



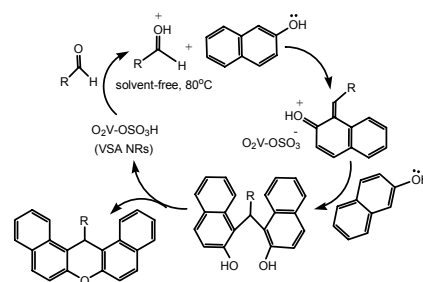
PREPARATION, CHARACTERIZATION AND USE OF VANADATESULFURIC ACID AS A NEW AND ECO-BENIGN NANOCATALYST FOR THE SYNTHESIS OF 14-ARYL-14H-DIBENZO[*a,j*] XANTHENES UNDER SOLVENT-FREE CONDITIONS

Masoud NASR-ESFAHANI* and Tooba ABDIZADEH

Department of Chemistry, Yasouj University, Yasouj, Iran

Received September 20, 2012

Vanadatesulfuric acid (VSA) is a recyclable and eco-benign catalyst for the preparation of biologically active 14-aryl-14-*H*-dibenzo [*a,j*]xanthenes by a one-pot condensation reaction of 2-naphthol and aldehydes under solvent-free conditions in high to excellent yields (80–93%) and in short reaction times (10–45 min). The nanocatalyst was characterized by FT-IR, XRD, XRF and TEM analysis. The present method offers several advantages such as simple procedure, short reaction time, high yields, simple workup, reusability of the catalyst and simple purification of the products.



INTRODUCTION

Xanthene heterocycles and derivatives are a key structural element of many biologically active compounds such as antibacterials,¹ antivirals² and anti-inflammatory agents,³ u-opiat agonist,⁴ antitumor,⁵ neuropharmacological,⁶ CNS stimulating⁷ as well as efficacy in antagonists for the paralyzing acting of zoxazolamine.⁸ They have also been used for photodynamic therapy,⁹ used as dyes¹⁰ and fluorescent material for visualization of biomolecules.¹¹ Xanthene-based compounds have also shown agricultural and bactericide activity, while some other benzoxanthenes are also utilized in industries as dyes in laser technologies.¹² Thus, synthesis of xanthene derivatives is currently of great importance.

Many procedures are disclosed to synthesize benzoxanthenes like reaction of 2-naphthol with

2-naphthol-1-methanol,¹³ formamide,¹⁴ and carbon monoxide.¹⁵ In spite of potential utility of aforementioned routes, these methods have many disadvantages such as low yields, the need for a prolonged reaction time, the use of toxic organic solvents, excess reagents and harsh reaction conditions. Because of these drawbacks, the reaction has been improved by mixing 2-naphthol with aldehydes in the presence of a catalyst such as acetic acid and sulfuric acid,¹⁶ acetic acid and hydrochloric acid,¹⁷ H₃PO₄ or HClO₄,¹⁸ *p*-toluenesulfonic acid,¹⁹ sulfamic acid,²⁰ I₂,²¹ Amberlyst-15,²² K₅CoW₁₂O₄₀,²³ LiBr,²⁴ HClO₄⁻,²⁵ SiO₂,²⁵ cyanuric chloride,²⁶ silica sulfuric acid,²⁷ heteropoly acid,²⁸ Dowex-50W,²⁹ and Selectfluor TM.³⁰ These methods show varying degrees of success as well as limitations due to a long reaction time, the use of toxic solvent,³¹ special apparatus and the use of toxic catalysts.²¹ Therefore, to avoid these limitations, the discovery of a new and

* Corresponding author: manas@mail.yu.ac.ir

efficient catalyst for the preparation of dibenzoxanthenes under mild and practical conditions is of prime interest.

Solid acid catalysts like heteropoly acids,³² Nafion-H,³³ silica sulfuric acid,³⁴ and silica phosphoric acid³⁵ with lower toxicity, higher stability and recyclability play a prominent role in organic synthesis under heterogeneous conditions. Solid acids have many advantages such as ease of handling, decreasing reactor and plant corrosion problems, and environmentally safe disposal.^{36,37}

It is well known in the protocol of green chemistry that its main objective is to perform reactions under solventless conditions using heterogeneous catalysts, in order to generate environmentally friendly chemical transformations.³⁸ In addition, it is important to note that an ideal synthesis is considered as one in which a target molecule is produced quantitatively in one step, from available and inexpensive raw materials, under environmentally harmless processes.³⁹

In continuation of above and our studies on the application of inorganic solid acid,⁴⁰ we found that anhydrous sodium metavanadate reacts with chlorosulfonic acid (1:1 mole ratio) to give nanorod particles of vanadatesulfuric acid (VSA). The reaction is performed easy, clean and without any workup (Scheme 1). It is to be noted that there is no gas production during the reaction.

In continuation of our programme on utility of solid acid in organic reactions, herein we were interested to examine vanadatesulfuric acid as proton source in the synthesis of 14-Aryl-14-*H*-dibenzo[*a,j*]xanthenes under solvent free condition.

