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Synthesis of benzoxanthene derivatives using Brønsted acidic ionic liquids (BAILs), 2-pyrrolidonium hydrogen sulfate and (4-sulfobutyl)tris(4-sulfophenyl) phosphonium hydrogen sulfate

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1. Introduction

The field of ionic liquids (ILs) is growing at a very fast rate, as the many beneficial properties of these liquids are identified and utilized [1]. Their role in electrochemistry [2–4], synthesis of nano structured materials [5], and reaction media and catalysis [6–11] were studied. Brønsted acidic ionic liquids (BAILs), as green media, are thought to be promising catalysts replacing cation-exchange resins or solid acids for the organic reactions [12].

Huang et al. have synthesized pyrrolidonium acidic ionic liquids and studied their catalytic activity for esterification of acetic acid and butanol for the first times [13]. Excellent conversions and selectivities were obtained using 2-pyrrolidonium hydrogen sulfate ([Hnhp][HSO₄]) [14].

Recently, a novel ionic liquid, (4-sulfobutyl)tris(4-sulfophenyl) phosphonium hydrogen sulfate, has been synthesized through the simple procedure and its catalytic activity for the oxathioacetalization was investigated under solvent-free conditions [15].

2-Hydroxy-1,4-naphthoquinone (Lawsone) is known as hennotannic acid and shows a red-orange dye in the leaves of the henna plant [16]. Naphthoquinone core of these derivative compounds were

ABSTRACT

Brønsted acidic ionic liquids (BAILs), 2-pyrrolidonium hydrogen sulfate and (4-sulfobutyl)tris(4-sulfophenyl) phosphonium hydrogen sulfate are found to be efficient catalysts for synthesis of 14-aryl-14H-dibenzo[a,i] xanthene-8,13-dione, 3,4-dihydro-1H-benzo[b]xanthene-1,6,11(2H,12H)-trione, and aryl-5H-dibenzo[b,i] xanthene-5,7,12,14(13H)-tetraone derivatives.

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reported to show fluorescence activities [17], biological properties, industrial applications and precursors in the synthesis of heterocyclic compounds [18]. Xanthenes and benzoxanthenes are important biologically active heterocycles [19]. They show antibacterial [20], antiflammatory [21] and antiviral activities [22] and can also be used in photodynamic therapy as well as antagonists for paralyzing the action of zoxozolamine [23].

In continuation of our research on applications of ionic liquids in organic synthesis [24], and our interest in the synthesis of reactive dyes based on 2-hydroxy-1,4-naphthoquinone encouraged us to the synthesis of a) 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones from β -naphthol, aromatic aldehydes and 2-hydroxy-1,4-naphthoquinone; b) 3,4-dihydro-1*H*-benzo[b]xanthene-1,6,11(2*H*,12*H*)-trione from 2-hydroxy-1,4-naphthoquinone, various aromatic aldehydes and dimedone; c) aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraones from 2-hydroxy-1,4-naphthoquinone, and various aromatic aldehydes in the presence of a catalytic amount of 2-pyrrolidonium hydrogen sulfate (IL1) and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (IL2) under thermal solvent-free conditions (Scheme 1).

2. Experimental

All reagents were purchased from Merck and Sigma-Aldrich and used without further purification. 2-Pyrrolidonium hydrogen sulfate

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Scheme 1. Synthesis of benzoxanthene derivatives using Brønsted acidic ionic liquids.

(IL1) [13] and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (IL2) [15] were prepared according to the reported procedure. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 400, 500 MHz instrument. IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica-gel polygram SILG/UV 254 plates.

2.1. Preparation of 2-pyrrolidonium hydrogen sulfate as ionic liquid

2-Pyrrolidone (20 mmol) was charged into a 150 mL three necked flask with magnetic stirrer. Then equimolar concentrated sulfuric acid (98 wt.%) was added dropwise slowly at room temperature. After the dropping was finished, the system was slowly heated up to 80 °C and stirred for 12 h. The mixture was washed with diethyl ether three times to remove non-ionic residues and dried in vacuum by a rotary evaporator to obtain the viscous clear 2-pyrrolidonium hydrogen sulfate [13].

