Scientific paper

# 1,4-Diazaniumbicyclo[2.2.2]octane Diacetate: As an Effective, New and Reusable Media for the Synthesis of 14-Aryl-14*H*-dibenzo[*a*,*j*]xanthenes

# Leila Zare Fekri\* and Hajar Saeedi Fard

Department of Chemistry, Payame Noor University, PO Box 19395-3697 Tehran, Iran

\* Corresponding author: E-mail: chem\_zare@yahoo.com

Received: 02-11-2015

#### Abstract

A general synthetic route to dibenzoxanthenes has been developed using 1,4-diazaniumbicyclo[2.2.2]octane diacetate as a new bis ionic liquid under thermal and solvent free condition. This method provides several advantages such as a simple work-up, environmental friendliness and shorter reaction time along with high yields. All of the synthesized compounds were characterized by infrared spectroscopy, <sup>1</sup>H and <sup>13</sup>C spectroscopy and elemental analyses.

Keywords: Solvent free, xanthenes, 1,4-diazaniumbicyclo[2.2.2]octane diacetate, β-naphthol

#### 1. Introduction

Research on xanthenes, especially benzoxanthenes, has emerged in organic synthesis due to their wide range of biological and therapeutic properties like antiviral,<sup>1</sup> antiinflammatory,<sup>1</sup> and antibacterial activities,<sup>1a,b</sup> as well as in photodynamic therapy<sup>2</sup> and as antagonists of the paralyzing action of zoxazolamine.<sup>3</sup> Xanthenes are also available from natural sources. Popularly known Santalin pigments have been isolated from a number of plant species.<sup>4</sup> Furthermore, due to their useful spectroscopic properties they are used as dyes,<sup>5</sup> in laser technologies,<sup>6</sup> and in fluorescent materials for visualization of biomolecules.<sup>7</sup> Many procedures have been disclosed on how to synthesize xanthenes and benzoxanthenes, such as cyclodehydrations,<sup>8</sup> trapping of benzynes by phenols,<sup>9</sup> alkylations of hetero atoms,<sup>10</sup> cyclocondensations between 2hydroxyaromatic aldehydes and 2-tetralone.<sup>11</sup> Benzaldehydes and acetophenones bearing tethered carbonyl chains underwent the intramolecular phenyl-carbonyl coupling reactions in the presence of samarium diiodide and hexamethylphosphoramide to afford xanthenes.<sup>12</sup> In addition, 14H-dibenzo[a,j]xanthenes and related products are prepared by the reaction of  $\beta$ -naphthol with formamide,<sup>1</sup> 1-hydroxymethylnaphthalen-2-ol<sup>13</sup> and carbon monoxide.<sup>14</sup> Recently, xanthenes were also synthesized by the condensation of aldehydes,  $\beta$ -naphthol and dimedone.15

Due to the environmental concerns, the use of benign solvents as alternatives to the volatile organic solvents is of high interest to organic chemists. The use of ionic liquids as reaction media and catalyst can offer a solution to the solvent emission and catalyst recycle problems.<sup>16,17</sup> Ionic liquids possess the advantages, like negligible vapor pressure, reasonable thermal stability and recyclability. They dissolve many organic and inorganic substrates and are tunable to specific chemical tasks.<sup>18</sup> Recently, ionic liquids have been successfully employed as solvents with concomitant catalytic activity for a variety of reactions.<sup>19</sup>

#### 2. Results and Discussion

As a part of our going interest for the development of efficient and environmentally friendly procedures for the synthesis of heterocyclic and pharmaceutical compounds,<sup>20–23</sup> an efficient, facile and solvent free procedure was introduced for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes (Scheme 1). For this purpose, the reaction of aromatic aldehydes and β-naphthols using a bis ionic liquid (1,4-diazaniumbicyclo[2.2.2]octane diacetate, DABCO-diacetate), was investigated for the first time. The procedure presented here not only gives the desired products in good yields, but also avoids the problems associated with the conventional solvents such as cost,

Fekri and Fard: 1,4-Diazaniumbicyclo[2.2.2]octane Diacetate: ...

handling, safety and pollution, and moreover the reaction times are reduced to a few minutes.

