Synthesis of 1,8-Dioxo-
Catalyzed by 1,1'-[BMIM][BF_4]
Ionic Liquid

Chapter 4
4.1. INTRODUCTION
The classical method for the synthesis of 1,8-dioxo-octahydroxanthenes involves the condensation of two molecules of dimedone (5,5-dimethyl-1,3-cyclohexanedione) with aromatic aldehydes [1-3]. The process involves the acid/base catalysed condensation reaction in alcohol to yield a 1,8-dioxooctahydroxanthenes as a final product [4].

![Chemical structure](image)

Xanthene derivatives have attracted considerable research interest in recent years due to their promising activity as positive allosteric modulators of metabotropic (mGlu) receptors [5] and potent nonpeptidic inhibitors of recombinant human calpain I [6]. They have been used as rigid carbon skeletons for the construction of new chiral bidentate phosphine ligands with potential applications in catalytic processes [7]. In particular, xanthenediones constitute a structural unit in a number of natural products [8] and have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring [9].

4.2. RECENT LITERATURE REVIEW
The mechanism of cyclocondensation reaction for the synthesis of 1,8-dioxooctahydroxanthene has been investigated by several groups [4, 10]. The accepted mechanistic pathway outlined in Scheme 4.2 involves the one-pot Knoevenagel condensation and Michael addition followed by cyclodehydration.
The knoevenagel condensation takes place between enol form of dimedone 2 and aldehyde 1 precursors to give α,β-unsatureted carbonyl compound 4. The compound 4 reacts as a Michael acceptor with 2 to form compound 5. The product 5 upon cyclodehydration gives the final product 3.

Numerous methods have been reported in the literature for the synthesis of 1,8-dioxo-octahydroxanthene derivatives. Many of these methods employed Bronsted acid/base, inorganic salts and ionic liquids as a catalyst along with conventional and non-conventional energy sources. However, some of these methods are plagued by the limitation of prolonged reaction times, poor yields, toxic solvents/catalyst and vigorous reaction conditions.


Jin, T.-S. et al. [12] reported p-dodecysulphonic acid catalyzed synthesis of xanthenediones in aqueous media. The aqueous method provides advantages over other methods having organic solvent in place of water.

phosphate as a neutral and efficient catalyst for the synthesis of xanthene derivatives in aqueous media. Bigdeli, M. A. et al. [15] carried out synthesis of xanthenes using trichloroisocyanuric acid as a catalyst. The protocol describes a catalytic reaction which uses organic molecules as a catalyst. Zhang, Z.-H. et al. [16] reported antimony trichloride/SiO₂ promoted synthesis of xanthenes. The new application of SbCl₃ dispersed on dry silica gel has been developed.


Dabiri, M. et al. [19] reported 1-methylimidazolium trifluoroacetate as an efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthene. The procedure gave high yield of xanthenes by using [Hmim][Tfa] acidic IL. Bazgir, A. et al. [20] reported dowex-50W promoted synthesis of 1,8-dioxo-octahydroxanthene derivatives under solvent free conditions. Das, B. et al. [21] used amberlyst-15 as an efficient reusable heterogeneous catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes. The procedure gave products with high yield.

Palaniappan, S. et al. [22] carried out polyaniline-p-toluenesulfonate salt catalyzed clean synthesis of 1,8-dioxo-octahydroxanthene in aqueous media. The catalyst showed versatility and reusability in the synthesis.

Fan, X. et al. [23] reported InCl₃·4H₂O promoted green preparation of xanthenedione derivative in [bmim][BF₄] ionic liquid.

4.3. OBJECTIVES

The objectives of the present work are as under
1) To carry out ionic liquid mediated synthesis of 1,8-dioxo-octahydroxanthene with mild and efficient procedure.
2) To carry out a study on effect of ionic liquid on reaction under different energy sources.
3) To carry out a spectroscopic characterization of synthesized xanthenes.
The work carried out to meet the said objective is described in the following sections. The synthesis of 1,8-dioxo-octahydroxanthene using conventional energy source, microwave irradiation, ultrasonication and solar energy are respectively covered in section 4a, 4b, 4c and 4d. The spectroscopic characterization is dealt with in section 4e with the spectral data of all the synthesized 1,8-dioxo-octahydroxanthene, some selected spectra are also put on view in the same section.
Synthesis of 1,8-dioxo-octahydroxanthene by Conventional energy source
4.4a.1. RESULTS AND DISCUSSION