2.2. Preparation of (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (IL1)

2.2.1. Preparation of zwitterions

Triphenylphosphine (20 mmol), 1,4-butane sulfonate (20 mmol) in equimolar quantities in toluene and brought to reflux. The mixture was stirred magnetically for 12 h at the refluxed temperature. Then, a white solid zwitterion was formed and washed repeatedly with ether three times after vacuum filtration. After dried in vacuum (110 °C), the product (zwitterion) was obtained in good yield (90%) and sufficient purity [15] as assessed by a Varian DRX-400 NMR spectroscopy. Spectroscopic data for the zwitterion: ¹H NMR (D₂O, 400 MHz) δ : 7.43–8.51 (m, 15H), 4.12 (s, 2H), 3.80 (s, 2H), 2.34 (s, 2H),

1.20 (s, 2H) ppm; ¹³C NMR (D₂O, 100 MHz,) δ: 143.90, 134.77, 131.42, 127.46, 37.97, 32.82, 23.74, 19.87 ppm (Scheme 2).

2.2.2. Preparations of (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (IL2)

In a three necked round bottomed flask equipped with a magnetic stirrer, a thermometer and a funnel, the quadruple molar sulfuric acid (40 mmol) was added to the zwitterions (10 mmol), then the mixture was stirred for 12 h at temperature from 80 to 150 °C to form the ionic liquid. Then, the IL phase was washed repeatedly with toluene and ether to remove non-ionic residues, and dried in vacuum (110 °C). A black viscous liquid was formed quantitatively in high purity as assessed by NMR spectroscopy. ¹H NMR (D₂O, 400 MHz) δ : 7.53 (d, *J*=6.8 Hz, 6H), 7.94 (d, *J*=6.4 Hz, 6H), 3.52 (t, *J*=7.6 Hz, 3H), 1.80–1.92 (m, 2H), 1.28–1.39 (m, 4H), 1.87 (s, 2H) ppm; ¹³C NMR (D₂O, 100 MHz) δ : 149.83, 135.42, 128.14, 122.43, 52.05, 26.64, 22.62, 20.63 ppm (Scheme 3).

2.3. Synthesis of 14-aryl-14H-dibenzo [a,i]xanthene-8,13-diones and 3,4-dihydro-1H-benzo[b]xanthene-1,6,11(2H,12H)-trione

A stirred mixture of arylaldehydes (1 mmol), β -naphthol or dimedone (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol), and



Triphenyl phosphine

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Scheme 2. Preparation of zwitterions.



Scheme 3. Preparation of Brønsted acidic ionic liquid (BAIL), (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (IL2).

2-pyrrolidonium hydrogen sulfate (0.08 g, 40 mol%, 0.4 mmol) or (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (0.07 g, 10 mol%, 0.1 mmol) was reacted in an oil bath at 100 °C for the appropriated times (Tables 1, 2). After completion of the reaction, it was cooled to room temperature. Then, 5 mL of water was added to the mixture. The ionic liquid was dissolved in water, and filtered for separation of the crude product. The separated product was washed twice with water (2×5 mL). The solid product was purified by recrystallization procedure in ethanol.

All of the desired product(s) were characterized by comparison of their physical data with those of known compounds. For recycling the catalysts, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused.

Select characterizations of the orange-red products j, k, and l are given below:

2.3.1. 14-(3,4,5-trimethoxylphenyl)-14H-dibenzo[a,i]xanthene-8,13dione (j)

Orange powder, M.p.: 288–290 °C; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 3.71 (s, 3H), 3.73 (s, 6H), 5.83(s, 1H), 6.57 (s, 2H), 7.41–7.56 (m, 4H), 7.74–7.77 (m, 1H), 7.82–7.89 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.06–8.13 (m, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.4, 178.38, 157.16, 153.18, 147.35, 138.70, 136.82, 135.21, 131.9, 131.3, 131.12, 130.85, 129.96, 129.7, 129.45, 128.60, 127.56, 125.69, 124.59, 123.84, 116.73, 116.56, 116.34, 105.88, 77.51, 77.09, 77.66, 60.72, 56.11, 35.28 ppm; IR

Table 1

Synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-diones.

