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### **Graphical Abstract**







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# Rapid, efficient and solvent-free synthesis of (un)symmetrical xanthenes catalyzed by recyclable sulfated polyborate

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ABSTRACT

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Keywords: Sulfated polyborate Xanthenes Dimedone Aldehyde β-naphthol The present study describes a rapid, simple and straightforward approach to the synthesis of 1,8-dioxo-octahydroxanthenes, 14-phenyl-14*H*-dibenzo[*a*, *j*]xanthene and tetrahydrobenzoxanthene-11-ones under solvent-free conditions using sulfated polyborate as a highly efficient catalyst. The procedure offers several advantages including cleaner reaction profile, mild reaction condition, economic, recyclable and environmentally benign catalyst, high yields, simple experimental and workup procedures. While non-extractive work up/purification, along with reusability of catalyst make this method economically affordable for large scale.

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Xanthene and its derivatives are the important class of organic compounds because of their pharmaceutical, biological and medicinal activities like anti-inflammatory,<sup>1</sup> antibacterial,<sup>2</sup> antiviral,<sup>3</sup> anti-depressants and anti-malarial agent,<sup>4</sup> These are antagonists of paralyzing action of Zoxazolamine<sup>5</sup> and in photodynamic therapy,<sup>6</sup> Furthermore, they have been used as valuable synthetic precursors for many organic compounds,<sup>7</sup> dyes,<sup>8</sup> pH sensitive fluorescent materials for the visualization of biomolecular assemblies,<sup>9</sup> and in laser technologies,<sup>10</sup> xanthenes like RO67-4853 (IC<sub>50</sub> BHK cell 114.4), Rhodamine and Amsacrine (IC<sub>50</sub> HCT-8 = 105 and L1210 = 32), are a very important class in pharmacological activity (Fig. 1).<sup>11,12</sup>

Several methods have been reported for the preparation of various xanthene derivatives. Among these methods, the condensation of aldehydes with  $\beta$ -naphthol, cyclic 1,3-dicarbonyl compounds and/or an equimolar mixture of  $\beta$ -naphthol and cyclic 1,3-dicarbonyl compounds are the simplest for the synthesis of symmetrical and unsymmetrical xanthenes. Various catalysts have been used for the preparation of these xanthenes e.g. SelectfluorTM, <sup>13</sup> KAl(SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O, <sup>14</sup> nano-TiO<sub>2</sub>.<sup>15</sup> PVSA, <sup>16</sup> MeSO<sub>3</sub>H, <sup>17</sup> Nano-ZnO, <sup>18</sup> silica sulfuric acid, <sup>19</sup> [Et<sub>3</sub>NSO<sub>3</sub>H]Cl <sup>20</sup> and SaSA<sup>21</sup> have been used for the preparation of 14-phenyl-14*H*dibenzo[*a,j*]xanthene; SbCl<sub>3</sub>/SiO<sub>2</sub>.<sup>22</sup> SiO<sub>2</sub>eReSO<sub>3</sub>H, <sup>23</sup> MCM-41-SO<sub>3</sub>H<sup>24</sup> dodecylbenzene sulfonic acid, <sup>25</sup> triethylbenzylammonium chloride, <sup>26</sup> diammonium







Fig. 1. Pharmacologically active xanthenes.

hydrogen phosphate,<sup>27</sup> nano-TiO<sub>2</sub>,<sup>28</sup> InCl<sub>3</sub>.4H<sub>2</sub>O,<sup>29</sup> FeCl<sub>3</sub>.8H<sub>2</sub>O,<sup>30</sup> NaHSO<sub>4</sub>,<sup>31</sup> silica (SiO<sub>2</sub>-Pr-SO<sub>3</sub>H),<sup>32</sup> and silica-supported preyssler nano particles<sup>33</sup> have been used for the preparation of 1,8-dioxooctahydroxanthenes and sulfamic acid,<sup>34</sup> SuSA,<sup>35</sup> dodecatungstophosphoric acid,<sup>36</sup> organocatalyst trityl chloride,<sup>37</sup> InCl<sub>3</sub>/P<sub>2</sub>O<sub>5</sub>,<sup>38</sup> (B(HSO<sub>4</sub>)<sub>3</sub>),<sup>39</sup> DSIMHS (ionic liquid)<sup>40</sup> and poly (AMPS-co-AA)<sup>41</sup> have been used for the preparation of tetrahydrobenzoxanthene-11-ones.