4.4a.1.1. Scheme

The synthesis of 1,8-dioxo-octahydroxanthene 3 (Scheme 4.4a.1) was carried out by one-pot reaction of various aromatic/heterocyclic aldehydes 1 and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) 2 in presence of carboxy functionalized ionic liquid [cmmim][BF₄] under conventional thermal heating in absence of any added catalyst. The most optimum reaction condition and the role of ionic liquid to accelerate the reaction are discussed in this section.

![Scheme 4.4a.1](image)

4.4a.1.2. Reaction optimization

Table 4.4a.1 Optimization data of reaction condition for the synthesis of 1,8-dioxo-octahydroxanthene as a function of reaction temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ionic liquidb</th>
<th>Temperature (°C)</th>
<th>Yield (%)d</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[cmmim][BF₄]</td>
<td>30</td>
<td>Intermediate</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>[cmmim][BF₄]</td>
<td>50</td>
<td>67</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>[cmmim][BF₄]</td>
<td>70</td>
<td>78</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>[cmmim][BF₄]</td>
<td>80</td>
<td>87</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>[cmmim][BF₄]</td>
<td>90</td>
<td>88</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>[cmmim][BF₄]</td>
<td>100</td>
<td>87</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>_c</td>
<td>80</td>
<td>0</td>
<td>6</td>
</tr>
</tbody>
</table>

aIn all the reactions condition were optimized for 100 % conversion

bReactions were carried out by using 200 mg IL

cReaction was run without IL, dIsolated yield
In initial experiments, the typical one-pot condensation of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) and benzaldehyde (mole ratio 2:1) was performed in the presence of \([\text{cmim}]\text{[BF}_4]\) without added co-solvent. In initial reaction, at 30 °C some milky white solid was observed within short period of time and TLC of reaction mixture also indicate the formation of a new compound with the presence of unreacted dimedone. At this stage the reaction was quenched by addition of water to the reaction mixture. Unfortunately, the melting point of the obtained compound does not match with expected product. At first sight, the \(^1\text{H}\) NMR spectrum of obtained product looked similar with the expected xanthene but in actual it showed one more singlet in the down field region compared to xanthenes (Figure 4.4a.1). The obtained \(^1\text{H}\) NMR spectrum indicated the formation of uncyclised intermediate (Scheme 4.4a.2). Reaction was run for 6 h, but the intermediate did not get cyclised to give 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione (Entry 1, Table 4.4a.1).

![Figure 4.4a.1 \(^1\text{H}\) NMR spectrum of uncyclised intermediate](image)

2-{[(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)(Aryl)methyl]-5,5-dimethylcyclohexane-1,3-dione (uncyclised intermediate)

Singlet of \(-\text{OH}\) indicate formation of uncyclised intermediate

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When the reaction was carried out at 50 °C (Entry 2), after 0.5 h TLC showed the formation of new compound other than intermediate. As the time goes the amount of targeted xanthene increased gradually. After, 6 h of reaction the yield of targeted 1,8-dioxo-octahydroxanthene were found to be 67 %. TLC of reaction mixture still indicated the presence of intermediate. To obtain xanthenes alone with more increased yield, rather than the mixture, the reaction mixture was stirred at different elevated reaction temperatures as shown in Entry 3, 4, 5 and 6. All these four conditions gave xanthenes with higher yield. It was observed that beyond 80 °C there was no effect of temperature on yield of the product. When the reaction was carried out in absence of ionic liquid (Entry 7) at 80 °C, the starting materials remained unchanged even after 6 h. It showed the importance of ionic liquid in acceleration of reaction.