To emphasize the effect of the ionic liquid, the model reaction between 4-chlorobenzaldehyde and  $\beta$ -naphthol was described and different acid catalysts were tested for this reaction. All the reactions were run with catalytic amounts of the catalysts. As can be seen in Table 1 satisfactory results were obtained only with DABCO-diacetate (entry 9).

To investigate the efficiency and generality of the reaction, various benzaldehyes were treated with  $\beta$ -naphthol under the above-described reaction conditions in the presence of DABCO-diacetate. The results are summarized in Table 2. Accordingly, we can see that all the reactions afforded the corresponding xanthenes **3a**-**p** in high yields.

On the other hand, the synthesis of xanthenes from hydrazones required shorter reaction times and provided the products in higher yields than was the case when starting from aldehydes. It seems that the conversion of aldehydes to the corresponding hydrazone derivatives helps to facilitate the nucleophilic addition of  $\beta$ -naphthol in comparison with the starting aldehydes. Because the hydrazones are unstable under acidic ionic liquid media, it helps to treat them better with  $\beta$ -naphthol.

After reaction, the ionic liquid was easily separated from the reaction medium by washing with distilled water (IL is soluble in water). The washed ionic liquid was distilled under vacuum to recover it and reuse it as a solvent in the subsequent reactions. After three successive runs, recycled ionic liquid showed no loss of efficiency with regard to the reaction time and yield (Table 3).



Scheme 1. Synthesis of benzoxanthenes using [DABCO]diacetate

Table 1. Effect of catalyst or media on the reaction of 4-chlorobenzaldehyde and  $\beta$ -naphthol

Entry	Catalyst	Catalyst amount/ 1mmol of substrate	Reaction conditions	Time (min)	Yield (%)
1	$H_2SO_4$	5 drops	Reflux	7200	34
2	<i>p</i> -ŤsOH	0.5 mmol	Reflux	3600	45
3	Montmorillonite K10	0.5 g	Reflux	120	81
4	HY-Zeolite	0.5 g	Reflux	120	68
5	$I_2$	0.5 mmol	Reflux	7200	15
6	<i>L</i> -proline	0.5 mmol	Reflux	3600	45
7	Nanoparticle $Fe_3O_4$	0.5 g	Reflux	60	83
8	Nanoparticle $Fe_3O_4$ @SiO <sub>2</sub>	0.5 mmol	Reflux	60	85
9	DBU-Ac	0.5 mmol	Heat, 80 °C	10	82
10	DABCO-diacetate	0.5 mmol	Heat, 80 °C	6	91
11	DABCO-diacetate	0.3 mmol	Heat, 80 °C	8	85
12	DABCO-diacetate	0.5 mmol	Heat, 60 °C	8	74

Fekri and Fard: 1,4-Diazaniumbicyclo[2.2.2]octane Diacetate: ...

	Dreadure a Dreadure h						
Entry	<b>Product</b> <sup>a</sup>	Time (min)	Yield (%) <sup>b</sup>	Time (min)	Yield $(\%)^b$	<b>m.p.</b> (°C)	Ref.
1	O <sub>2</sub> N 3a	5	94	3	98	310-311	1, 24, 25
2	CI J 3b	6	91	3.5	97	287–288	1, 24, 25
3	Br 3c	6	89	4	95	294–295	1, 24,25
4	F 3d	5.5	87	4	94	239–240	1, 24, 25
5	O <sub>2</sub> N Generation of the second	8	83	5	91	293–294	1, 24, 25
6		5	94	3	97	210–211	1
7	Cl Gl Gl J J J J J J J J J J J J J J J J	8	87	5.5	94	215–216	1, 24, 25
8	Br	6	92	4	93	192–193	1, 24,25

Table 2. Synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes and comparison of efficiency of [DABCO]diacetate

Fekri and Fard: 1,4-Diazaniumbicyclo[2.2.2]octane Diacetate: ...