Each of these methods has their own advantages but also suffer from one or more disadvantages such as prolonged reaction time, low yields, use of hazardous, expensive and excess of catalysts, use of organic solvents for reaction and work up, harsh reaction conditions, tedious workup procedure, difficult recovery and reusability of the catalysts, many of them are not eco-friendly.

In addition, only a few are used for the synthesis of the above-mentioned three kinds of xanthenes. Therefore, it is worth to find more convenient methods for the synthesis of xanthenes and its derivatives.

Having the above points in mind, herein we report a rapid and efficient synthesis of 1,8-dioxooctahydroxanthenes, 14phenyl-14*H*-dibenzo[*a*,*j*]xanthene and tetrahydrobenzoxanthene-11-ones in the presence of sulfated polyborate under solvent-free conditions.

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12-substituted tetrahydrobenzoxanthene-11-ones

**Scheme 2.** Synthesis of various xanthene derivatives catalyzed by sulfated polyborate.

A literature search revealed that boric acid catalyzes many useful organic transformations above  $100^{\circ}$ C.<sup>42,43</sup> Boric acid dehydrates above  $100^{\circ}$ C and turns to its polymeric forms, which could be the active species catalyzing the reaction.<sup>44</sup> Dehydrative polymerization of boric acid liberates water molecules which may hamper the progress of the reaction.

This persuades us to develop a polymeric boric acid catalyst with mild Bronsted acidity. To accomplish this boric acid was dehydrated at 200 °C to convert it into its polymeric Lewis acid form and then sulfonated to introduce the mild Bronsted acid character.<sup>45</sup> Boron being an electron deficient element and electron withdrawing effect of adjacent sulfate enhances its Lewis acidity; hence sulfated polyborate has both Lewis as well as Bronsted acid characters (Scheme 1).

In perpetuate green, practical and convenient catalytic methods for the current interest in commercial process and organic synthesis. The sulfated polyborate was prepared from readily available boric acid, as economic and non-toxic starting material, characterized and effectively applied for various organic transformations.<sup>45-53</sup> Herein its applicability in the promotion of the synthesis of different types of xanthenes derivatives. All reactions are performed under mild conditions during relatively short reaction time in good to high yields (Scheme 2).

For initial screening, the study was designed for the synthesis of 1,8-dioxo-octahydroxanthenes from benzaldehyde (1 mmol); a representative substrate and dimedone (2 mmol) reaction to investigate the suitability of sulfated polyborate as a catalyst at different reaction conditions. The results are summarized in (Table 1).

#### Table 1

Effect of catalyst loading and temperature for the synthesis of 9-phenyl-1,8-dioxo-octahydroxanthenes.<sup>a</sup>

| Entry | Catalyst<br>(wt %) | Temperature<br>(°C) | Time<br>(min) | Yield <sup>b</sup><br>(%) |
|-------|--------------------|---------------------|---------------|---------------------------|
| 1     | -                  | 100                 | 180           | NR <sup>c</sup>           |
| 2     | 2.5                | 100                 | 60            | 30                        |
| 3     | 5                  | 100                 | 40            | 50                        |
| 4     | 7.5                | 100                 | 30            | 70                        |
| 5     | 10                 | 100                 | 3             | 99                        |
| 6     | 10                 | r.t.                | 180           | NR <sup>c</sup>           |
| 7     | 10                 | 50                  | 60            | 45                        |
| 8     | 10                 | 70                  | 30            | 70                        |

 $^{\rm a}$  Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol).  $^{\rm b}$  Isolated yield.  $^{\rm c}$  No Reaction

#### Table 2

The effect of the solvents on the synthesis of 9-phenyl-1,8-dioxo-octahydroxanthenes.<sup>a</sup>

| Entry | Solvent      | Temperature<br>(°C) | Time<br>(min) | Yield <sup>b</sup><br>(%) |
|-------|--------------|---------------------|---------------|---------------------------|
| 1     | Solvent free | 100                 | 05            | 98                        |
| 2     | EtOH         | reflux              | 60            | 70                        |
| 3     | MeCN         | reflux              | 60            | 20                        |
| 4     | THF          | reflux              | 60            | 30                        |
| 5     | Water        | reflux              | 60            | NR <sup>c</sup>           |
| 6     | Toluene      | reflux              | 60            | 60                        |
| 7     | DMF          | 100                 | 60            | 65                        |

 $^a$  Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol). Sulfated polyborate (10 w%) b Isolated yield.  $^c$  No Reaction

Effect of the catalyst loading on time and yield of the reaction was assessed (Table, 1, entries 1-5). The reaction does not proceed in the absence of a catalyst (Table 1, entry 1) while proceeding with the presence (Table 1, entry 2). An increase of the catalyst loading increased the product yield with a reduction in reaction time (Table 1, entries 3-5). The catalyst loading beyond 10 wt % was not advantageous, hence a 10 wt % catalyst loading was chosen for further study.