RESULTS AND DISCUSSION

In this work, we wish to report an efficient and convenient procedure for the synthesis of dibenzo xanthenes from the alkyl or aryl aldehydes using

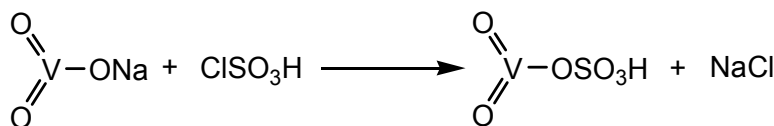
nanorod particles of vanadatesulfuric acid as catalyst (Scheme 2).

Characterization of vanadatesulfuric acid

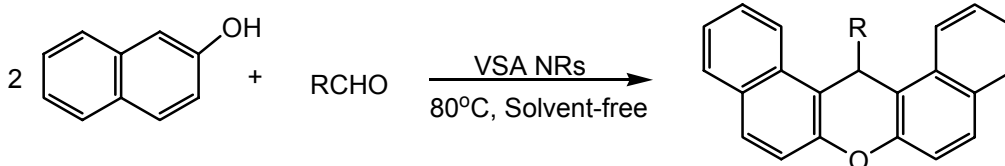
FT-IR spectroscopy is an effective tool, which determines the changes in structure of molecular species in a system. Fig. 1 exhibits the IR spectra of sodium metavanadate as substrate and Vanadatesulfuric acid. The infrared vibration bands found for NaVO₃ are assigned as follows (Fig. 1(A)): In these spectra, several absorptions appear which are apparently the result of V-O stretching modes for each of several, different oxygen atoms according to the particular location or arrangement within the lattice.⁴¹ At lower frequency, a broad and general absorption occurs which is apparently caused by lower frequency VO bonding. Here, the V-O stretching mode is observed as a medium band located at 950 cm⁻¹. These two spectra tend to locate the “normal” position for this stretching vibration between oxygen and vanadium. Other broad bands are present in the spectrum of sodium metavanadate, centering at 845 and 690 cm⁻¹. The VO₃- structure consists of VO bondings of variable bond lengths, some of which vibrate at lower frequencies than others. The 950 cm⁻¹ band has been assigned to a VO bond, which is considerably shorter than other bonds in the structure; the 845 cm⁻¹ band very probably arises from the stretching modes of the longer VO bonds.

For vanadatesulfuric acid, the infrared vibration bands are consigned as follows (Fig. 1(B)):

The bands found at 3450 and 1640 cm⁻¹ are attributed to the stretching and bending vibration of -OH group, respectively. The bands at 1050, and 1180 cm⁻¹ are assigned for the sulfonic acid bonds, S-OH, S=O stretching, and S=O asymmetric stretching, respectively. The bands appearance in 960, 840 and 603 cm⁻¹ related to V=O and V-O stretching.



Scheme 1



Scheme 2

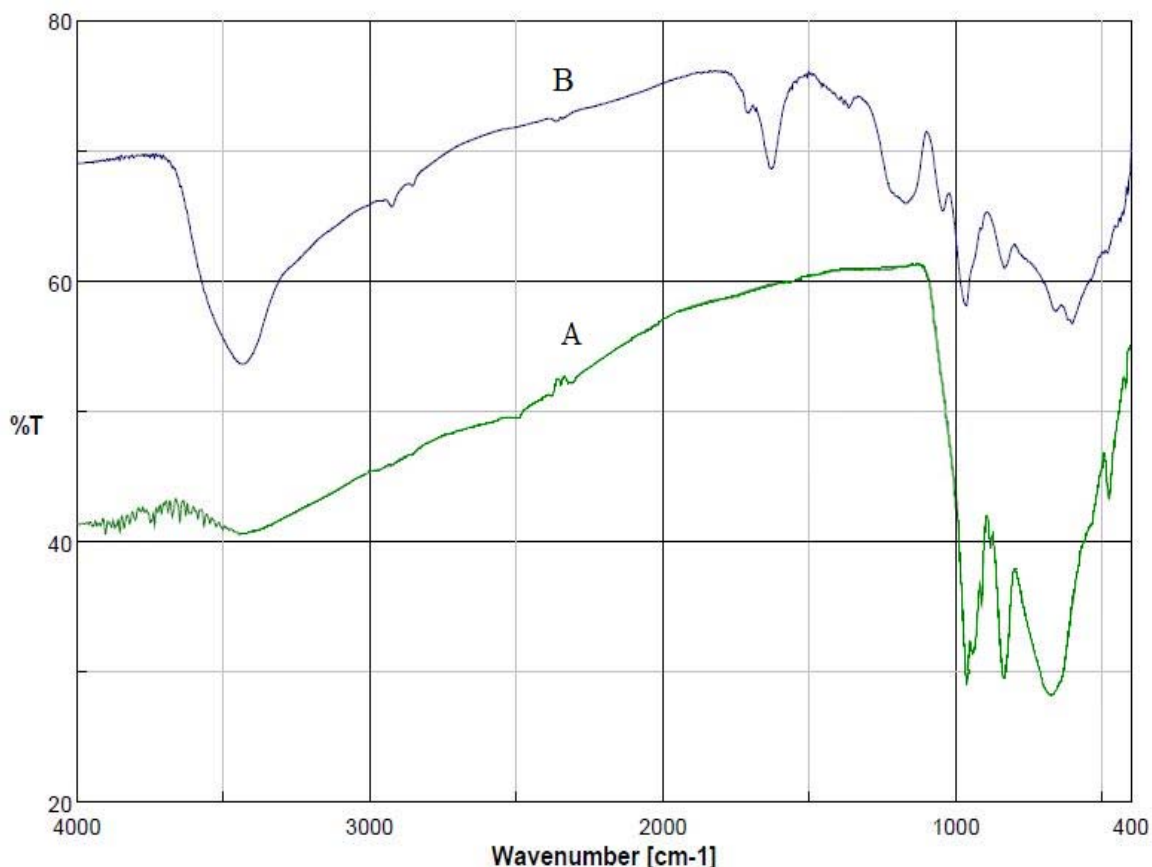


Fig. 1 – FT-IR spectra of A: sodium metavanadate; B: vanadatesulfuric acid.