Entry	Substrate	IL1		IL2	
		Time (min)	Yield (%) ^a	Time (min)	Yield (%) ^a
a	Benzaldehyde	35	90	9	92
b	4-Nitrobenzaldehyde	25	91	7	94
с	3-Nitrobenzaldehyde	28	96	4	90
d	2,4-di Cholorobenzaldehyde	30	90	5	88
e	3,4-di Cholorobenzaldehyde	28	85	7	88
f	2-Cholorobenzaldehyde	20	90	4	97
g	4-Cholorobenzaldehyde	25	90	2	96
ĥ	4-Methylbenzaldehyde	30	80	8	85
i	4-Methoxybenzaldehyde	32	83	10	87
	3,4,5-Trimethoxybenzaldehyde	37	82	10	89
j	The corresponding 14-aryl-14 <i>H</i> -dibenzo[a,i] xanthene-8,13-diones was synthesized for the first time				
k	2,5-Dimethoxybenzaldehyde The corresponding 14-aryl-14 <i>H</i> -dibenzo[a,i] xanthene-8,13-diones was synthesized for the first time	34	86	12	92

^a Yields refer to the isolated pure products. The desired pure products were characterized by comparison of their physical data (melting points, IR, ¹H and ¹³C NMR) with those of known compounds [25–27]. The reaction was carried out under thermal solvent-free conditions in an oil bath at 100 °C.

Table 2	
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Synthe	esis of 3,4	4-dihydro-1	H-benzo[b]xanthene-	1,6,11(2H,12H)	-triones
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Entry	Substrate	IL1		IL2		
		Time (min)	Yield (%) ^{a,b}	Time (min)	Yield (%) ^{a,b}	
L	Benzaldehyde	30	84	20	92	
M	4-Nitrobenzaldehyde	25	90	15	97	
Ν	4-Methylbenzaldehyde	35	80	15	97	
0	4-Cholorobenzaldehyde	30	87	10	83	
Р	3-Nitrobenzaldehyde	25	88	10	80	
Q	4-Bromobenzaldehyde	35	83	7	95	
R	4-Fluorobenzaldehyd	35	78	20	92	
S	2-Cholorobenzaldehyde	40	93	15	97	
Т	3-Bromobenzaldehyde	35	78	10	97	

^a Yields refer to the pure isolated products.

^b The structure of all known products were confirmed by comparison of their spectral data (FT-IR, ¹H NMR, ¹³C NMR) with those of known samples in the literature [27].

(KBr) (ν_{max} , cm⁻¹): 3035, 1700, 1655, 1636, 1617, 1589, 1543, 1507, 1458, 1286, 1213, 1126, 1092; Anal. Calcd (%) for C₃₀H₂₂O₆: C, 75.30; H, 4.63; Found: C, 75.27; H, 4.65.

2.3.2. 14-(2,5-dimethoxylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (k)

Orange powder, M.p.: 260 °C; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 3.63 (s, 3H), 3.92 (s, 3H), 6.11 (s, 1H), 6.61–6.58 (m, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 6.84 (d, *J* = 2.8 Hz, 1H), 7.37–7.50 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.74–7.80 (m, 3H), 8.09 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 178.5, 178.18, 157.4, 153.7, 151.1, 147.0, 135.1, 133.4, 131.7, 131.9, 131.1, 130.1, 129.3, 129.1, 128.4, 127.3, 125.4, 124.5, 124.1, 117.5, 117.2, 116.8, 116.2, 113.1, 112.1, 57.0, 55.5, 30.0 ppm; IR (KBr) (ν_{max} , cm⁻¹): 3034, 1698, 1655, 1637, 1590, 1542, 1508, 1499, 1458, 1289, 1214, 1182, 1155; Anal. Calcd (%) for C₂₉H₂₀O₅: C, 77.67; H, 4.50; Found: C, 77.47; H, 4.64.

2.3.3. 12-phenyl-3,4-dihydro-1H-benzo[b]xanthene-1,6,11(2H,12H)-trione (l)

Orange powder; mp: 264–265 °C,; ¹H NMR (500 MHz, DMSO-*d*₆): δ =0.94 (3H, s), 1.07 (3H, s), 2.15 and 2.31 (2H, s), 2.67 (2H, s), 4.88 (1H, s), 7.10–7.15 (1H, m), 7.21–7.32 (2H, m), 7.43–7.46 (2H), 7.80– 7.91 (3H, m), 7.99–8.07 (1H, m). ¹³C NMR (125 MHz, DMSO-*d*₆): δ =26.9, 28.9, 32.4, 32.7, 40.1, 113.6, 124.2, 126.2, 126.5, 127.2, 128.7, 128.8, 129.0, 130.9, 131.4, 134.6, 135.0, 143.2, 149.5, 163.4, 177.5, 183.2, 196.3 ppm. IR (KBr) (v_{max} , cm⁻¹): 2926, 1678, 1606. Anal. Calcd for C₂₅H₂₀O₄: C, 78.11; H, 5.24%. Found: C, 78.21; H, 5.29%.