Temperature played an important role in the synthesis of xanthenes (Table 1, entry 6 - 8). The temperature effect was examined at ambient, 50, 70 and 100 °C under the solvent free condition with sulfated polyborate as a catalyst. The reaction does not proceed at room temperature. While increasing temperature to 100 °C resulted in increased product yield in shorter reaction time (Table 1, entries 5, 7 and 8). Therefore, this was the optimum temperature for performing the reaction.

The effect of various solvents on time and yield of the reaction was ascertained (Table 2, entries 2-7). In ethanol, reaction proceeds smoothly with longer reaction time (Table 2, entries 2). The reaction in MeCN, THF, water, toluene, and DMF

#### Table 3

Sulfated polyborate catalyzed synthesis of 1,8-dioxooctahydroxanthenes.<sup>a</sup>



| Entry | Aldehyde                            | Time  | Yield <sup>b</sup> | M.P. °C |                       |
|-------|-------------------------------------|-------|--------------------|---------|-----------------------|
|       | (R)                                 | (min) | (%)                | Obs.    | L.it                  |
| 1     | C <sub>6</sub> H <sub>5</sub>       | 3     | 99                 | 203-205 | 205-20654             |
| 2     | $2-O_2N-C_6H_4$                     | 4     | 97                 | 244-246 | 246-248 <sup>56</sup> |
| 3     | $2-HO-C_6H_4$                       | 5     | 95                 | 204-205 | 202-205 <sup>55</sup> |
| 4     | 3-Br-C <sub>6</sub> H <sub>4</sub>  | 5     | 97                 | 284-286 | 281-282 <sup>54</sup> |
| 5     | 3-Cl-C <sub>6</sub> H <sub>4</sub>  | 5     | 98                 | 185-187 | 186-187 <sup>54</sup> |
| 6     | $3-O_2N-C_6H_4$                     | 5     | 95                 | 169-171 | 167-168 <sup>54</sup> |
| 7     | $4-CH_3O-C_6H_4$                    | 4     | 97                 | 251-253 | 250-251 <sup>54</sup> |
| 8     | $4-HO-C_6H_4$                       | 4     | 95                 | 245-247 | 246-248 <sup>55</sup> |
| 9     | 4-Br-C <sub>6</sub> H <sub>4</sub>  | 5     | 97                 | 260-263 | 263-265 <sup>56</sup> |
| 10    | $4-Cl-C_6H_4$                       | 4     | 98                 | 235-236 | 236-237 <sup>54</sup> |
| 11    | $4-CH_3-C_6H_4$                     | 4     | 97                 | 232-234 | 230-232 <sup>55</sup> |
| 12    | $4-O_2N-C_6H_4$                     | 4     | 96                 | 228-230 | 229-230 <sup>54</sup> |
| 13    | 2-Thienyl                           | 6     | 96                 | 198-200 | 201-20458             |
| 14    | 5-methylfuran-2-yl                  | 6     | 96                 | 192-194 | NA <sup>c</sup>       |
| 15    | Indol-3-yl                          | 7     | 97                 | 255-257 | 256-257 <sup>53</sup> |
| 16    | $C_3H_7$                            | 5     | 95                 | 130-132 | 135-137 <sup>64</sup> |
| 17    | C <sub>6</sub> H <sub>5</sub> CH=CH | 7     | 95                 | 172-174 | $177 - 178^{54}$      |
| 18    | $c-C_{6}H_{11}$                     | 5     | 97                 | 178-180 | NA <sup>c</sup>       |

<sup>a</sup>Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol), sulfated polyborate (10 w%) at 100 °C solvent-free. <sup>b</sup> Isolated yield, <sup>c</sup>not available in the literature