Fig. 2(b) shows the XRD pattern of VSA. A number of prominent Bragg reflections reveal that the resultant particles of Vanadatesulfuric acid have a monoclinic structure (Space group: $P2_1/m$; $a = 12.170 \text{ \AA}$, $b = 3.602 \text{ \AA}$, $c = 7.780 \text{ \AA}$, JCPDS card no. 16-0601). The size of the VSA particles was also determined from X-ray line broadening using the Debye-Scherrer formula ($D = 0.9\lambda/\beta\cos\theta$, where D is the average crystalline size, λ is the X-ray wavelength used, β is the angular line width at half maximum intensity, and θ is the Bragg's angle). For the (001) reflection the average size of the VSA particles was estimated to be around 16 nm. The morphology and size of VSA were investigated by transmission electron microscopy (TEM) (Fig. 2a). They had needle-like morphology with a narrow size distribution from 15 to 20 nm and a mean size of 17 nm, confirming the results calculated from Scherrer's equation. The presence of some larger particles should be attributed to aggregating or overlapping of smaller particles. In addition, elemental analysis of catalyst was performed by means of X-ray fluorescence

analysis (XRF) that the obtain result confirmed the elemental composition of VSA.

Effect of solvent and catalyst concentration on the synthesis of 14-phenyl-14-*H*-dibenzo[*a,j*]xanthenes

We initially investigated the catalytic activity of VSA in the synthesis of dibenzoxanthenes under different reaction conditions. For comparison of the results between solvent and solvent-free conditions, the solvent effect in the condensation of benzaldehyde and 2-naphthol in the presence of vanadatesulfuric acid as a model has been also studied. As shown in Table 1, among the tested solvents, such as ethanol, methanol, water, acetonitrile, chloroform and a solvent-free system, the best result was obtained after 20 min under solvent-free condition in excellent yield (93%) compared to solvent conditions with longer time (10 h) and lower yields (55-72%). Therefore, we choose solvent-free condition for the catalytic synthesis of dibenzoxanthene derivatives.

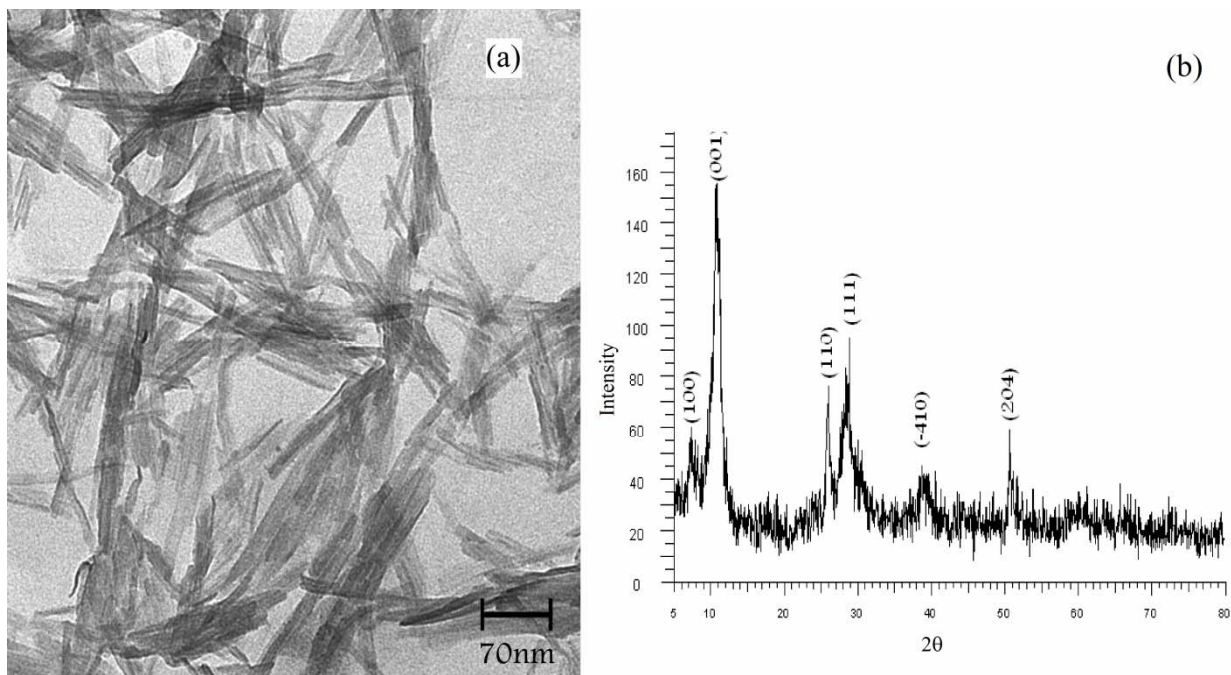


Fig. 2 – (a) The TEM image showing needle-like VSA particles of 15-20 nm in size; (b) Powder X-ray diffraction pattern of the VSA particles.

