# A New LiBr-Catalyzed, Facile and Efficient Method for the Synthesis of 14-Alkyl or Aryl-14*H*-dibenzo[*a*,*j*]xanthenes and Tetrahydrobenzo[*b*]pyrans under Solvent-Free Conventional and Microwave Heating

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**Abstract:** An efficient method for the synthesis of 14-alkyl or aryl-14H-dibenzo[a,j]xanthenes and tetrahydrobenzo[b]pyrans under solvent-free conventional and microwave heating using lithium bromide, is described.

**Key words:** xanthenes, tetrahydrobenzo[*b*]pyrans, solvent-free, lithium bromide, microwave irradiation



Scheme 1

Xanthenes and particularly benzoxanthenes constitute an important group of oxygen heterocycles which have extended conjugation conferring interesting spectroscopic properties and as such have many applications in laser methodologies.<sup>1,2</sup> Benzoxanthene derivatives have shown good promise as sensitizers in photodynamic therapy (PDT), a well known method of controlling the localized tumours.<sup>3</sup> Additionally, these compounds also have promising antibacterial,<sup>4</sup> antiviral<sup>5</sup> and antiinflammatory activities<sup>6</sup> and can be used as luminescent sensors.<sup>7</sup>

Methods reported for the production of xanthenes include aryne cycloaddition to phenols,<sup>8</sup> intramolecular coupling of aldehydes and ketones,<sup>9</sup> cyclodehydration,<sup>10</sup> and from precursors like formamide,<sup>11</sup> toxic carbon monoxide,<sup>12</sup> protected aldehydes<sup>13</sup> and finally 2-napthol-1-methanol.<sup>14</sup> Several of these methods involve harsh reaction conditions or long reaction time leaving considerable scope for development of further clean, facile and efficient process for the synthesis of these important molecules. We and others<sup>15</sup> have been using LiBr as a mild Lewis acid in many chemical transformations,<sup>16</sup> including the Friedel-Crafts reaction, preparation of acylals, opening of epoxides, Knoevenagel condensation, Bigginelli condensation, Ehrlich-Sachs reaction. In most of these reported reactions, the LiBr is almost neutral.<sup>16</sup> We have also been active in the area of microwave heating under solvent free conditions.<sup>17,18</sup> In continuation of our investigations with LiBr and microwave heating we describe herein a new efficient and facile method for the production of xanthenes using LiBr under solvent free condition by applying conventional as well as microwave heating (Scheme 1).

SYNLETT 2006, No. 12, pp 1928–1932 Advanced online publication: 24.07.2006 DOI: 10.1055/s-2006-947339; Art ID: D03806ST © Georg Thieme Verlag Stuttgart · New York In a typical example, benzaldehyde (2 mmol),  $\beta$ -naphthol (4 mmol) and LiBr (0.3 mmol) were mixed and stirred for 5 minutes at room temperature and then the temperature was raised to 130 °C and maintained for 65 minutes (Method A). After completion of reaction (TLC), the reaction mixture was cooled to room temperature and water (20 mL) was added. The solid thus obtained was filtered and recrystallized with ethanol to afford colorless crystals of 14-phenyl-14*H*-dibenzo[a,j]xanthene (**3a**), in 82% yield, mp 184–85 °C (lit.<sup>10a</sup> mp 185 °C; entry 1, Table 1). Similarly, other aldehydes were reacted with  $\beta$ -naphthol to afford various xanthene derivatives 3b-k (Table 1). When the reaction was carried out under microwave irradiation (Method B), equivalent results were obtained and the xanthene derivatives were obtained in 77-86% yield (Table 1). The reaction proved to be very reproducible and could be carried out in a domestic microwave oven as well as a purpose designed Prolabo Microwave Module Synthwave S-402.

In the course of optimization of the reaction conditions, increase in reaction time did not prove fruitful. About 15 mol% of LiBr seems to be the optimum amount of Lewis acid and higher amounts of catalyst (20 mol%) did not improve the yields while decreasing the amount of catalyst decreases the yield. The reaction works well with aromatic aldehydes (entry 1–9, Table 1) as well as aliphatic aldehydes (entries 10 and 11, Table 1), giving various xanthene derivatives in 77–86% yields. As can be seen in Table 1, the method is general and tolerates a variety of functional groups.