#### Table 4

Sulfated polyborate catalyzed synthesis of 14-substituted-14*H*-dibenzo[a,j]xanthene.<sup>a</sup>

| $\sim$ |  |       |                    |         |                       |
|--------|--|-------|--------------------|---------|-----------------------|
| 2      |  |       |                    |         |                       |
| Entry  | Aldehyde   | Time  | Yield <sup>b</sup> | M.P. °C |                       |
|        | (R)  | (min) | (%)                | Obs.    | L.it                  |
| 1      | C <sub>6</sub> H <sub>5</sub>                    | 3     | 99                 | 184-186 | 186-188 <sup>54</sup> |
| 2      | $2-Cl-C_6H_4$                                    | 5     | 97                 | 210-212 | 209-211 <sup>54</sup> |
| 3      | $2-O_2N-C_6H_4$                                  | 8     | 94                 | 216-218 | 214-215 <sup>57</sup> |
| 4      | $3-O_2N-C_6H_4$                                  | 8     | 95                 | 220-222 | 215-217 <sup>54</sup> |
| 5      | 3-Cl-C <sub>6</sub> H <sub>4</sub>               | 6     | 97                 | 205-207 | 207-209 <sup>54</sup> |
| 6      | 3-Br-C <sub>6</sub> H <sub>4</sub>               | 6     | 97                 | 185-187 | 186-188 <sup>57</sup> |
| 7      | $4-CH_3O-C_6H_4$                                 | 7     | 95                 | 204-206 | 200-202 <sup>54</sup> |
| 8      | $4-O_2N-C_6H_4$                                  | 5     | 94                 | 316-318 | 312-314 <sup>54</sup> |
| 9      | 4-Br-C <sub>6</sub> H <sub>4</sub>               | 5     | 95                 | 295-297 | 296-298 <sup>54</sup> |
| 10     | 4-Cl-C <sub>6</sub> H <sub>4</sub>               | 8     | 95                 | 282-285 | 284-286 <sup>54</sup> |
| 11     | 4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> | 5     | 95                 | 220-223 | 225-227 <sup>57</sup> |
| 12     | C <sub>6</sub> H <sub>6</sub> CH <sub>2</sub>    | 6     | 94                 | 172-174 | 171-174 <sup>59</sup> |
| 13     | C <sub>3</sub> H <sub>7</sub>                    | 6     | 95                 | 172-175 | 171-175 <sup>59</sup> |
| 14     | <i>c</i> -C <sub>6</sub> H <sub>11</sub>         | 5     | 96                 | 170-172 | 173-174 <sup>61</sup> |

 $^a$  Reaction conditions: benzaldehyde (1 mmol),  $\beta$ -naphthol (2 mmol), sulfated polyborate (10 w%) at 100 °C solvent-free.  $^b$  Isolated yield.

resulted in poor yields with longer reaction time (Table 2, entries 3-7). None of the solvents presented the advantage of time and yield over solvent free condition. Hence, the solvent free condition was regarded as best for the cost and environmental acceptability. In all the experiments, the products were isolated by aqueous quenching followed by filtration and washing with water.

To study the substrate scope, optimized reaction conditions were applied to various aldehydes with dimedone and/or  $\beta$ -naphthol. All the substrate variants reacted well and afforded high yields of the corresponding xanthene derivatives within shorter reaction time (Table 3, 4 and 5). Several electron-releasing or electron-withdrawing substituents at *ortho, meta* and *para* positions of aromatic aldehydes showed no significant

#### Table 5

Sulfated polyborate catalyzed synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones.<sup>a</sup>



| Entry | Aldehyde   | Time  | Yield <sup>b</sup> | M.P. °C |                       |
|-------|--|-------|--------------------|---------|-----------------------|
|       | (R)  | (min) | (%)                | Obs.    | L.it                  |
| 1     | C <sub>6</sub> H <sub>5</sub>                    | 6     | 97                 | 145-147 | 148-151 <sup>54</sup> |
| 2     | $2-HO-C_6H_4$                                    | 7     | 91                 | 220-224 | 223-225 <sup>62</sup> |
| 3     | $2-O_2N-C_6H_4$                                  | 9     | 90                 | 176-178 | $178 - 180^{54}$      |
| 4     | 3-O2N-C6H4                                       | 8     | 92                 | 165-167 | 167-170 <sup>54</sup> |
| 5     | 3-Br-C <sub>6</sub> H <sub>4</sub>               | 7     | 94                 | 158-160 | 161-164 <sup>54</sup> |
| 6     | 3-Cl-C <sub>6</sub> H <sub>4</sub>               | 9     | 90                 | 173-175 | 175-178 <sup>54</sup> |
| 7     | $4-CH_3O-C_6H_4$                                 | 8     | 95                 | 210-212 | 208-20954             |
| 8     | $4-HO-C_6H_4$                                    | 9     | 90                 | 225-227 | 223-225 <sup>56</sup> |
| 9     | 4-Br-C <sub>6</sub> H <sub>4</sub>               | 10    | 91                 | 186-188 | 185-187 <sup>54</sup> |
| 10    | 4-Cl-C <sub>6</sub> H <sub>4</sub>               | 9     | 92                 | 175-178 | 178-179 <sup>54</sup> |
| 11    | 4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> | 10    | 90                 | 174-178 | 176-188 <sup>54</sup> |
| 12    | $4-O_2N-C_6H_4$                                  | 7     | 91                 | 179-180 | 175-178 <sup>54</sup> |
|       |  |       |                    |         |                       |