	D 1 //	Procedure a		Procedure b			
Entry	Product <sup>a</sup>	Time (min)	Yield $(\%)^b$	Time (min)	Yield $(\%)^b$	m.p. (°C)	Ref.
9	F J Ji	6.5	94	5	98	262–263	1, 24, 25
10	но зј	10	87	6	93	145–146	1, 24, 25
11	H <sub>3</sub> C 3K	9	89	5.5	95	227–228	1, 24, 25
12	H <sub>3</sub> CO 31	10	86	6	92	205–206	1, 24, 25
13	H <sub>3</sub> CO H <sub>3</sub> CO J 3m	12	82	8	90	260–261	1, 24, 25
14	STORE 3n	8	80	6	85	181–182	1, 24, 25
15	0 0 0 0 0 0 0 0 0 0	12	89	7	96	194–196	25
16	H <sub>3</sub> C <sub>N</sub> H <sub>3</sub> C 3p	13	85	7	95	189–190	_

<sup>*a*</sup> All products were characterized by the comparison of their physical constants with those of authentic samples and by the help of IR and NMR spectroscopy. <sup>*b*</sup> Yields based upon the starting aldehyde.

Table 3. Evaluation of reusability of the ionic liquid for the synthesis of 3b

12H), 14.11 (s, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.9, 44.5, 175.8 ppm.

Run	1	2	3	4	5
Time (min)	6	6	6	7	7
Yield (%)	91	90	88	90	88
m.p. (°C)	287-288	287–289	288-290	287–288	287–289

In the proposed mechanistic pathway, initially the aldehyde and  $\beta$ -naphthol are activated via dipolarization by DABCO-diacetate, followed by the nuclophilic attack of 2 equivalents of the  $\beta$ -naphthol to activate the aldehyde and finally via dehydration, the product **3** is produced. To investigate the efficiency of this method, the comparison between this method and some of those previous reported for the synthesis of **3b** was carried out (Table 4).

3. 2. General Procedure for the Preparation of 3a-n

A mixture of the aldehyde (1 mmol),  $\beta$ -naphthol (2 mmol) and [DABCO]diacetate (0.5 mmol) was heated at 80 °C for the required reaction time according to the Table 1. After completion of the reaction, as indicated by TLC, the reaction product was extracted by CHCl<sub>3</sub>/H<sub>2</sub>O. After evaporation of the organic solvent, the crude product was obtained and recrystallized from EtOH and dried to afford the compounds **3a–p** as powders.

The filtrate was concentrated under reduced pressure and washed with diethyl ether. Then, it was dried in a

Table 4. Comparison of synthesis of compound 3b in this method with some of the previously reported methods

Entry	Catalyst	Condition	Time (min)	Yield (%)	Ref.
1	Selectfluor <sup>TM</sup>	stir at 125 °C	420	95	1
2	Polytungstozincate acid	80 °C/Solvent-free	90	88	24
3	CoPy <sub>2</sub> Cl <sub>2</sub>	85 °C, neat conditions	120	95	25
4	Alum	Water, 100 ° C	240	90	26
5	SiO <sub>2</sub> –ZnCl <sub>2</sub>	Stir, 100°C	40	83	27
6	[Et <sub>3</sub> N-SO <sub>3</sub> H]Cl	Sonication, 80 °C	40	93	28
7	$Mg(BF_4)_2$ doped in $[BMim][BF_4]$	Neat, 80 °C	15	94	29
8	DABCO-dihydroAc	procedure a	6	91	This work
9	DABCO-dihydroAc	Procedure b	3.5	97	This work

#### 3. Experimental

Chemicals were purchased from Merck and Fluka. All solvents used were dried and distilled according to the standard procedures. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were determined on a Shimadzu FT-IR 8600 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined on a Bruker 400 DRX Avance instrument at 400 and 100 MHz, respectively. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyzer.

#### 3. 1. Preparation of 1,4-Diazaniumbicyclo [2.2.2]octane diacetate, [DABCO] diacetate, as a Novel Bis Ionic Liquid

A mixture of 1,4-diazabicyclo[2.2.2]octane (10 mmol) and acetic acid (20 mmol) was irradiated with microwaves (180 W) for 2 min at 100 °C three times. After completion of the reaction, the mixture was washed with diethyl ether ( $3 \times 10$  mL). The organic product was extracted from the liquid phase and evaporated under vacuum to produce the desired ionic liquid.