Encouraged by these results we were delighted to observe this protocol, could safely be extended to a three-component coupling reaction involving equimolar quantity of aldehyde 1, 5,5-dimethyl-1,3-cyclohexanedione (4) and active methylene compounds 5. Tetrahydrobenzo[b]pyrans **6a–e** were obtained in excellent yields (Scheme 2, Table 2) without the formation of any side products.

Entry	Aldehyde	Product <sup>a</sup>	Method A <sup>b</sup>		Method B <sup>b</sup>		Mp (°C)
			Time (min)	Yield (%) <sup>c</sup>	Time (min)	Yield (%) <sup>c</sup>	
1	СНО	<b>3</b> a	65	82	4.0	83	184-85 <sup>10a</sup>
2	Br-CHO	3b	60	83	3.5	81	295–97 <sup>10a</sup>
3	MeO — CHO	3c	70	80	4.5	82	203–04
4	Вг СНО	3d	65	81	3.5	80	190–92
5	СІ—СНО	3e	60	84	3.0	86	287-89 <sup>10b</sup>
6	СІ	3f	65	80	3.5	80	214–15
7		3g	60	84	3.5	85	309-10 <sup>10a</sup>
8	O <sub>2</sub> N CHO	3h	70	81	4.0	84	210–11
9	Me-CHO	<b>3</b> i	65	82	3.0	82	227-29 <sup>10a</sup>
10	EtCHO	3ј	75	78	4.5	79	112–13
11	МеСНО	3k	75	77	4.5	78	172-7313

 Table 1
 LiBr-Mediated Synthesis of 14-Alkyl or Aryl-14H-dibenzo[a,j]xanthenes<sup>19</sup>

<sup>a</sup> The products were characterized by comparison of their melting points and spectral (IR, <sup>1</sup>H NMR) data with those of authentic samples. <sup>b</sup> Method A: reaction carried out under thermal condition in solvent-free conditions. Method B: reactions carried out under microwave irradi-

ation in solvent-free conditions.

<sup>c</sup> Isolated yields after recrystallization.

Results of the investigation involving thermal (method A) as well as microwave (method B) irradiation are presented in Table 2.

In a typical example, benzaldehyde (2 mmol), 5,5-dimethyl-1,3-cyclo-hexanedione (2 mmol), malononitrile (2 mmol) and LiBr (0.3 mmol) were mixed and stirred for 5 minutes at room temperature. The reaction mixture was then maintained at 90 °C for 55 minutes (Method A). After completion of the reaction (TLC), the reaction mixture was cooled to room temperature and water (20 mL) was added. The solid thus obtained was filtered and recrystallized with ethanol to afford colorless crystals of 2-amino-3-cyano-4-phenyl-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (**6a**), 84% yield, mp 232–234 °C (lit.<sup>21</sup> mp 233–234 °C; entry 1, Table 2). Similarly, other tetrahydrobenzo[b]pyrans **6b–e** were obtained (Table 2) by the reaction of aldehydes, 5,5-dimethyl-1,3-cyclohexanedione and active methylene compounds. When the reaction was carried out under microwave irradiation (Method B), equivalent results were obtained and the tetrahydrobenzo[b]pyran derivatives were obtained in 81–86% yield (Table 2).

It is worth mentioning here that we did not observe the formation of 3,3,6,6-tetramethyl-9-aryl-1,8-dioxo-octa-hydroxanthenes **7** which would arise by the reaction of 5,5-dimethyl-1,3-cyclohexanedione with aldehyde. Evidently it appears that R<sup>1</sup>CH<sub>2</sub>CN being activated competes successfully in condensation with the aldehyde so the formation of 3,3,6,6-tetramethyl-9-aryl-1,8-dioxo-octa-hydroxanthenes **7** is suppressed.



Scheme 2

 Table 2
 LiBr-Mediated Synthesis of Tetrahydrobenzo[b]pyrans<sup>20</sup>

Entry	Aldehyde	$\mathbb{R}^1$	Product <sup>a</sup>	Method A <sup>b</sup>		Method B <sup>b</sup>		Mp (°C) <sup>21</sup>
				Time (min)	Yield (%) <sup>c</sup>	Time (min)	Yield (%) <sup>c</sup>	
1	СНО	CN	6a	55	84	8.0	84	232–234
2	СІ—СНО	CN	6b	50	86	7.5	86	216–218
3	MeO-CHO	CN	6c	60	82	8.5	81	199–200
4	СНО	CO <sub>2</sub> Et	6d	60	80	8.5	82	191–193
5	СІ—СНО	CO <sub>2</sub> Et	6e	60	82	8.5	85	257–258

<sup>a</sup> Melting points, IR, <sup>1</sup>H NMR were in accordance with those of authentic samples.