<sup>a</sup> Reaction conditions: benzaldehyde (1 mmol), β-naphthol (1 mmol) & dimedone (1 mmol), sulfated polyborate (10 w%) at 100 °C solvent-free <sup>b</sup> Isolated yield





effect on product yield and time. This protocol is also extendable to aliphatic/alicyclic/aromatic/heteroaromatic aldehydes (Table 3).

On the other side, this protocol is also applicable to dimedone (Table 3) or  $\beta$ -naphthol (Table 4) variants to afford symmetrical xanthene with similar product time and yield. It could be concluded that the aldehydes substituted with electron-withdrawing groups and electron-donating groups reacted very well and produced the corresponding xanthenes in good to excellent yields in shorter times. This protocol is also extendable to aliphatic/alicyclic aldehydes (Table 4).

The synthesis of unsymmetrical xanthenes *via* reaction of various aldehydes with dimedone and  $\beta$ -naphthol. In all cases, aldehydes bearing electron-donating group, electron-withdrawing groups and aldehydes containing halogens showed high product yield and short reaction time (Table 5).

Recyclability of the catalyst is an important attribute for the industrial suitability. Therefore, reusability of the catalyst in the model reaction under optimized reaction condition was evaluated. In this study, after completion of each reaction cycle, water was added and the product was filtered off. The filtrate was evaporated in vacuum rotary evaporator to recover catalyst. Recovered catalyst was recycled for four times with no significant loss in catalytic activity (Fig. 2).

The plausible mechanism, at first, the aldehyde could have been activated by the H<sup>+</sup> from sulfated polyborate, followed by the carbonyl carbon is attacked by the nucleophilic  $\beta$ -naphthol (a) or cyclohexanedione derivatives (b) to form the Knoevenagel products. The subsequent addition of these fragments to another mole of (a) and/or (b), gives the acyclic adducts intermediate, which undergoes intramolecular dehydrative cyclization with the participation of two hydroxyl groups to afford the xanthene derivatives.

#### Conclusion

In conclusion, in this study, we have successfully applied sulfated polyborate as a highly efficient catalyst for the preparation of symmetrical and unsymmetrical xanthenes derivatives. Ease of preparation and handling of the catalyst, high reaction rates, simple procedure, high yields of the products with no side reactions and solvent-free conditions are the key advantages of this method.

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Scheme 3. A plausible mechanism for sulfated polyborate catalyzed synthesis of xanthene derivatives.

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- 65. General procedure for the synthesis of symmetrical xanthenes: A mixture of aldehyde (1 mmol), dimedone/ β-naphthol (2 mmol) and sulfated polyborate (10 wt %) was heated at 100 °C in an oil bath. The reaction was monitored by thin layer chromatography. After completion of the reaction, the mixture was cooled to room temperature and quenched in water; solid precipitated was filtered at vacuum pump, washed with water (3 X 5 mL), dried under vacuum and recrystallized from ethanol to afford the pure product.
- 66. General procedure for the synthesis of unsymmetrical xanthenes: A mixture of aldehyde (1 mmol), β-naphthol (1 mmol), dimedone (1 mmol) and sulfated polyborate (10 wt %) was heated at 100 °C in an oil bath. The reaction was monitored by thin layer chromatography. After completion of the reaction, the mixture was cooled to room temperature and quenched in water; solid precipitated was filtered at vacuum pump, washed with water (3 X 5 mL), dried under vacuum and recrystallized from ethanol to afford the pure product.