Analytical data for DABCO-diacetate: yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.16 (s, 2H), 3.01 (s,

vacuum evaporator to recover the ionic liquid for the subsequent use.

#### 3. 3. Analytical Data for the Synthesized Compounds

**14-(4-Nitrophenyl)-14***H***-dibenzo**[*a*,*j*]**xanthene** (**3a**): yellow solid; m.p. 310–311 °C; IR (KBr) *v* 3065, 1623, 1554, 1352, 1221 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.7 (s, 1H), 7.69–8.05 (m, 12H), 8.34 (d, *J* = 8.7 Hz, 2H), 8.58 (d, *J* = 8.2 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  38.9, 121.8, 122.5, 125.2, 126.5, 127.1,131.8, 132.4, 132.9, 135.2, 136.5, 136.6, 136.9, 147.3, 151.9 ppm; Anal Calc. for C<sub>27</sub>H<sub>17</sub>NO<sub>3</sub>: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.43; H, 4.21, N, 3.52.

**14-(4-Chlorophenyl)-14***H***-dibenzo[***a***,***j***]xanthene (3b): Brown solid; m.p. 287–288 °C; IR (KBr)** *v* **3068, 1646, 1556, 1487, 1233, 1121 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) \delta 6.49 (s, 1H), 7.12 (dd,** *J* **= 2.0 Hz,** *J* **= 6.4 Hz, 2H), 7.42-7.45 (m, 2H), 7.46–7.49 (m, 2H), 7.51 (s, 2H), 7.58–7.62 (m, 2H), 7.82 (d,** *J* **= 9.2 Hz, 2H), 7.86 (d,** *J* **= 8.0 Hz, 2H), 8.34 (d,** *J* **= 8.4 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) \delta 36.7, 115.9, 119.0, 124.9, 126.3, 126.9, 130.2, 130.3, 133.0, 134.5, 135.7, 139.2, 139.8, 146.1,**  151.4 ppm; Anal. Calcd for C<sub>27</sub>H<sub>17</sub>ClO: C, 82.54; H, 4.36. Found: C, 82.58; H, 4.29.

**14-(4-Bromophenyl)-14***H***-dibenzo[***a***,***j***]xanthene (3c): Brown solid; m.p. 294–295 °C; IR (KBr)** *v* **3123, 1654, 1537, 1481, 1223, 1126 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) \delta 6.74 (s, 1H), 7.35 (d,** *J* **= 8.4 Hz, 2H), 7.48 (t,** *J* **= 7.2 Hz, 2H), 7.56–7.66 (m, 6H), 7.95 (d,** *J* **= 8.8 Hz, 4H), 8.66 (d,** *J* **= 8.4 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) \delta 35.8, 112.9, 118.3, 125.1, 126.7, 126.8, 131.9, 132.3, 133.6, 134.9, 135.0, 139.1, 140.8, 145.2, 153.5 ppm; Anal. Calcd for C<sub>27</sub>H<sub>17</sub>BrO: C, 74.15; H, 3.92. Found: C, 74.09; H, 3.99.** 

**14-(2-Nitrophenyl)-14H-dibenzo**[*a,j*]**xanthene** (*3e*): Yellow solid; m.p. 293-294 °C; IR (KBr) *v* 3354, 3018, 1625, 1556, 1367, 1289, 1109 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.57 (s, 1H), 7.23–8.76 (m, 16H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  34.7, 119.2, 121.4, 123.5, 124.9, 125.0, 126.4, 129.0, 130.4, 130.8, 131.9, 133.9, 136.6, 137.2, 143.3, 145.5, 150.2 ppm; Anal. Calcd for C27H17NO3: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.42; H, 4.20, N, 3.51.