Table 1

Solvent effect on the reaction of benzaldehyde and β -naphthol catalyzed by VSA

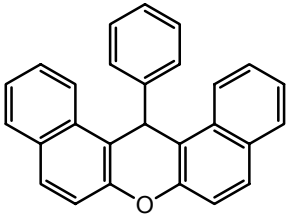
Product	Solvent	Time(h)	Yield(%)
	CH ₃ CH ₂ OH	10	77
	CH ₃ OH	10	70
	H ₂ O	10	62
	CH ₃ CN	10	52
	CHCl ₃	10	60
	Solvent-free	20min	93

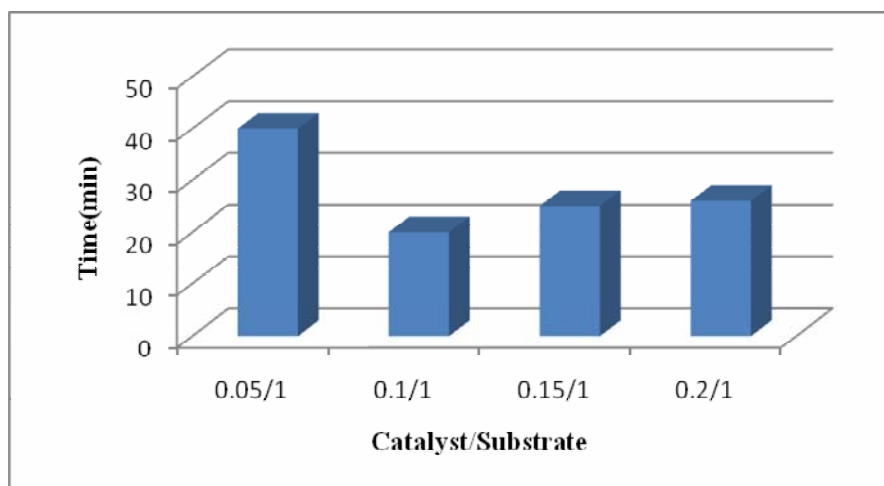
Fig. 3 illustrates the effect of catalyst molar ratio on the conversion time of benzaldehyde as typical substrate under solvent-free conditions. It is important to note that no 14-aryl-14H-dibenzo[*a,j*]xanthene derivatives were afforded when the reactions were performed in the absence of VSA nanorod particles in the reaction mixture. With increasing the catalyst, the reaction time is decreased up to 10% of catalyst molar ratio that was found to be an optimum amount in current conditions. The higher amount of catalyst was found that have not a notable effect on the reaction time.

Therefore, this reaction was developed with other aldehydes, and the results are summarized in Table 2. The time of reactions were within

10-45 min, and high yields of 14-aryl or alkyl-14H-dibenzo[*a,j*]xanthenes were obtained.

To use of VSA NRs in large scale synthesis especially in chemical laboratory, a typical reaction was performed for synthesis of **1** with tenfold amounts of reactants and catalyst with respect to one mentioned in the experimental section. The results showed the yield of 90% in these conditions that is comparable with one in Table 2.

The plausible mechanism in which VSA has catalyzed this transformation is shown in Scheme 3. The reaction likely proceeds via initial formation of intermediate (I). This intermediate reacted with another molecule of 2-naphthol to afford the corresponding benzoxanthenes.



^a Based on disappearance of benzaldehyde. For 0/1 catalyst to substrate after 10 h the conversion was 0%.

Fig. 3 – The catalyst amount effect on the synthesis of 14-phenyl-14*H*-dibenzo [*a,j*]xanthenes.^a

Table 2

Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives in presence of VSA as catalyst^a