<sup>b</sup> Reaction condition: aldehyde **1** (2 mmol), 5,5-dimethyl-1,3-cyclohexanedione (**4**, 2 mmol), active methylene compound **5** (2 mmol) and LiBr (0.30 mmol) were heated to reflux (Method A) or irradiated in a microwave oven at 500 W (Method B) for the appropriate time as shown in Table 2.

<sup>c</sup> Isolated yields after recrystallization.

In conclusion, we have developed a quick, clean and simple method for the synthesis of 14H-dibenzo[a,j]xanthenes and tetrahydrobenzo[b]pyrans under solvent-free conditions using thermal as well as microwave heating. Further merits of this method are its generality, shorter reaction times and easy work-up. The catalyst used here is near neutral in nature unlike previously used Brønsted acids or strong dehydrating agents such as POCl<sub>3</sub>.

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- (19) General Procedure for the Synthesis of 14-Alkyl or Aryl Dibenzo[a,j]xanthenes Method A.
   A mixture of aldehyde (2 mmol), β-naphthol (4 mmol) and

A mixture of aldehyde (2 mmol), β-naphthol (4 mmol) and LiBr (0.3 mmol) were mixed and stirred for 5 min at r.t. and then temperature was raised to 130 °C and maintained for the appropriate time given in Table 1. After completion of reaction (TLC), the reaction mixture was cooled to r.t. and  $H_2O$  (20 mL) was added and the mixture stirred for 5 min. The solid thus obtained was filtered and the crude product obtained was purified by recrystallization from EtOH.

#### Method B.

A mixture of aldehyde (2 mmol,),  $\beta$ -naphthol (4 mmol) and LiBr (0.3 mmol) were irradiated in a domestic microwave oven at 500 W for the appropriate time according to Table 1. After completion of reaction (TLC), the reaction mixture was cooled to r.t. and H<sub>2</sub>O (20 mL) was added and the mixture stirred for 5 min. The solid thus obtained was filtered and the crude product obtained was purified by recrystallization from EtOH.

### (20) General Procedure for the Synthesis of Tetrahydrobenzo[b]pyran – Method A.

A mixture of aldehyde (2 mmol,), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), active methylene compound (2 mmol) and LiBr (0.6 mmol) was mixed and stirred for 5 min at r.t. and then heated at 90 °C for the appropriate time given in Table 2. After completion of reaction (TLC), the reaction mixture was cooled to r.t.,  $H_2O$  (20 mL) was added and the mixture stirred for 5 min. The solid thus obtained was filtered and the crude product obtained was purified by recrystallization from EtOH.

Method B.

A mixture of aldehyde (2 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), active methylene compound (2 mmol) and LiBr (0.6 mmol) was irradiated in a domestic microwave oven at 500 W for the appropriate time according to Table 2. After completion of reaction (TLC), the reaction mixture was cooled to r.t.,  $H_2O$  (20 mL) was added and the mixture stirred for 5 min. The solid thus obtained was filtered and the crude product obtained was purified by recrystallization from EtOH.

(21) (a) Wang, X. S.; Shi, D. Q.; Tu, S. J.; Yao, C. S. Synth. Commun. 2003, 33, 119..(b) Selected Characterization Data. 14-Phenyl-14H-dibenzo[a,j]xanthene (3a, Table 1, Entry 1).

 $\begin{array}{l} Mp \ 184-85 \ ^{\circ}C. \ IR \ (KBr): \ 3030, \ 1612, \ 1242 \ cm^{-1}. \ ^{1}H \ NMR \\ (200 \ MHz, \ CDCl_3): \ \delta = 6.75 \ (s, 1 \ H), \ 7.10-8.10 \ (m, \ 17 \ H). \\ Anal. \ Calcd \ for \ C_{27}H_{18}O: \ C, \ 90.47; \ H, \ 5.06. \ Found: \ C, \ 90.55; \\ H, \ 5.15. \end{array}$ 

## 14-(4-Methoxyphenyl)14-*H*-dibenzo[*a*,*j*]xanthene (3c, Table 1, Entry 3).

Mp 203–04 °C. IR (KBr): 3035, 1621, 1581, 1252. cm<sup>-1. 1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.50 (s, 3 H), 6.45 (s, 1 H), 6.73 (d, *J* = 9.3 Hz, 2 H), 7.36–7.92 (m, 12 H), 8.36 (d, *J* = 9.3 Hz, 2 H). Anal. Calcd for C<sub>28</sub>H<sub>20</sub>O<sub>2</sub>: C, 86.57; H, 5.19. Found: C, 86.35; H, 5.29.