4.4a.1.3. Characteristic data showing the synthesis of 1,8-dioxo-octahydroxanthene

Based on above optimization, a number of 1,8-dioxo-octahydroxanthene were successfully synthesized using 200 mg of IL at 80 °C from condensation of a variety of aldehydes with dimedone. The various aldehydes employed and the characteristic data for them are shown in Table 4.4a.2.
### Table 4.4a.2 Characteristic data for all synthesized 1,8-dioxo-octahydroxanthene

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Reaction Time(^a) (h)</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Ph—</td>
<td>2.5</td>
<td>87</td>
</tr>
<tr>
<td>3b</td>
<td>4-(\text{O}_2\text{N}-\text{C}_6\text{H}_4)-</td>
<td>2.0</td>
<td>83</td>
</tr>
<tr>
<td>3c</td>
<td>2-(\text{Cl}-\text{C}_6\text{H}_4)-</td>
<td>3.0</td>
<td>84</td>
</tr>
<tr>
<td>3d</td>
<td>3-(\text{Cl}-\text{C}_6\text{H}_4)-</td>
<td>2.5</td>
<td>78</td>
</tr>
<tr>
<td>3e</td>
<td>4-(\text{Cl}-\text{C}_6\text{H}_4)-</td>
<td>2.5</td>
<td>82</td>
</tr>
<tr>
<td>3f</td>
<td>2-(\text{O}_2\text{N}-\text{C}_6\text{H}_4)-</td>
<td>2.5</td>
<td>76</td>
</tr>
<tr>
<td>3g</td>
<td>3-(\text{O}_2\text{N}-\text{C}_6\text{H}_4)-</td>
<td>3.0</td>
<td>83</td>
</tr>
<tr>
<td>3h</td>
<td>4-(\text{H}_3\text{C}-\text{C}_6\text{H}_4)-</td>
<td>2.0</td>
<td>78</td>
</tr>
<tr>
<td>3i</td>
<td>4-(\text{MeO}-\text{C}_6\text{H}_4)-</td>
<td>3.0</td>
<td>81</td>
</tr>
<tr>
<td>3j</td>
<td>4-(\text{HO}-\text{C}_6\text{H}_4)-</td>
<td>2.0</td>
<td>76</td>
</tr>
<tr>
<td>3k</td>
<td>4-(\text{HO},\text{3-MeO-C}_6\text{H}_3)-</td>
<td>3.0</td>
<td>85</td>
</tr>
<tr>
<td>3l</td>
<td>2-(\text{Br-C}_6\text{H}_4)-</td>
<td>2.5</td>
<td>80</td>
</tr>
<tr>
<td>3m</td>
<td>3-(\text{Br-C}_6\text{H}_4)-</td>
<td>3.0</td>
<td>84</td>
</tr>
<tr>
<td>3n</td>
<td>4-(\text{F-C}_6\text{H}_4)-</td>
<td>2.0</td>
<td>88</td>
</tr>
<tr>
<td>3o</td>
<td>2,5-((\text{MeO})_2-\text{C}_6\text{H}_3)-</td>
<td>3.5</td>
<td>89</td>
</tr>
<tr>
<td>3p</td>
<td>3,4-((\text{MeO})_2-\text{C}_6\text{H}_3)-</td>
<td>3.0</td>
<td>84</td>
</tr>
<tr>
<td>3q</td>
<td>3,4,5-((\text{MeO})_3-\text{C}_6\text{H}_2)-</td>
<td>3.0</td>
<td>78</td>
</tr>
<tr>
<td>3r</td>
<td>2-(\text{HO}-\text{C}_6\text{H}_4)-</td>
<td>2.0</td>
<td>82</td>
</tr>
<tr>
<td>3s</td>
<td>2-(\text{Furyl})-</td>
<td>2.5</td>
<td>85</td>
</tr>
<tr>
<td>3t</td>
<td>2-(\text{Thienyl})</td>
<td>2.5</td>
<td>81</td>
</tr>
<tr>
<td>3u</td>
<td>2-(\text{Pyridyl})</td>
<td>3.0</td>
<td>86</td>
</tr>
</tbody>
</table>

\(^a\)All the reactions were run till the completion as indicated by TLC

\(^b\)yield after crystallization

From this data, it was noticed that all the aldehydes having electron donating/withdrawing substituent reacted smoothly in shorter reaction time to afford the 1,8-dioxo-octahydroxanthene in very good to excellent isolated yields. All the reactions were monitored by TLC and preceded till the completion of the reaction (as indicated by TLC). All the synthesized xanthenes were homogeneous on TLC and pure enough for further practical
use. However, all the compounds were crystallized by using ethanol and the % yield was calculated after the crystallization step. All the compounds were characterized by melting point, $^1$H NMR, $^{13}$C NMR and DEPT-135 spectral techniques. Additional confirmation for the structures is also obtained by IR and mass spectrometric studies for representative samples from the series. All the data were in agreement with the cited literature.