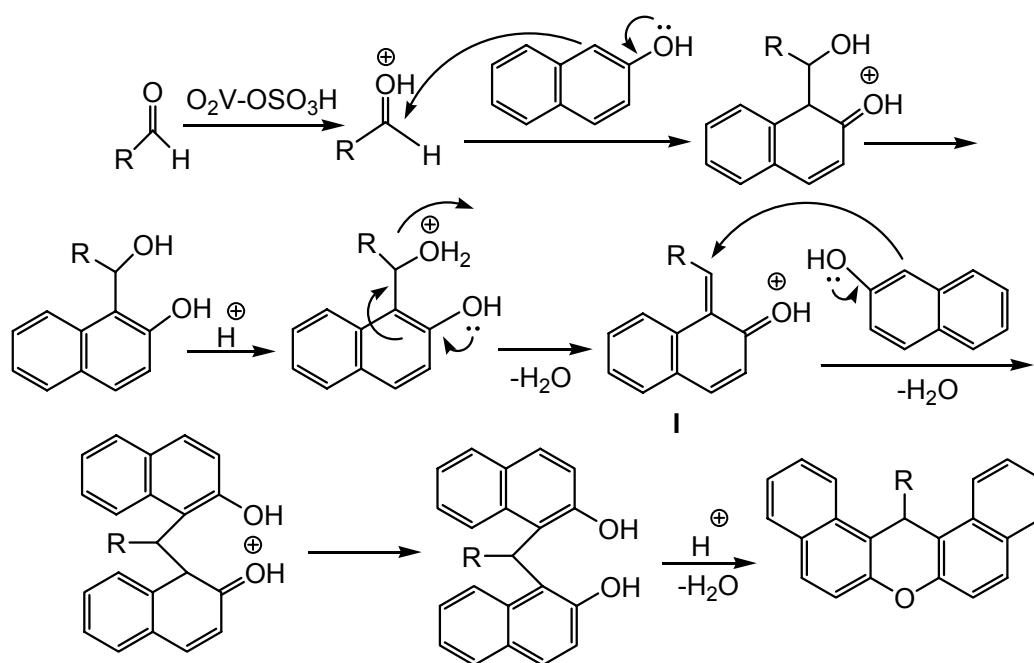
Entry	R	Time (min)	Yield ^b (%)	Mp (°C)	
				Found	Reported
1	C ₆ H ₅	20	93	180-181	182-183
2	4-CH ₃ -C ₆ H ₄	20	85	225-227	227-228
3	4-CH ₃ O-C ₆ H ₄	15	88	231-233	230-232
4	4-Cl-C ₆ H ₄	10	90	288-290	287-288
5	4-NO ₂ -C ₆ H ₄	15	92	308-310	310-311
6	3-NO ₂ -C ₆ H ₄	20	87	212-214	210-211
7	2,4-Cl ₂ -C ₆ H ₃	20	86	225-227	227-228
8	4-Br-C ₆ H ₄	15	92	292-294	295-296
9	2-Cl-C ₆ H ₄	25	90	215-217	214-215
10	2-CH ₃ O-C ₆ H ₄	40	80	261-263	258-260
11	2-NO ₂ -C ₆ H ₄	20	93	211-213	214-215
12	4-HO-C ₆ H ₄	30	88	135-137	139-140
13	3-Br-C ₆ H ₄	20	91	188-190	190-191
14	2-HO-C ₆ H ₄	30	82	124-126	127-128
15	CH ₃ CH ₂ CH ₂	45	80	149-151	152-154

Table 2 (continued)

16	2-Cl-6-F-C ₆ H ₃	35	89	232-233	-
17	2,4-CH ₃ -C ₆ H ₃	25	90	196-197	-
18	2-Br-C ₆ H ₄	25	92	216-217	-
19	2,4-HO-C ₆ H ₃	30	90	234-236	-

^a All products were characterized by ¹H NMR, ¹³C NMR and IR spectroscopy and comparison with these reported in the literature.⁴²

^b Isolated yields.



Scheme 3

Table 3

Reusability of vanadatesulfuric acid in the synthesis of 14-phenyl-14H-dibenzo[*a,j*]xanthenes

Cycles	Isolated yield ^a (%)
Fresh	93
1	90
2	88
3	85
4	82

^a Catalyst could be recycled by washing with ethanol and dried at 100 °C for 2h

To achieve the reaction efficiency of recovered catalyst, the reaction mixture of **1** was filtered and washed with ethanol twice to give Vanadatesulfuric acid. The recovered acid was dried and used again for synthesis of **1** that led to the yield of 90% (Table 3). It can also be recovered and reused at least four times without noticeable losing activity.

Comparative results

In order to show the ability of our method with respect to previous reports, some of our results in comparison to some other methods are summarized in Table 4. As shown, the yield/time ratio of the present method is better or comparable with the other reported results.

Table 4
Comparison of efficiency of various catalysts in synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes

Entry	Catalyst	Condition	Time (h)	Yield (%)	Ref.
1	VSA	Solvent-free/80 °C	10-45 min	80-93	This work
2	<i>p</i> -Toluenesulfonic acid	1,2-dichloroethane (reflux)	15-24	83-95	[19]
3	Sulfamic acid	Solvent-free/125 °C	6-11	74-93	[20]
4	I ₂	Solvent-free/90 °C	2.5-5	82-95	[21]
5	Amberlyst-15	Solvent-free/125 °C	0.5-2	80-94	[22]
6	LiBr	Solvent-free/130 °C	1-2	80-84	[24]
7	Silica sulfuric acid	Solvent-free/80 °C	0.5-2	80-96	[27]
8	Heteropoly acid	Solvent-free/100 °C	0.5-1.5	80-91	[28]
9	Dowex-50W	Solvent-free/100 °C	1-2	78-91	[29]
10	Selectfluor™	Solvent-free/125°C	6-12	74-93	[30]

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka and Aldrich chemical companies. Transmission electron microscopy was studied using a Philips, CM-10 TEM instrument operated at 100 kV. X-ray diffraction analysis was carried out using a D8ADVANCE, Bruker X-ray diffractometer. Elemental analysis of VSA was performed on a S4 Pioneer Bruker X-ray fluorescence analyzer. Melting points were determined using a Barnstead Electrothermal (BI 9300) apparatus and are uncorrected. IR spectra were obtained using a FT-IR JASCO-680 spectrometer instrument. NMR spectra were taken with a Bruker 400 MHz Ultrashield spectrometer at 400 MHz (¹H) and 125 MHz (¹³C) using DMSO-d₆ as the solvent with TMS as the internal standard.