**14-(3-Nitrophenyl)-14H-dibenzo**[*a,j*]**xanthene** (**3f**): Yellow solid; m.p. 210–211 °C; IR (KBr) *v* 3054, 2936, 1556, 1489, 1343, 1223 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.55 (s, 1H), 7.23–7.81 (m, 13H), 8.32 (d, *J* = 8.5 Hz, 2H), 8.56 (s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  34.7, 119.2, 121.4, 123.5, 125.0, 126.4, 129.0, 130.4, 130.8, 131.9, 133.7, 133.9, 136.6, 137.2, 143.3, 145.5, 150.2 ppm; Anal. Calcd for C<sub>27</sub>H<sub>17</sub>NO<sub>3</sub>: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.34; H, 4.22, N, 3.54.

**14-(3-Bromophenyl)-14***H***-dibenzo[***a***,***j***]xanthenes (3h): Yellow solid; m.p. 192–193 °C; IR (KBr)** *v* **3015, 2926, 1612, 1476, 1321, 1212 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-***d***<sub>6</sub>, 400 MHz) δ 6.61 (s, 1H), 6.65–7.11 (m, 2H), 7.32 (d,** *J* **= 7.6 Hz, 2H), 7.51–7.53 (m, 5H), 7.65–7.81 (m, 2H), 7.85–7.89 (m, 4H), 8.14 (d,** *J* **= 7.8 Hz, 1H); <sup>13</sup>CNMR (DMSO-***d***<sub>6</sub>, 100 MHz) δ 32.1, 114.3, 115.4, 123.3 (two carbons), 128.9, 129.1, 129.3, 129.7 (two carbons), 129.8, 130.5, 130.6, 130.9, 131.8, 132.2, 145.5, 149.6 ppm; Anal. Calcd for C<sub>27</sub>H<sub>17</sub>BrO: C, 74.15; H, 3.92. Found: C, 74.25; H, 3.94.** 

**14-(3-Fluorophenyl)-14***H***-dibenzo[***a***,***j***]xanthene (3i): Brown solid; m.p. 262–263 °C; IR (KBr)** *v* **3143, 1568, 1412, 1254, 1117, 1078 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) \delta 6.51 (s, 1H), 6.77–8.24 (m, 16H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) \delta 37.3, 113.0, 113.5, 116.1 (d, <sup>3</sup>***J***<sub>C-F</sub> = 2.6 Hz), 117.1, 119.8, 120.1, 121.9, 124.3 (d, <sup>3</sup>***J***<sub>C-F</sub> = 2.8 Hz), 124.8, 128.0, 129.1, 129.7, 130.1 (d, <sup>2</sup>***J***<sub>C-F</sub> = 28.3 Hz), 134.5 (d, <sup>2</sup>***J***<sub>C-F</sub> = 33.4 Hz), 147.8 (d, <sup>1</sup>***J***<sub>C-F</sub> = 160.2 Hz), 151.2 ppm; Anal.Calcd for C<sub>27</sub>H<sub>17</sub>FO: C, 86.15; H, 4.55; F, 5.05. Found: C, 86.09; H, 4.54.**  **14-(4-Hydroxyphenyl)-14***H***-dibenzo**[*a*,*j*]**xanthene (3j**): Pink solid; m.p. 145–146 °C; IR (KBr) *v* 3414, 1609, 1512, 1464, 1235, 1123 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.76 (br, s, 1H), 6.37(s, 1H), 6.52–8.87 (m, 16H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  34.3, 116.7, 118.0, 118.4, 123.2, 124.6, 126.1, 126.7, 128.4, 130.8, 132.4, 132.8, 139.9, 146.8, 157.1 ppm; Anal. Calcd for C<sub>27</sub>H<sub>18</sub>O<sub>2</sub>: C, 86.61; H, 4.85. Found: C, 86.63; H, 4.78.

**14-(4-Methylphenyl)-14H-dibenzo**[*a*,*j*]**xanthene (3k)**: White solid; m.p. 227–228 °C; IR (KBr) *v* 3013, 2923,1634, 1589, 1487, 1492, 1233 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.32 (s, 3H), 6.42 (s, 1H), 6.78 (d, *J* = 9.6 Hz, 2H), 7.54–8.09 (m,12H), 8.43 (d, *J* = 8.9 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  23.1, 36.2, 113.6, 117.1, 126.2, 126.7, 128.2, 129.5, 131.4, 132.2, 133.2, 134.1, 144.8, 148.6, 149.8, 151.5 ppm; Anal. Calcd for C<sub>28</sub>H<sub>20</sub>O: C, 90.29; H; 5.41. Found: C, 90.34; H; 5.42.