2.4. Synthesis of aryl-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraones

A stirred mixture of aldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (2 mmol) and 2-pyrrolidonium hydrogen sulfate (0.08 g, 40 mol%, 0.4 mmol) or (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (0.07 g, 10 mol%, 0.1 mmol) were reacted in an oil bath at 100 °C for the appropriated times (Table 3). After completion of the reaction, it was cooled to room temperature. Then, 5 mL of water was added to the mixture. The ionic liquid was dissolved in water, and filtered for separation of the crude product. The separated product was washed twice with water (2×5 mL). The solid product was purified by recrystallization procedure in ethanol.

All of the desired product(s) were characterized by comparison of their physical data with those of known compounds. For recycling the catalysts, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused.

Table 3

Tuble 5	
Synthesis	of arvl-5H-dibenzolb.ilxanthenes.

Entry	Aromatic aldehyde	IL1		IL2		
		Time (min)	Yield (%) ^{a,b}	Time (min)	Yield (%) ^{a,b}	
А	Benzaldehyde	30	90	10	95	
В	4-Cholorobenzaldehyde	25	95	9	98	
С	4-Bromobenzaldehyde	25	97	5	96	
D	4-Flourobenzaldehyde	20	86	7	90	
E	4-Methylbenzaldehyde	20	85	7	89	
F	2-Cholorobenzaldehyde	17	96	10	92	
G	3-Nitrobenzaldehyde	20	95	10	95	
Н	4-Methoxybenzaldehyde	28	89	15	90	
Ι	4-Nitrobenzaldehyde	25	90	12	91	

^a Yields refer to the pure isolated products.

^b The structure of all known products were confirmed by comparison of their spectral data (FT-IR, ¹H NMR, ¹³C NMR) with those of known samples in the literature [28–30].

3. Results and discussions

In order to be able to carry out preparation of 14-aryl-14*H*-dibenzo [a,i]xanthene-8,13-diones derivatives in a more efficient way minimizing the time, temperature and amount of catalyst, the reaction of β -naphthol, benzaldehyde, and 2-hydroxy-1,4- naphthoquinone was selected as model system and the catalyst reactivity at different reaction temperatures (80, 100, 110 and 120 °C) and the different amounts of catalyst (0.05, 0.08, 0.1, 0.12 g) were investigated. The best result was obtained by carrying out the reaction with 1.0:1.0:1.0 molar ratios of β -naphthol, benzaldehyde, 2-hydroxy-1,4-naphthoquinone, in the presence of 2-pyrrolidonium hydrogen sulfate (0.08 g, 40 mol%, 0.4 mmol) under solvent-free conditions at 100 °C. The reaction was completed in 35 min with 90% yield.

In addition, mentioned optimized procedure was applied for Brønsted acidic ionic liquid, (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate. The best result was obtained by carrying out the reaction with 1.0:1.0:1.0 molar ratios of β -naphthol, benzaldehyde, 2-hydroxy-1,4-naphthoquinone, in the presence of (BAIL), (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (0.07 g, 10 mol%, 0.1 mmol) under solvent-free conditions at 100 °C. The reaction was completed in 9 min with 92% yield.

We also examined the model reaction being conducted with concentrated sulfuric acid (98% w/w) as catalyst under the same conditions to compare ionic liquids with hazardous H_2SO_4 (0.4 mmol) under solvent-free conditions at 100 °C. The reaction was completed in 45 min with 74% yield. The corrosive properties of sulfuric acid are accentuated by its highly exothermic reactions. The danger is greater with concentrated sulfuric acid and also it isn't good via green chemistry view. It couldn't be reused and recycled for next reactions and not environmentally safe.

In summary, the preparation of IL is straightforward to escape from disadvantages of H₂SO₄. 2-pyrrolidonium hydrogen sulfate and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate are recyclable catalysts and reuseable several times without any loss of their activity. High conversions, shorter reaction times, cleaner reaction, simple experimental and work-up procedures are advantages of these procedures.

Using these optimized reaction conditions, the scope and efficiency of the reaction were explored for the synthesis of 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones derivatives (products: a-k) through direct condensation of β -naphthol (1 mmol), aromatic aldehyde (1 mmol) and 2-hydroxy-1,4-naphthoquinone (1 mmol) (Table 1) and 3,4-dihydro-1H-benzo[b]xanthene-1,6,11(2*H*,12*H*)-triones derivatives (products: L–T) through direct condensation of dimedone (1 mmol), aromatic aldehyde (1 mmol) and 2-hydroxy-1,4-naphthoquinone (1 mmol), 4-naphthoquinone (1 mmol) (Table 2).