Preparation of nanorod vanadatesulfuric acid

Anhydrous sodium metavanadate was prepared by drying of sodium metavanadate monohydrate (NaVO₃ · H₂O, MW = 139.94) in the oven at 250 °C for 4 hours.

To a mixture of chlorosulfonic acid (0.1 mol, 11.6 g, 7.7 mL) and dry CHCl₃ (25 mL) in 250 mL round bottom flask in an ice-bath, anhydrous sodium metavanadate (0.1 mol, 12.2 g) was added gradually with stirring. After the completion of addition of anhydrous sodium metavanadate, the reaction mixture was shaken for 1 h. Then 50 mL of cold water was added to the reaction mixture and stirred for 10 minutes. The mixture was filtered and a dark red solid of Vanadatesulfuric acid, 16.3 g (91%), Mp 256 °C (dec.) was obtained. Characteristic IR bands (KBr, cm⁻¹): 3540-3300 (OH, bs), 1640 (OH, m), 1250-1140 (S=O, bs), 1050 (S-O, m), 960 (V=O, m), 840 (V=O, m), 630 (V-O, m) (Fig. 1(B)).

General procedure for the preparation of 14-Aryl-14H-dibenzo[a,j]xanthenes

In a round-bottomed flask the aldehyde (1mmol), 2-naphthol (2 mmol) and VSA (10 mol%) were mixed

thoroughly. The flask was heated at 80 °C with concomitant stirring. After completion of the reaction confirmed by TLC (eluent: EtOAc:n-hexane, 1:4), hot ethanol (10 mL) was added and filtered and separated solid catalyst. The solvent was evaporated and the crude products were recrystallized from ethanol, gave the pure products in 80-93% yields based on the starting aldehyde (Table 2). The products were characterized by IR, ¹H NMR, ¹³C NMR and via comparison of their melting points with the reported ones. Spectroscopic data of new compounds:

14-(2-Chloro-6-Fluorophenyl)-14H-dibenzo[a,j]xanthene

(**16**): Mp: 232-233 °C; R_f = 0.65 (*n*-hexane:ethyl acetate = 3:1); IR (KBr): 3205, 2959, 1651, 1599, 1521, 1484, 1376, 1342, 1238, 1160, 1027, 832, 747 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 6.68 (s, 1H), 6.92 (m, 1H), 7.11 (m, 1H), 7.42 (d, *J* = 1.2 Hz, 1H), 7.46-7.51 (m, 2H), 7.54 (d, *J* = 17.6 Hz, 2H), 7.64 (m, 2H), 7.95 (m, 4H), 8.74 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (125 MHz, DMSO-d₆) δ (ppm): 35.09, 111.99, 117.43, 122.03, 124.29, 127.11, 128.44, 128.90, 129.87, 129.94, 130.44, 131.23, 149.04, 153.24. Anal. Calcd. for C₂₇H₁₆ClFO: C, 78.93; H, 3.93; Cl, 8.63; F, 4.62; O, 3.89; found: C, 78.8; H, 3.9.

14-(2,4-Dimethylphenyl)-14H-dibenzo[a,j]xanthene (**17**):

Mp: 196-197 °C; R_f = 0.53 (*n*-hexane:ethyl acetate = 3:1); IR (KBr): 3055, 2958, 1620, 1594, 1510, 1458, 1350, 1248, 1158, 1035, 964, 815, 739, 684 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 2.01 (s, 3H), 2.41 (s, 3H), 6.71 (s, 1H), 6.83 (m, 2H), 7.44 (m, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.55 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 4H), 8.42 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (125 MHz, DMSO-d₆) δ (ppm): 18.76, 20.10, 35.82, 115.85, 117.12, 123.79, 124.26, 126.59, 128.58, 129.17, 129.62, 130.65, 131.11, 131.70, 132.10, 134.56, 135.42, 139.73, 147.97. Anal. Calcd. for C₂₉H₂₂O: C, 90.12; H, 5.74; O, 4.14; found: C, 90.2; H, 5.8.

14-(2-Bromophenyl)-14H-dibenzo[a,j]xanthene (**18**):

Mp: 216-217 °C; R_f = 0.49 (*n*-hexane:ethyl acetate = 3:1); IR (KBr): 3055, 2964, 1621, 1592, 1515, 1458, 1428, 1353, 1248, 1139, 1063, 964, 826, 733, 677 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 6.68 (s, 1H), 6.94 (m, 1H), 7.13 (m,

1H), 7.42 (m, 2H), 7.48-7.53 (m, 2H), 7.55 (d, $J = 20.0$ Hz, 2H), 7.62-7.68 (m, 2H), 7.95 (d, $J = 20.0$ Hz, 4H), 8.76 (d, $J = 11.2$ Hz, 2H); ^{13}C NMR (125 MHz, DMSO- d_6) δ (ppm): 36.68, 116.94, 117.89, 118.24, 120.57, 123.39, 124.62, 126.91, 128.73, 128.79, 129.49, 130.52, 130.94, 131.79, 133.30, 144.66, 148.25. Anal. Calcd. for $\text{C}_{27}\text{H}_{17}\text{BrO}$: C, 74.15; H, 3.92; Br, 18.27; O, 3.66; found: C, 74.2; H, 3.8.