**14-(4-Methoxyphenyl)-14***H***-dibenzo**[*a*,*j*]**xanthene (31**): yellow solid; m.p. 205–206 °C; IR (KBr) *v* 3123, 2876, 1675, 1609, 1588, 1437, 1387, 1276 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.53 (s, 3H), 6.54 (s, 1H), 6.73 (d, *J* = 8.7 Hz, 2H),7.56–7.76 (m, 12H), 8.67 (d, *J* = 8.7 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  36.9, 53.2, 112.6, 117.8, 118.9, 124.0, 124.1, 126.8, 129.1, 127.8, 130.9, 137.0, 137.8, 151.3, 152.5, 153.2 ppm; Anal. Calcd for C<sub>28</sub>H<sub>20</sub>O<sub>2</sub>: C, 86.57; H; 5.19. Found: C, 86.41; H; 5.20.

**14-Phenyl-14***H***-dibenzo[***a***,***j***]xanthene (***3n***): White solid; m.p. 181–183 °C; IR (KBr)** *v* **3089, 2911, 1623, 1580, 1542, 1437, 1256, 1177cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) \delta 6.51 (s, 1H), 6.98–7.02 (m, 1H), 7.14–7.18 (m, 2H), 7.40–7.44 (m, 2H), 7.50 (d,** *J* **= 8.8 Hz, 2H), 7.53–7.55 (m, 2H), 7.59–7.61 (m, 2H), 7.81 (d,** *J* **= 8.8 Hz, 2H), 7.84 (d,** *J* **= 8.0 Hz, 2H), 8.40 (d,** *J* **= 8.4 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) \delta 31.3, 114.2 (two carbons), 121.2,123.5, 125.6, 127.8 (two carbons), 129.1 (two carbons), 133.4, 135.6, 145.2, 149.3, 159.1 ppm; Anal. Calcd for C<sub>27</sub>H<sub>18</sub>O: C, 90.47; H, 5.06. Found: C, 90.41; H, 5.13.** 

**3-(14***H***-Dibenzo[***a***,***j***]xanthen-14-yl)chromen-4-one (<b>3o**): Light yellow solid; m.p. 194–196 °C; IR (KBr) *v* 3143, 1623, 1576, 1423, 1278, 1208, 1181 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.10 (s, 1H), 6.52 (s, 1H), 7.56–8.05 (m, 16 H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  36.7, 55.4, 112.2, 114.3, 117.6, 118.1, 118.5, 118.9, 123.6, 125.2, 129.8, 131.2, 133.7, 136.1, 139.6, 143.1, 147.4, 151.3, 161.1 ppm; Anal. Calcd for C<sub>30</sub>H18O3: C, 84.49; H, 4.25. Found: C, 84.37; H, 4.21.

**14-(4-***NN***-Dimethylphenyl)-14***H***-dibenzo[***a***,***j***]xanthene (<b>3p**): yellow solid; m.p. 189–190 °C; IR (KBr) *v* 3112, 1632, 1514, 1445, 1232, 1212, 1209, 1123 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.01 (s, 6H), 6.83 (s, 1H), 7.39–7.49

(m, 3H), 7.54–7.67 (m, 4H), 7.78–7.85 (m, 3H), 7.91–7.99 (m, 2H), 8.03 (d, J = 9.2 Hz, 1H), 8.20 (s, 1H), 8.69 (d, J = 8.4 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  34.2, 75.2, 113.2, 115.1, 117.6, 118.1, 119.1, 122.7, 125.3, 129.8, 130.9, 134.8, 143.1, 144.6, 149.1, 163.2 ppm; Anal. Calcd for C<sub>29</sub>H<sub>23</sub>NO: C, 86.75; H, 5.77; N, 3.49. Found: C, 86.77; H, 5.56; N, 3.65.