4.4a.1.4. Mechanism

The IL $[^\text{cmmim}][\text{BF}_4]$ promotes the reaction due to its inherent Brønsted acidity. The -COOH proton of $[^\text{cmmim}][\text{BF}_4]$ is capable of bonding with the carbonyl oxygen of dimedone as well as aldehyde. The capacity of IL to form the bond with substrate may push the reaction in to the forward direction. Based on this, the mechanism for the reaction is given as under (Scheme 4.4a.2).

4.4a.2. CONCLUSION

In conclusion, the presented method is an easy and general method for the synthesis of 1,8-dioxo-octahydroxanthene via condensation reaction between aldehydes and dimedone in presence of catalytic amount of ionic liquid. The method works in absence of hazardous solvent, under mild reaction conditions, produces compounds in good yields and with nearly
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complete recovery of ionic liquid. The activity of ionic liquid persisted for next six runs with almost same efficiency with the same reactants.

4.4a.3. EXPERIMENTAL

All the reactants were of research grade and used as obtained without any further purification. The reactions were performed in 25 mL round bottom flask equipped with a refluxing condenser and magnetic stirrer in a preheated oil bath.

4.4a.3.1. General procedure for the synthesis of 1,8-dioxo-octahydroxanthene

A mixture of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), aldehyde (1 mmol) and [cmmim][BF$_4$] (200 mg) was charged into a 25 mL flask equipped with a condenser and magnetic needle. The reaction mixture was stirred on a preheated oil bath at 80 °C for appropriate time as shown in Table 4.4a.2. After completion of reaction (as indicated by TLC) the reaction mixture was poured onto crushed ice (~20 gm) and stirred well. The solid separated was washed with ice cold water and then crystallized from hot ethanol to afford pure 1,8-dioxo-octahydroxanthenes. The combined aqueous filtrate was subjected to vacuo at 80 °C under reduced pressure (10 mmHg) for 4 h to leave behind the IL in near complete recovery, pure enough to recycle. The recovered ionic liquid was found to be equally effective for at least six cycles in the synthesis of 3a.

4.4a.3.2. Recyclability of ionic liquid

The recycled ionic liquid was found to be equally effective for next six run in to the model reaction of dimedone and benzaldehyde. After the product separation through filtration the aqueous filtrate was put in to vacuum oven at 80 °C for 4 h. The efficiency of recovered ionic liquid in six reaction cycle is shown in terms of reaction yield by using plot diagram (Figure 4.4a.2).
Figure 4.4a.2 Recyclibility of [cmmim][BF$_4$] in model reaction of benzaldehyde and dimedone.
Synthesis of 1,8-dioxo-octahydroxanthene by Microwave irradiation
4.4b.1. RESULTS AND DISCUSSION

4.4b.1.1. Scheme
Microwave assisted cyclocondensation reaction was carried out by using a variety of aromatic/heterocyclic aldehydes 1 with dimedone 2 to afford 1,8-dioxo-octahydroxanthenes 3 (Scheme 4.4b.1) in the presence of carboxy functionalized ionic liquid [cmmim][BF₄]. The combined effect of microwave along with ionic liquid is discussed in this section.

4.4b.1.2. Reaction optimization
The ultimate goal was to synthesize the xanthenes under microwave irradiations in presence of ionic liquid without any added solvent or catalyst. Therefore, initially the reaction on a neat mixture of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) with benzaldehyde (1 mmol) was carried out in presence of [cmmim][BF₄] (200 mg) under microwave irradiation. The series of experimentation with respect to the power level of the MW set-up was also optimized. Upon optimization, it was found that the best result was obtained when the reaction mixture was irradiated at 40% power level (280 W) for time of 2 min. The presence of about 200 mg of IL ensures the homogeneity of the reaction mixture in particular when solid aldehydes are employed with dimedone. The optimization of power levels was checked with reference to reaction time, yield and purity of product. The data are shown in Table 4.4b.1.
Table 4.4b.1 Data representing the optimum condition for the synthesis of 1,8-dioxo-octahydroxanthene under microwave set up