14-(2,4-Dihydroxyphenyl)-14H-dibenzo[*a,j*]xanthene (19): Mp: 234-236 °C; Rf = 0.58 (n-hexane:ethyl acetate = 3:1); IR (KBr): 3256 (br), 2955, 1688, 1626, 1593, 1515, 1455, 1434, 1350, 1227, 1160, 1120, 1032, 813, 747 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm): 5.36 (s, 1H), 7.09 (dd, $J = 6.4$ Hz, $J = 2.4$ Hz, 1H), 7.12 (m, 2H), 7.14 (s, 1H), 7.23-7.27 (m, 2H), 7.36-7.40 (m, 2H), 7.51 (dd, $J = 4.8$ Hz, $J = 1.6$ Hz, 3H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.74-7.77 (m, 3H), 9.91 (s, 1H); ^{13}C NMR (125 MHz, DMSO- d_6) δ (ppm): 36.25, 102.13, 108.58, 118.56, 122.59, 125.46, 125.94, 126.07, 127.50, 127.66, 128.08, 129.26, 132.65, 134.54, 137.73, 145.47, 155.23. Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{O}_3$: C, 83.06; H, 4.65; O, 12.29; found: C, 83.1; H, 4.7.

CONCLUSIONS

In summary, a novel and highly efficient method for the synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes has been achieved by the condensation reaction of aldehydes with 2-naphthol using catalytic amount of the reusable and environmentally benign vanadatesulfuric acid (VSA) as a solid acid nanorod catalyst under solvent-free conditions. The attractive features of this protocol are simple procedure, short reaction time, high yields, simple workup, reusability of the catalyst and simple purification of the products. Furthermore, this method is also expected to find application in organic synthesis due to the low cost of the catalyst. This approach could make a valuable contribution to the existing processes in the field of benzoxanthene synthesis.

Acknowledgements: We are thankful to Yasouj University for partial support of this work.

REFERENCES

1. T. Hideo, *Jpn. Tokkyo Koho JP.*, **1981**, 56005480; T. Hideo, *Chem. Abstr.*, **1981**, 9580922b.
2. R. W. Lambert, J. A. Martin, J. H. Merrett, K. E. B. Parkes and G. J. Thomas, *PCT Int. Appl. WO*, **1997**, 9706178; R. W. Lambert, J. A. Martin, J. H. Merrett, K. E. B. Parkes and G. J. Thomas, *Chem. Abstr.*, **1997**, 126, 212377y.
3. J. P. Poupelin, G. Saint-Ruf, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf and R. Lacroix, *Eur. J. Med. Chem.*, **1978**, *13*, 67-71.
4. R. H. B. Galt, M. J. Horbury, R. J. Pearce and J. S. Shaw, *J. Med. Chem.*, **1989**, *32*, 2357-2362.
5. G. W. Rewcastle, G. J. Atwell, L. Zhuang, B. C. Baguley and W. A. Denny, *J. Med. Chem.*, **1991**, *34*, 217-222.
6. C. Kaiser, A. M. Pavloff, E. Garvey, P. J. Fowler, D. H. Tedeschi, C. L. Zirkle, E. A. Nodiff and A. J. Saggiomo, *J. Med. Chem.*, **1972**, *15*, 665-673.
7. J. W. Lewis and M. J. Readhead, *J. Med. Chem.*, **1970**, *13*, 525-527.
8. G. Saint-Ruf, H. T. Hieu and J. P. Poupelin, *Naturwissenschaften*, **1975**, *62*, 584-585.
9. J. P. Poupelin, G. Saint-Ruf, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Emouf and R. Lacroix, *Eur. J. Med. Chem.*, **1978**, *13*, 67-71.
10. B. B. Bhowmik and P. Ganguly, *Spectrochim. Acta A.*, **2005**, *61*, 1997-2003.
11. C. G. Knight and T. Stephens, *Biochem. J.*, **1989**, *258*, 683-689.
12. O. Sirkecioglu, N. Talinli and A. Akar, *J. Chem. Res. (S)*, **1995**, 502-506.
13. R. N. Sen and N. N. Surkar, *J. Am. Chem. Soc.*, **1925**, *47*, 1079-1091.
14. P. Papini and R. Cimmarusti, *Gazz. Chim. Ital.*, **1947**, *77*, 142-145.
15. K. Ota and T. Kito, *Bull. Chem. Soc. Jpn.*, **1978**, *49*, 1167-1168.
16. R. J. Sarma and J. B. Baruah, *Dyes Pigments*, **2005**, *64*, 91-92.
17. (a) J. A. Van Allan, D. D. Giannini and T. H. Whitesides, *J. Org. Chem.*, **1982**, *47*, 820-823.
18. A. Khoramabadi-zad, Z. Kazemi and H. A. Rudbari, *J. Korean Chem. Soc.*, **2002**, *46*, 541-544.
19. A. R. Khosropour, M. M. Khodaei and H. Moghannian, *Synlett*, **2005**, *6*, 955-958.
20. B. Rajitha, B. S. Kumar, Y. T. Reddy, P. N. Reddy and N. Sreenivasulu, *Tetrahedron Lett.*, **2005**, *46*, 8691-8693.
21. (a) B. Das, B. Ravikanth, R. Ramu, K. Laxminarayana and B. V. Rao, *J. Mol. Cat. A:Chem.*, **2006**, *255*, 74-77; (b) M. A. Pasha and V. P. Jayashankara, *Bioorg. Med. Chem. Lett.*, **2007**, *17*, 621-623.
22. S. Ko and C. F. Yao, *Tetrahedron Lett.*, **2006**, *47*, 8827-8829.
23. L. Nagarapu, S. Kantevari, V. C. Mahankhali and S. Apuri, *Cat. Commun.*, **2007**, *8*, 1173-1177.
24. A. Saini, S. Kumar and J. S. Sandhu, *Synlett*, **2006**, 1928-1932.
25. M. A. Bigdeli, M. M. Heravi and G. H. Mahdavinia, *J. Mol. Cat. A:Chem.*, **2007**, *275*, 25-29.
26. M. A. Bigdeli, M. M. Heravi and G. H. Mahdavinia, *Cat. Commun.*, **2007**, *8*, 1595-1599.
27. (a) H. R. Shaterian, M. Ghashang and A. Hassankhani, *Dyes Pigments*, **2008**, *76*, 564-568; (b) M. Seyyedhamzeh, P. Mirzaei and A. Bazgir, *Dyes Pigments*, **2008**, *76*, 836-839.
28. M. M. Amini, N. Seyyedhamzeh and A. Bazgir, *Appl. Catal. A:Gen.*, **2007**, *323*, 242-245.
29. G. I. Shakibaei, P. Mirzaei and A. Bazgir, *Appl. Catal. A:Gen.*, **2007**, *325*, 188-192.
30. P. S. Kumar, B. S. Kumar, B. Rajitha, P. N. Reddy, N. Sreenivasulu and Y. T. Reddy, *Arkivoc*, **2006**, *12*, 46-50.
31. A. R. Khosropour, M. M. Khodaei and H. Moghannian, *Synlett*, **2005**, 955-958.
32. H. Firouzabadi and A. A. Jafari, *J. Iran. Chem. Soc.*, **2005**, *2*, 85-114.
33. (a) M. A. Zolfigol, D. Habibi, B. F. Mirjalili and A. Bamoniri, *Tetrahedron Lett.*, **2003**, *44*, 3345-3349; (b) M. A. Zolfigol, I. Mohammadpoor-Baltork, D. Habibi, B.