### 4. Conclusion

In conclusion, we have investigated the ionic liquid 1,4-diazaniumbicyclo[2.2.2]octane diacetate as a mild and efficient media for the synthesis of substituted 14-aryl-14*H*-dibenzo[a,j]xanthenes. The remarkable advantages offered by this method are: the catalyst is inexpensive, non-toxic, easy to handle and reusable, alowing simple work-up procedure, short reaction times, high yields of the products with better purity and offers green aspects by avoiding toxic catalysts and hazardous solvents. To the best of our knowledge this is the first report on synthesis of alkyl- or aryl-14*H*-dibenzo[a,j]xanthene derivatives using ionic liquid 1,4-diazaniumbicyclo[2.2.2]octane diacetate.

#### 5. Acknowledgement

Financial support from the Research Council of Payame Noor University of Rudsar branch is sincerely acknowledged.

#### 6. References

- 1. (a) P. S. Kumar, B. Sunil Kumar, B. Rajitha, P. Narsimha Reddy, N. Sreenivasulu, Y. Thirupathi Reddy, *Arkivoc* **2006**, (*xii*), 46–50;
  - (b) V. S. Patil, V. S. Padalkar, K. R. Phatangare, P. G. Umape,
    B. N. Borase, N. Sekar, *J. Heterocycl. Chem.* 2015, *52*, 124–129. http://dx.doi.org/10.1002/jhet.1998
- R. M. Ion, D. Frackowiak, A. Planner, K. Wiktorowicz, *Acta Biochim. Pol.* 1998, 45, 833–845.
- G. Saint-Ruf, H. T. Hieu, J. P. Poupelin, *Naturwissenschaften* 1975, 62, 584–585.

http://dx.doi.org/10.1007/BF01166986

- 4. (a) A. Arnone, L. Merlini, G. Nasini, *Tetrahedron Lett.* **1972**, *13*, 3503–3506;
  - http://dx.doi.org/10.1016/S0040-4039(01)94083-3

(b) B. Ravindranath, T. R. Sheshadri, *Phytochemistry* **1973**, *12*, 2781–2790;

http://dx.doi.org/10.1016/0031-9422(73)85099-X

(c) J. Kinjo, H. Uemura, T. Nohara, M. Yamashita, N. Marubayashi, K. Yoshihira, *Tetrahedron Lett.* **1995**, *36*, 5599– 5602. http://dx.doi.org/10.1016/00404-0399(50)10710-

 A. Banerjee, A. K. Mukherjee, *Stain Technol.* 1981, 56, 83–85. http://dx.doi.org/10.3109/10520298109067286

- M. Ahmad, T. A. King, K. Ko Do, B. H. Cha, J. J. Lee, *Phys. D: Appl. Phys.* 2002, *35*, 1473–1476. http://dx.doi.org/10.1088/0022-3727/35/13/303
- 7. C. G. Knight, T. Stephens, *Biochem. J.* **1989**, *258*, 683–661. http://dx.doi.org/10.1042/bj2580683
- 8. (a) A. Bekaert, J. Andrieux, M. Plat, *Tetrahedron Lett.* 1992, *33*, 2805–2806; http://dx.doi.org/10.1016/S0040-4039(00)78863-0
  (b) J. Sarma, J. B. Baruah, *Dyes Pigm.* 2005, *64*, 91–92. http://dx.doi.org/10.1016/j.dyepig.2004.03.010
- 9. D. W. Knight, P. B. Little, *Synlett* **1998**, 1141–1143. http://dx.doi.org/10.1055/s-1998-1878
- 10. (a) R. Vazquez, M. C. de la Fuente, L. Castedo, D. Domínguez, *Synlett* 1994, 433–434; http://dx.doi.org/10.1055/s-1994-22878
  (b) H. Ishibashi, K.Takagaki, N. Imada, M. Ikeda, *Synlett* 1994, 49–50. http://dx.doi.org/10.1055/s-1994-22734
- A. Jha, J. Beal, *Tetrahedron Lett.* 2004, 45, 8999–9001. http://dx.doi.org/10.1016/j.tetlet.2004.10.046
- 12. C.-W. Kuo, J.-M. Fang, *Synth. Commun.* **2001**, *31*, 877–892. http://dx.doi.org/10.1081/SCC-100103323
- 13. R. N. Sen, N. N. Sarkar, J. Am. Chem. Soc. 1925, 47, 1079–1091. http://dx.doi.org/10.1021/ja01681a023
- K. Ota, T. Kito, Bull. Chem. Soc. Jpn. 1976, 49, 1167–1168. http://dx.doi.org/10.1246/bcsj.49.1167
- M. A. Ghasemzadeh, Acta. Chim. Slov. 2015, 62, 977–985. http://dx.doi.org/10.17344/acsi.2015.1501
- T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2084. http://dx.doi.org/10.1021/cr980032t
- 17. R. Sheldon, *Chem.Commun.* **2001**, 2399–2407. http://dx.doi.org/10.1039/b107270f
- J. K. Lee, M. J. Kim, J.Org.Chem. 2002, 67, 6845–6847. http://dx.doi.org/10.1021/jo026116q
- T. S. Li, Z. H. Zhang, F. Yang, C. G. Fu, J. Chem. Res. 1998, 1, 38. http://dx.doi.org/10.1039/a703694i
- 20. L. Synth. Commun. 2011, 41, 2323–2330. http://dx.doi.org/10.1080/00397911.2010.502990
- M. Nikpassand, L. Zare, M. Saberi, *Monatsh. Chem.* 2012, 143, 289–293. http://dx.doi.org/10.1007/s00706-011-0575-6