<table>
<thead>
<tr>
<th>Entry</th>
<th>Power levels in Watt</th>
<th>Reaction time (min)</th>
<th>% Yield</th>
<th>Purity of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140</td>
<td>5.5</td>
<td>48</td>
<td>Contained intermediate along with final product</td>
</tr>
<tr>
<td>2</td>
<td>210</td>
<td>4.0</td>
<td>61</td>
<td>Contained intermediate in minor amount</td>
</tr>
<tr>
<td>3</td>
<td>240</td>
<td>3.0</td>
<td>81</td>
<td>Purity was fine</td>
</tr>
<tr>
<td>4</td>
<td>280</td>
<td>2.0</td>
<td>92</td>
<td>Loss of yield</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>2.0</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>420</td>
<td>2.0</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>450</td>
<td>2.0</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>490</td>
<td>2.0</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>560</td>
<td>2.0</td>
<td>42</td>
<td>Contained some degraded product</td>
</tr>
<tr>
<td>10</td>
<td>700</td>
<td>2.0</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

*Reactions were run till the completion as indicated by TLC

4.4b.1.3. Characteristic data showing the MW assisted synthesis of 1,8-dioxo-octahydroxanthene

After finding the optimized condition, all the reactions with a variety of aldehydes were carried out by using 200 mg of IL at 40% power level (280 Watt) for the appropriate time shown in Table 4.4b.2. It was observed that all the aldehydes having electron donating/withdrawing group reacted smoothly within a short period of time to give a 1,8-dioxo-octahydroxanthene in excellent isolated yield. The various aldehydes employed along with dimedone and their characteristic data are shown in Table 4.4b.2.
Table 4.4b.2 Characteristic data for synthesized 1,8-dioxo-octahydroxanthenes under MW irradiation at 40% power level (280 W)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Reaction Time&lt;sup&gt;a&lt;/sup&gt; (min)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Ph−</td>
<td>2</td>
<td>92</td>
</tr>
<tr>
<td>3b</td>
<td>4-O&lt;sub&gt;2&lt;/sub&gt;N-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>2</td>
<td>95</td>
</tr>
<tr>
<td>3c</td>
<td>2-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>3</td>
<td>91</td>
</tr>
<tr>
<td>3d</td>
<td>3-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>2</td>
<td>88</td>
</tr>
<tr>
<td>3e</td>
<td>4-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>2</td>
<td>94</td>
</tr>
<tr>
<td>3f</td>
<td>2-O&lt;sub&gt;2&lt;/sub&gt;N-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>3g</td>
<td>3-O&lt;sub&gt;2&lt;/sub&gt;N-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>3</td>
<td>89</td>
</tr>
<tr>
<td>3h</td>
<td>4-H&lt;sub&gt;3&lt;/sub&gt;C-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>3i</td>
<td>4-MeO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>4</td>
<td>87</td>
</tr>
<tr>
<td>3j</td>
<td>4-HO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>4</td>
<td>83</td>
</tr>
<tr>
<td>3k</td>
<td>4-HO,3-MeO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>3l</td>
<td>2-Br-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>3</td>
<td>87</td>
</tr>
<tr>
<td>3m</td>
<td>3-Br-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>3</td>
<td>93</td>
</tr>
<tr>
<td>3n</td>
<td>4-F-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>2</td>
<td>94</td>
</tr>
<tr>
<td>3o</td>
<td>2,5-(MeO)&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>3p</td>
<td>3,4-(MeO)&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>4</td>
<td>86</td>
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<tr>
<td>3q</td>
<td>3,4,5-(MeO)&lt;sub&gt;3&lt;/sub&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;−</td>
<td>4</td>
<td>83</td>
</tr>
<tr>
<td>3r</td>
<td>2-HO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>3s</td>
<td>2-Furyl−</td>
<td>2</td>
<td>78</td>
</tr>
<tr>
<td>3t</td>
<td>2-Thienyl</td>
<td>2</td>
<td>89</td>
</tr>
<tr>
<td>3u</td>
<td>2-Pyridyl</td>
<td>3</td>
<td>91</td>
</tr>
</tbody>
</table>

<sup>a</sup>All the reactions were run till completion as indicated by TLC

<sup>b</sup>% yield after crystallization

All the synthesized compounds were pure enough for all further practical purpose. However, all the compounds were crystallized by using ethanol as a solvent. All the compounds were characterized by melting point, <sup>1</sup>H NMR, <sup>13</sup>C NMR and DEPT-135 spectral techniques. Additional confirmation for the structures is also obtained by IR and mass spectrometric studies for some
representative samples from the series. All the data were in agreement with the cited literature.