Table 4

Comparison of catalyzed method with different synthesis methods of 14-phenyl-14Hdibenzo[a,j]xanthenes.

Entry	Catalyst	Time	Yield	Reference
		(min)	%	
1	HClO ₄ -SiO ₂ /110 °C	60	90	[25]
2	SiO ₂ -Cl/110 °C	45	88	[26]
3	P-TSA/H ₂ O Reflux	600	88	[29]
4	2-Pyrrolidonium hydrogen sulfate (IL1)	35	90	Present
				work
5	4-Sulfobutyl)tris(4-sulfophenyl)phosphonium	9	92	Present
	hydrogen sulfate (IL2)			work

Interestingly, a variety of aldehydes including *ortho-*, *meta-*, and *para-*substituted aryl aldehydes participated well in this reaction and gave the corresponding benzoxanthene derivatives in good to excellent yield without formation of any by-products such as aryl-5*H*-dibenzo[b,i]xanthene.

We also found that a mixture of aromatic aldehydes (1 mmol), and 2-hydroxy-1,4-naphthoquinone (2 mmol) in the presence of a catalytic amount of 2-pyrrolidonium hydrogen sulfate (0.08 g, 40 mol%, 0.4 mmol) and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (0.07 g, 10 mol%, 0.1 mmol) as reusable catalysts at 100 °C under solvent-free conditions, afforded aryl-5*H*-dibenzo[b,i]xanthene derivatives (products: A–I) (Table 3).

To show the merit of the present work in comparison with reported results in the literature, we compared results of mentioned ionic liquids, 2-pyrrolidonium hydrogen sulfate and (4-sulfobutyl)tris (4-sulfophenyl)phosphonium hydrogen sulfate, with reported catalysts such as HClO₄–SiO₂ [25], SiO₂–Cl [26], and *P*-TSA [29] in the synthesis of 14-phenyl-14*H*-dibenzo[a,j]xanthenes from the reaction of β -naphthol, benzaldehyde and 2-hydroxy-1,4-naphthoquinone (Table 1, entry 1). As shown in Table 4, the ionic liquid can act as suitable catalyst with respect to reaction times and yield of the products.

The proposed mechanism is described according to literature [29] for preparation of aryl-5*H*-dibenzo[b,i]xanthene-5,7,12,14 (13*H*)-tetraone in the presence of Brønsted acidic ionic liquid (BAIL) such as 2-pyrrolidonium hydrogen sulfate (Scheme 4). Brønsted acidic ionic liquid with hydrogen bonding can activate the carbonyl groups of aldehyde to decrease the energy of transition state. Then



Scheme 4. Proposed mechanism for condensation reaction of aromatic aldehydes, and 2-hydroxy-1,4-naphthoquinone in the presence of catalytic amount of 2-pyrrolidonium hydrogen sulfate (IL1).



Fig. 1. The investigation of the recycling of 2-pyrrolidonium hydrogen sulfate (IL1) and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (IL2) based on benzaldehyde, β -naphthol and 2-hydroxy-1,4-naphthoquinone (Table 1, entry 1).

nucleophilic attack of 2-hydroxy-1,4-naphthoquinone, resulted in the formation of intermediate (I), and it is followed by the protonation and nucleophilic attack of 2-hydroxy-1,4-naphthoquinone giving the intermediate (II). Their subsequent intermolecular interaction leads to cyclization and dehydration to give the aryl-5*H*-dibenzo[b,i] xanthene-5,7,12,14 (13*H*)-tetraone.

We also investigated the recycling of the catalysts under solvent-free conditions using a model reaction of benzaldehyde, β -naphthol and 2hydroxy-1,4-naphthoquinone (Table 1, entry 1) using 2-pyrrolidonium hydrogen sulfate and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate as catalysts. After completion of the reaction, the reaction mixture was cooled to room temperature, and the ionic liquid was dissolved in water. For recycling the catalyst, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused. The recovered catalysts were reused five times without any loss of their activities (Fig. 1).