## 14-(3-Bromophenyl)-14-*H*-dibenzo[*a*,*j*]xanthene (3d, Table 1, Entry 4).

Mp 190–92 °C. IR (KBr): 3040, 1613, 1245. cm<sup>-1.</sup> <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 6.62$  (s, 1 H), 7.21–20 (m, 16 H). Anal. Calcd for C<sub>27</sub>H<sub>17</sub>BrO: C, 74.15; H, 3.92. Found: C, 74.21; H, 3.86. UV (CHCl<sub>3</sub>):  $\lambda_{max} = 245, 266, 335$  nm.

# 14-(4-Nitrophenyl)-14*H*-dibenzo[*a,j*]xanthene (3g, Table 1, Entry 7).

Mp 309–10 °C. IR (KBr): 3070, 1615, 1540, 1355, 1245. cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.20–7.90 (m, 12 H), 8.15 (d, *J* = 9.0 Hz, 2 H), 8.55 (d, *J* = 9.0 Hz, 2 H). 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, 80.29; H, 4.10; N, 3.55. UV (CHCl<sub>3</sub>):  $\lambda_{max}$  245, 259, 335 nm. **14-(4-Methylphenyl)-14***H***-dibenzo[***a***,***J***]xanthene (3i, Table 1, Entry 9).** 

Mp 227–29 °C. IR (KBr): 3038, 1618, 1240 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.30 (s, 3 H), 6.55 (s, 1 H), 7.15–7.95 (m, 16 H). Anal. Calcd for C<sub>28</sub>H<sub>20</sub>O: C, 90.29; H, 5.41. Found: C, 90.41; H, 5.49.

## 14-Ethyl-14*H*-dibenzo[*a*,*j*]xanthene (3j, Table 1, Entry 10).

Mp 112–13 °C. IR (KBr): 3045,2901, 1615, 1221 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 0.98$  (t, J = 6.1 Hz, 3 H) 1.64

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(d, J = 6.1 Hz, 3 H), 5.60 (q, J = 6.1 Hz, 1 H) 7.09–7.97 (m, 12 H). Anal. Calcd for C<sub>23</sub>H<sub>18</sub>O: C, 89.00; H, 5.85. Found: C, 89.12; H, 5.76.

**2-Amino-3-cyano-4-phenyl-7,7-dimethyl-5-oxo-4***H***-5,6,7,8-tetrahydrobenzo**[*b*]**pyran (6a, Table 2, Entry 1).** Mp 232–234 °C. IR (KBr): 3392, 3288, 2934, 2198, 1685, 1601 cm<sup>-1.</sup> <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 0.97$  (s, 3 H), 1.04 (s, 3 H), 2.18 (d, *J* = 14.5 Hz, 1 H), 2.23 (d, *J* = 14.5 Hz, 1 H), 2.50–2.60 (br s, 2 H), 4.30 (s, 1 H), 6.10 (s, 2 H), 7.20–7.40 (m, 5 H). Anal. Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.58; H, 6.08; N, 9.40. Ethyl-2-Amino-4-phenyl-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran Carboxlate (6d, Table 2, Entry 4).

Mp 191–193 °C. IR (KBr): 3420, 2960, 2925, 1749, 1598, 1358 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 1.0$  (s, 3 H), 1.06 (s, 3 H), 1.21 (t, J = 7.5 Hz), 2.14 (d, J = 14.0 Hz, 1 H), 2.25 (d, J = 14.0 Hz, 1 H), 2.49 (br s, 2 H), 4.19 (q, J = 7.5 Hz), 4.27 (s, 1 H), 5.84 (s, 2 H), 7.10–7.35 (m, 5 H). Anal. Calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>: C, 70.38; H, 6.74; N, 4.11. Found: C, 70.30; H, 6.83; N, 4.07.