4.4b.1.4. Mechanism

The mechanism for the IL-MW induced protocol for the synthesis of xanthenes follows the same path as shown in section 4.4a.1.4.

4.4b.2. CONCLUSION

The IL-MW induced protocol described a novel and environmentally benign method for the synthesis of 1,8-dioxo-octahydroxanthene. The combined effect of microwave and ionic liquid makes the procedure more efficient compare to conventional acid/base catalyzed thermal processes. The ionic liquid catalyzed reaction under microwave irradiations gave a new methodology apt for the development.

4.4b.3. EXPERIMENTAL

All the reactants were of research grade and used as obtained without any further purification. The reactions were performed in scientific microwave system (Catalyst system 'CATA-R', 700 W).

4.4b.3.1. General procedure for the synthesis of 1,8-dioxo-octahydroxanthene under microwave irradiation

A mixture of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), aldehyde (1 mmol) and [cmmim][BF₄] (200 mg) was charged into a 25mL flask. The mixture was stirred gently with a spatula for a few seconds to ensure a homogeneous mixing of reactants with ionic liquid. Then, reaction mixture was subjected to microwave irradiation at 40% power level (CATA-R, 700 W) for appropriate time shown in Table 4.4b.2. After completion of reaction (as indicated by TLC) the reaction mixture was poured onto crushed ice (~20 gm) and stirred well. The solid separated was washed with ice cold water and then crystallized from hot ethanol to afford pure 1,8-dioxo-octahydroxanthenes. The combined aqueous filtrate was subjected to vacuo at 80 °C under reduced pressure (10 mmHg) for 4 h to leave behind the IL in
near complete recovery, pure enough to recycle. The recovered ionic liquid was found to be equally effective for at least six cycles in the synthesis of 3a under microwave irradiations at 40% power level.

### 4.4b.3.2. Recyclability of ionic liquid

In the present study the reusability of ionic liquid was checked by running a model reaction of benzaldehyde and dimedone in recycled ionic liquid. It was found that ionic liquid was equally effective for at least six runs. The plot diagram showing the efficacy of recycled ionic liquid is shown in Figure 4.4b.1.

![Recyclibility of [cmmim][BF₄] in model reaction of benzaldehyde and dimedone under microwave irradiations.](image)

**Figure 4.4b.1** Recyclibility of [cmmim][BF₄] in model reaction of benzaldehyde and dimedone under microwave irradiations.
Synthesis of 1,8-dioxo-octahydroxanthene by Ultrasonic Irradiation
4.4.1. RESULTS AND DISCUSSION

4.4.1.1. Scheme

The efficient synthesis of 1,8-dioxo-octahydroxanthene compounds has been carried out by one-pot condensation of aromatic/heterocyclic aldehydes 1 with dimedone 2 (Scheme 4.4.1) in presence of [cmmim][BF₄] under ultrasonic irradiations. The reaction proceeded under mild conditions with minimal or no waste. The optimum reaction condition and the role of ionic liquid and ultrasonic irradiation to accelerate the reaction are discussed in detail in this section.

![Scheme 4.4.1](image)

4.4.1.2. Reaction optimization

Table 4.4.1 Optimization data for the synthesis of 1,8-dioxooctahydroxanthene under ultrasound irradiations

<table>
<thead>
<tr>
<th>Entry</th>
<th>IL/co-solvent</th>
<th>Reaction condition</th>
<th>Time (min)ᵃ</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No IL/2 mL MeOH</td>
<td>RT, )))</td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>[cmmim][BF₄]/1 mL MeOH</td>
<td>RT, )))</td>
<td>50</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>[cmmim][BF₄]/1 mL MeOH</td>
<td>50 °C, )))</td>
<td>50</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>[cmmim][BF₄]/no co-solvent</td>
<td>RT, )))</td>
<td>180</td>
<td>28ᵇ</td>
</tr>
<tr>
<td>5</td>
<td>[cmmim][BF₄]/1 mL MeOH</td>
<td>RT, stirring</td>
<td>180</td>
<td>Intermediate</td>
</tr>
</tbody>
</table>