4. Conclusion

We have developed a green and straightforward protocol for the synthesis of 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones, aryl-5*H*-dibenzo[b,i]xanthene-5,7,12,14(13*H*)-tetraones and 3,4-dihydro-1*H*-benzo[b]xanthene-1,6,11(2*H*,12*H*)-triones using two molecular liquids, 2-pyrrolidonium hydrogen sulfate (0.08 g, 40 mol%, 0.4 mmol) and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (0.07 g, 10 mol%, 0.1 mmol) as catalysts under thermal solvent-free conditions. This procedure provides several advantages such as cleaner reactions, easier workup, reduced reaction times and reusable catalysts.

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References

- [1] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Germany, 2008.
- [2] D.R. Macfarlane, M. Forsyth, Adv. Mater. 13 (2001) 957.
- [3] M.C. Buzzeo, R.G. Evans, R.G. Compton, Chem. Phys. Chem. 5 (2004) 1106.
- [4] R. Hagiwara, Y. Ito, J. Fluorine Chem. 105 (2000) 221.
- [5] M. Antonietti, D.B. Kuang, B. Smarsly, B. Yong, Z. Angew, Chem. Int. Ed. 43 (2004) 4988.
- [6] H. Jain, J.O. Whittingham, MRS Bull. 25 (2000) 11.
- [7] F. Shi, Y.L. Gu, Q.H. Zhang, Y.Q. Deng, Catal. Surv. Asia 8 (2004) 179.
- [8] P. Kubisa, Prog. Polym. Sci. 29 (2004) 3.
- [9] C. Baudenquin, J. Baudoux, J. Levillain, D. Cahard, A.C. Gaumont, J.C. Plaquevent, Tetrahedron-Asymmetry 14 (2003) 3081.
- [10] H. Zhao, S.V. Malhotra, Aldrichim. Aceta. 35 (2002) 75.
- [11] C.M. Gordon, Appl. Catal. 222 (2001) 101.
- [12] T. Duan, W. You-Ting, Z. Zheng, G. Jiao, H. Xing-Bang, Z. Zhi-Bing, Ind. Eng. Chem. Res. 50 (2011) 1989.
- [13] B. Huang, Y. Wang, K. Zhang, Y. Fang, B. Zhou, Chin. J. Catal. 28 (2007) 743.
- [14] B. Huang, Z. Li, Y. Wang, K. Zhang, Y. Fang, Acta. Chim. Sinica 15 (2008) 1837.
- [15] B. Shaohua, C. Lu, J. Yongjun, Y. Jianguo, Chin. J. Chem. 28 (2010) 2119.
- [16] B. Huang, Z. Li, Y. Wang, K. Zhang, Y. Fang, Acta. Chim. Sinica 15 (2008) 1837.
- [17] A.C. Dweek, Int. J. Cosmet. Sci. 24 (2002) 287.
- [18] M.M.D. Oliveira, M.C.F. Linardi, M.R.P. Sampaio, J. Pharm. Sci. 67 (1978) 562.
- [19] B. Søballe, K.P. Robert, Microbiology 145 (1999) 1817.
- [20] T. Hideu, J.P. Tokkyo Koho, Chem. Abstr. 95 (1981) 80922b 56005480, 1981.
- [21] R.W. Lamberk, J.A. Martin, J.H. Merrett, K.E.B. Parkes, G.J. Thomas, Chem. Abstr. 126 (1997) P212377y W09706178; 1997.
- [22] J.P. Poupelin, G. Saint-Rut, O. Fussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, R. Lakroix, Eur. J. Med. Chem. 13 (1978) 67.
- [23] G. Saint-Ruf, H.T. Hieu, J.P. Poupelin, Naturwissenschaften 62 (1975) 584.
- [24] H.R. Shaterian, M. Arman, F. Rigi, J. Mol. Liq. 158 (2011) 145.
- [25] L.Q. Wu, Y.F. Wu, C.G. Yang, L.M. Yang, L.J. Yang, J. Braz. Chem. Soc. 221 (2010) 941.
- [26] L. Wu, J. Zhang, L. Fang, C. Yang, F. Yan, Dye. Pigment. 86 (2010) 93.
- [27] M. Dabiri, Z. Noroozi Tisseh, A. Bazgir, J. Heterocycl. Chem. 47 (2010) 1062.
- [28] A. Rahmati, Chin. Chem. Lett. 21 (2010) 761.
- [29] A. Bazgir, Z. Noroozi Tisseh, P. Mirzaei, Tetrahedron Lett. 49 (2008) 5165.
- [30] Z. Noroozi Tisseh, C. Azimi, P. Mirzaei, A. Bazgir, Dye. Pigment. 79 (2008) 273.