22. L. Zare, N.O. Mahmoodi, A.Yahyazadeh, M. Nikpassand, Ultrason. Sonochem. 2012, 19, 740–744. http://dx.doi.org/10.1016/j.ultsonch.2011.11.008

- 23. L. Zare Fekri, M. Nikpassand, K. Hassanpour, *Curr. Org. Syn.* **2015**, *12*, 76–79.
- http://dx.doi.org/10.2174/1570179411666140806005614 24. M. Mohammadpour Amini, Y. Fazeli, Z. Yassaee, S. Feizi, A. Bazgir, *Open Catal .J.* **2009**, *2*, 40–44. http://dx.doi.org/10.2174/1876214X00902010040
- 25. J. Venu Madhav, B. Suresh Kuarm, B. Rajitha, *Arkivoc* **2008**, *(ii)*, 204–209.
- M. Baghbanzadeh, M. Shakouri Nikchen, E. Arzroomchilar, Bioorg. *Med. Chem. Lett.* 2008, *18*, 436–438. http://dx.doi.org/10.1016/j.bmcl.2007.07.008
- 27. H. A. Soliman, A. Y. Mubarak, A. El-Mekabati, S. S. Elmorsy, *Chem. Sci. Trans.* **2014**, *3*, 819–825.

Fekri and Fard: 1,4-Diazaniumbicyclo[2.2.2]octane Diacetate: ...

 A. Zare, A. R. Moosavi-Zare, M. Merajoddin, M. A. Zolfigol, T. Hekmat-Zadeh, A. Hasaninejad, A. Khazaei, M. Mokhlesi, V. Khakyzadeh, F. Derakhshan-panah, M. H. Beyzavi, E. Rostami, A. Arghoon, R. Roohandeh. *J. Mol. Liq.* 2012, *167*, 69–77. http://dx.doi.org/10.1016/j.molliq.2011.12.012

29. K. Rad-Moghadam, S. C. Azimi, *J. Mol. Catal.* **2012**, *363*, 465–469. http://dx.doi.org/10.1016/j.molcata.2012.07.026

## Povzetek

Razvili smo splošno sintezno pot do dibenzoksantenov z uporabo 1,4-diazanijumbiciklo[2.2.2]oktan diacetata kot nove bis ionske tekočine pod termičnimi pogoji brez prisotnosti topil. Ta metoda predstavlja kar nekaj prednosti, kot so enostavnost izolacije, okoljska sprejemljivost in krajši reakcijski časi ob hkratnem doseganju višjih izkoristkov. Vse sintetizirane spojine smo karakterizirali s pomočjo infrardeče spektroskopije, <sup>1</sup>H in <sup>13</sup>C magnetne resonančne spektroskopije in elementnih analiz.