- F.Mirjalili and A. Bamoniri, *Tetrahedron Lett.*, **2003**, *44*, 8165-8167; (c) B. F. Mirjalili and A. Bamoniri, *Phosphorus Sulfur and Silicon*, **2004**, *179*, 2189-2193.
34. (a) M. A. Zolfigol, *Tetrahedron*, **2001**, *57*, 9509-9511; (b) M. A. Zolfigol and A. Bamoniri, *Synlett*, **2002**, 1621-1624; (c) M. A. Zolfigol, F. Shirini, A. Ghorbani Choghamarani and I. Mohammadpoor-Baltork, *Green Chem.*, **2002**, *4*, 562-564; (d) M. A. Zolfigol, H. Nasr-Isfahani, S. Mallakpour and M. Safaiee, *Synlett*, **2005**, 761-764.
35. M. A. Zolfigol, F. Shirini, K. Zamani, E. Ghofrani and S. Ebrahimi, *Phosphorus Sulfur and Silicon*, **2004**, *179*, 2177-2182.
36. A. Corma, *Current Opinion in Solid State & Materials Science Current Chemistry*, Ltd. 2, **1997**, p. 63-75.
37. A. Corma and H. Garcia, *Catal. Today*, **1997**, *38*, 257-308.
38. P. T. Anastas and T. C. Williamson, "Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes", Oxford University Press, New York, 1998.
39. P. A. Wender, S. L. Handy and D.L. Wright, *Chem. Ind.*, **1997**, 765-769.
40. (a) M. Nasr-Esfahani, B. Karami, M. Montazerzohori and K. Abdi, *J. Heterocycl. Chem.*, **2008**, *45*, 1183-1185; (b) M. Nasr-Esfahani, M. Montazerzohori, M. Moghadam, I. Mohammadpoor-Baltork and S. Moradi, *Phosphorus Sulfur and Silicon*, **2010**, *185*, 261-266; (c) M. Nasr-Esfahani, M. Montazerzohori and T. Gholampour, *Bull. Korean Chem. Soc.*, **2010**, *31*, 3653-3657; (d) M. Nasr-Esfahani, M. Montazerzohori and S. Mehrizi, *J. Heterocycl. Chem.*, **2011**, *48*, 249-254; (e) M. Nasr-Esfahani, S.J. Hoseini and F. Mohammadi, *Chinese J. Catal.*, **2011**, *32*, 1484-1489.
41. L. D. Frederickson and D. M. Hausen, *Anal. Chem.*, **1963**, *35*, 818-827.
42. (a) R. Kumar, G. C. Nandi, R. K. Verma and M. S. Singh, *Tetrahedron Lett.*, **2010**, *51*, 442-445; (b) B. F. Mirjalili, A. Bamoniri and A. Akbari, *Chinese Chem. Lett.*, **2011**, *22*, 45-48; (c) A. K. Bhattacharya, K. C. Rana, M. Mujahid, I. Sehar and A. K. Saxena, *Bioorg. Med. Chem. Lett.*, **2009**, *19*, 5590-5593; (d) H. Eshghi, M. Bakavoli, H. A. Moradi, *Chinese Chem. Lett.*, **2008**, *19*, 1423-1426.

