An efficient and convenient approach to the synthesis of 3,3,6,6-tetramethyl-9-aryl-1,8-dioxo-octahydroxanthene derivatives using inexpensive boric acid as the catalyst (10 mol%) is described. The use of water as reaction medium is the most important feature of this reaction.
RESULTS AND DISCUSSION

In view of the surprising lack of literature report on the truly economical and environmentally benign methods for the synthesis of 9-aryl-1, 8-dioxo-octahydroxanthene derivatives, we thought it was worthwhile to develop the practical, general, mild and environmentally benign protocol for the synthesis of 9-aryl-1, 8-dioxo-octahydroxanthene derivatives. In order to meet the objective of such a protocol, the use of catalyst which would be environmentally benign, stable to air and moisture, and inexpensive was at the forefront of our scheme of things. Thus in view of our objective of the development of environmentally benign protocol for the synthesis of titled compounds, we though the boric acid would be prime and suitable choice to be employed as catalyst for the same. To further illustrate the utility of water as solvent and role of PTCs in organic synthesis, we chose to study the cyclocondensation reaction of aldehyde and 5,5-dimethyl-1,3-cyclohexanediene in water. In view of making the process inexpensive we preferred boric acid as an inexpensive and efficient catalyst and TBAB as a phase transfer catalyst.

As a starting point for the development of boric acid catalyzed synthesis of 9-aryl-1, 8-dioxooctahydroxanthene in water, cyclocondensation reaction involving benzaldehyde (3 mmol) and 5,5-dimethyl-cyclohexa-1,3-dione (3 mmol) in the presence of 10 mol% of boric acid and TBAB (1 mmol) in water under reflux was performed. We were pleased to find that the corresponding cyclocondensation reaction product was obtained in 84% isolated yield within 10 h. To check out whether there is a need for catalyst to perform the present reaction in a practical way; we repeated the above experiment under same reaction conditions as above but without using boric acid. We found that this time the corresponding cyclocondensation product was obtained only in 30 % yield despite the reaction being continued for 15h. Thus, this finding confirmed the pivotal role of the boric acid as a catalyst in the present reaction. With good results being obtained in the reaction of benzaldehyde, next, a variety of aromatic aldehydes were examined under our optimized reaction conditions (TABLE 1).

The results are summarized in TABLE 1. Thus it is seen that aromatic aldehydes possessing both electron withdrawing and electron releasing substituents underwent the cyclocondensation reaction smoothly to afford the corresponding products in high yield. It was found that the nature of the substituents on aldehydes did not have detrimental effect on the product yields. Moreover, the reaction can also be applied to $\alpha$-$\beta$-unsaturated aldehydes, (TABLE 1, entry 10), such as cinnamaldehyde giving the corresponding product in high yield. In all the examples, studied generally >70% yield of the corresponding 9-aryl-1, 8-dioxooctahydroxanthene were obtained within 10 h. A broad range of functional groups such as halides, cyano, alkoxy, nitro (entries, 7-9) were tolerated under the present reaction conditions which clearly evident the functional groups compatibility of the present method. The work-up is very easy and the products can be obtained in high purity by mere washing the reaction mixture with water to remove the boric acid catalyst followed by recrystallization with ethanol. Thus this novel approach not only preserves the simplicity but consistently produced the

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Reaction time (h)</th>
<th>Product Yield (%c)</th>
<th>M. p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_6$H$_5$</td>
<td>10</td>
<td>3a</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>4-CH$_3$C$_6$H$_4$</td>
<td>12</td>
<td>3b</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>4-CH$_3$OCC$_6$H$_4$</td>
<td>11</td>
<td>3c</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>4-HOC$_6$H$_4$</td>
<td>13</td>
<td>3d</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>4-HO-3-CH$_3$OCC$_6$H$_3$</td>
<td>12</td>
<td>3e</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>4-CIC$_6$H$_4$</td>
<td>11</td>
<td>3f</td>
<td>77</td>
</tr>
<tr>
<td>7</td>
<td>4-NO$_2$C$_6$H$_4$</td>
<td>10</td>
<td>3g</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>3-NO$_2$C$_6$H$_4$</td>
<td>12</td>
<td>3h</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>2-NO$_2$C$_6$H$_4$</td>
<td>14</td>
<td>3i</td>
<td>73</td>
</tr>
<tr>
<td>10</td>
<td>C$_6$H$_5$CH=CH</td>
<td>15</td>
<td>3j</td>
<td>74</td>
</tr>
</tbody>
</table>

*Isolated yield
structurally diverse 9-aryl-1, 8-dioxo-octahydroxanthenes in high yields in an environmentally benign and resource effective process.

