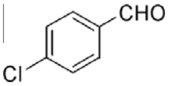
Colorless crystals; m.p. 184–185 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.46 (s, 1H, CH), 6.96 (t, *J* = 7.2 Hz, 1H, ArH), 7.12 (t, *J* = 7.2 Hz, 2H, ArH), 7.36–7.58 (m, 8H, ArH), 7.74–7.81 (m, 4H, ArH), 8.37 (d, *J* = 8.4 Hz, 2H, ArH) ppm; IR (KBr): 3070, 3020, 1620, 1590, 1430, 1400, 1250, 1150, 1075, 825, 740 cm^{-1}.

Table 1
Comparison of the amount of catalyst and yields using conventional heating and ultrasound irradiation for the synthesis of 14 (phenyl)-14*H*-dibenzo[*a*,*j*]xanthene.

Entry	Amount of catalyst (mg)	Method A		Method B	
		Yield (%)[a]	Time (min)	Yield (%)[a]	Time (min)
1	0	–	360	–	120
2	5	65	120	92	40
3	10	94	60	95	20
4	15	94	60	95	20
5	20	92	60	96	20

[a] Isolated yields.

Table 2
P(4-VPH)HSO_4 catalyzed synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes.[a]

Entry	Aldehyde	Method A		Method B		Mp (°C)
		Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]	
1		55	94	20	97	184–185
2		72	93	20	90	230–231
3		45	94	20	92	239–240
4		65	96	20	95	297–298
5		72	94	20	92	295–260
6		72	92	20	90	213–215
7		70	96	20	95	312–314
8		78	94	20	87	259–260
9		76	92	20	94	179–180
10		72	90	20	94	204–205
11		57	92	20	88	214–216
12		54	93	20	88	210–213
13		52	96	20	92	290–292

[a] Products were characterized by ^{1}H NMR, IR and melting point and also by comparison with the reported in literature data [10].

[b] Isolated yields.

Table 3
Comparison of our results with results obtained by other groups.[a]

Catalyst	Conditions	Time (h)	Yield (%)	References
$K_5CoW_{12}O_{40}\cdot 3H_2O$	Neat/125 °C	2	91	29
I2	Neat/90 °C	2.5	90	30
p-TsOH	Neat/125 °C	4	89	10
LiBr	Neat/130 °C	1	82	31
Amberlyst-15	Neat/125 °C	2	94	32
Sulfamic acid	Neat/125 °C	8	93	18
Cellulose sulfuric acid	Neat/110 °C	1.5	81	33
P(4-VPH)HSO_4	Neat/100 °C	55 min	94	This work
	Ultrasonic/35 kHz	20 min	97	

[a] Based on the synthesis of 14-(phenyl)-14*H*dibenzo[*a*,*j*]xanthene.

Table 4
The recycling of P(4-VPH)HSO_4 in synthesis of 14-(phenyl)-14*H*dibenzo[*a*,*j*]xanthene under ultrasound irradiation.

Entry	Time (min)	Yield (%)[a]
1	20	97
2	20	97
3	20	94
4	25	93
5	30	92

[a] Isolated yields.

3.3.2. 14-(4-Methylphenyl)-14H-dibenzo[a, j]xanthene (Table 1, entry 2)

Colorless crystals; m.p. 227–228 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.11 (s, 3H, CH_3), 6.43 (s, 1H, CH), 6.93 (d, *J* = 7.8 Hz, 2H, ArH), 7.22–7.36 (m, 8H, ArH), 7.42–7.81 (m, 4H, ArH), 8.37 (d, *J* = 8.4 Hz, 2H, ArH) ppm; IR (KBr): ν = 3068, 3022, 1620, 1590, 1512, 1395, 1248, 1110, 810, 740 cm^{-1}.

3.3.3. 14-(2-Nitrophenyl)-14H-dibenzo[a.j]xanthene (Table 1, entry 5)

Yellow crystals; m.p. 293 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *d* = 7.52 (s, 1H) 7.10–8.56 (m, 16H) ppm; IR (KBr): 3060, 1595, 1525, 1350, 1240, 1140, 810, 750 cm^{-1}.

4. Conclusion

We described herein solid acid P(4-VPH)HSO_4 catalyzed highly efficient, one-pot, green protocol for the synthesis of aryl-14-*H*-dibenzo[*a*, *j*]xanthenes by the condensation of an aldehyde and 2-naphthol under ultrasound irradiation in excellent yields. The present methodology offers several advantages such as simple procedure, low cost, easy work-up, short reaction times and milder conditions.

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