Mechanistically, the reaction will proceed through Knoevenagel condensation \((1+2 \rightarrow 6)\) followed by Michael addition \((1+6 \rightarrow 8)\) to form 1,5-dicarbonyl compound \((8)\) which finally undergoes cyclodehydration to form 9-aryl-1,8-dioxo-octahydroxanthene \((3)\). The role of boric acid is to enhance enolic (nucleophilic) character of dimedone required essentially for the Knoevenagel condensation and Michael addition.

**EXPERIMENTAL**

Melting points are uncorrected. IR spectra were recorded on a Shimadzu FTIR-1710 spectrophotometer. \(^1\)HNMR spectra were recorded at 400 MHz in CDCl\(_3\) using TMS as internal standard. The representative spectral analysis for few of the products is given below:

**General experimental procedure**

The aromatic aldehyde (3 mmol), 5,5-dimethyl-1,3-cyclohexanedione (6 mmol), boric acid (10 mol%) and TBAB (1 mmol) were mixed in 20 mL of water. The resulting reaction mixture was refluxed in a 100 mL round bottom flask for the time as indicated in TABLE 1. The reaction progress was monitored by TLC. The reaction mixture was cooled to room temperature and the solid product was filtered off and dried. The crude product was purified by recrystallization method using ethanol to afford 9-aryl-1,8-dioxo-octahydroxanthene in good to excellent yield.

(i) 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-P-tolyl 2H-xanthene-1,8(5H,9H)-dione (3b)

Crystalline yellow solid, M. p. 218-219\(^\circ\)C (Lit.\(^9\) melting point: 217-218\(^\circ\)C). IR (KBr, cm\(^{-1}\)): 3016, 2958, 2924, 1680, 1664, 1510, 1195, 1165, 1020, 999, 931, 840, 765, 715.

\(^1\)HNMR (CDCl\(_3\)): \(\delta = 1.01\) (s, 6H, 2CH\(_3\)), 1.11 (s, 6H, 2CH\(_3\)), 2.20 (s, 4H, 2CH\(_2\)), 4.72 (s, 1H, ArCH), 7.03 (d, J = 10.4 Hz, 2H, ArH), 7.19 (d, J = 10.8 Hz, 2H, ArH).

(ii) 9-(4-chlorophenyl)3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2H-xanthene-1,8(5H,9H)-dione (3f)

Crystalline yellow solid, M. p. 228-229\(^\circ\)C (Lit.\(^9\) melting point: 228-230\(^\circ\)C). IR (KBr, cm\(^{-1}\)): 3016, 2958, 2875, 1680, 1660, 1489, 1361, 1197, 1087, 852, 717.

\(^1\)HNMR (CDCl\(_3\)): \(\delta = 1.00\) (s, 6H, 2CH\(_3\)), 1.12 (s, 6H, 2CH\(_3\)), 2.20 (s, 4H, 2CH\(_2\)), 4.73 (s, 1H, ArCH), 7.20 (d, J = 8.4 Hz, 2H, ArH), 7.25 (d, J = 8.4 Hz, 2H, ArH).

(iii) 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-styryl-2H-xanthene-1,8(5H,9H)-dione (3j)

Crystalline yellow solid, M. p. 175-176\(^\circ\)C (Lit.\(^9\) melting point: 175-177\(^\circ\)C) \(^1\)HNMR (CDCl\(_3\)): \(\delta = 1.11\) (s, 12H, 4CH\(_3\)), 2.29 (s, 4H, 2CH\(_2\)), 2.43 (s, 4H,
The synthesis of 9-aryl-1,8-dioxo-octahydroxanthene is characterized by the following merits: (a) non-toxic, inexpensive and readily available nature of boric acid (b) use of aqueous medium is the most striking feature (c) easy work-up (d) preparative simplicity (e) high yields. In conclusion, we have demonstrated an environmentally benign three component condensation of aromatic aldehyde and two equivalents of dimedone to form 9-aryl-1,8-dioxo-octahydroxanthene using boric acid in aqueous medium.

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