ᵃAll the reactions were run till completion as indicated by TLC
ᵇDimedone remains sparingly soluble under this condition

To find out the optimum reaction condition, the model reaction of benzaldehyde with dimedone was carried out under different reaction conditions. Initially, the reaction was carried out in absence of ionic liquid.
by adding 2 mL methanol as a solvent (Entry 1, Table 4.4c.1). After 180 min, under ultrasound irradiations the starting materials were recovered back from the reaction mixture. After that, the sonochemical reaction with same substrate was carried out by taking 200 mg of [cmmim][BF₄] with 1 mL methanol as a co-solvent (Entry 2) (MeOH was used as a co-solvent because dimedone is sparingly soluble in IL at ambient temperature). It is notable that the product 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione formed absolutely within a short time period. To check out the influence of temperature the same reaction was carried out at 50 °C (Entry 3). It was noticed that there was no any significant change observed in reaction time and yield by increasing the temperature. When sole [cmmim][BF₄] was taken as a reaction medium, the significant decrease in the yield was observed (Entry 4). It was observed that the poor solubility of dimedone in reaction media under this condition (Temperature 30 °C) may be the main cause for decrease in yield. No significant formation of product was observed, when the reaction was conducted under silent conditions (simple stirring without ultrasound irradiations) (Entry 5).

4.4c.1.3. Characteristic data showing the sonochemical synthesis of 1,8-dioxo-octahydroxanthene

The sonochemical synthesis of xanthenes using 200 mg IL containing 1 mL MeOH was observed the most optimum condition for the synthesis of xanthenes in maximum yields at ambient temperature in the absence of any added catalyst. Hence, all further reactions with various aldehydes were carried out under this condition. A variety of aldehydes including electron withdrawing/donating functional groups were subjected to the sonochemical reactions in the IL to afford the xanthenes in very good isolated yields in short reaction times. The different aldehydes employed along with dimedone and the characteristic data of the obtained products are shown in Table 4.4c.2.
Table 4.4c.2. Characteristic data for the synthesized 1,8-dioxo-octahydroxanthenes under ultrasonication

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Reaction Time&lt;sup&gt;a&lt;/sup&gt; (min)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Ph−</td>
<td>50</td>
<td>87</td>
</tr>
<tr>
<td>3b</td>
<td>4-O&lt;sub&gt;2&lt;/sub&gt;N−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>60</td>
<td>85</td>
</tr>
<tr>
<td>3c</td>
<td>2-Cl−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>65</td>
<td>86</td>
</tr>
<tr>
<td>3d</td>
<td>3-Cl−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>55</td>
<td>82</td>
</tr>
<tr>
<td>3e</td>
<td>4-Cl−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>55</td>
<td>81</td>
</tr>
<tr>
<td>3f</td>
<td>2-O&lt;sub&gt;2&lt;/sub&gt;N−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>70</td>
<td>83</td>
</tr>
<tr>
<td>3g</td>
<td>3-O&lt;sub&gt;2&lt;/sub&gt;N−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>60</td>
<td>87</td>
</tr>
<tr>
<td>3h</td>
<td>4-H&lt;sub&gt;3&lt;/sub&gt;C−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>55</td>
<td>78</td>
</tr>
<tr>
<td>3i</td>
<td>4-MeO−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>45</td>
<td>85</td>
</tr>
<tr>
<td>3j</td>
<td>4-HO−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>80</td>
<td>79</td>
</tr>
<tr>
<td>3k</td>
<td>4-HO,3-MeO−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>85</td>
<td>81</td>
</tr>
<tr>
<td>3l</td>
<td>2-Br−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>45</td>
<td>84</td>
</tr>
<tr>
<td>3m</td>
<td>3-Br−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>55</td>
<td>86</td>
</tr>
<tr>
<td>3n</td>
<td>4-F−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>45</td>
<td>88</td>
</tr>
<tr>
<td>3o</td>
<td>2,5-(MeO)&lt;sub&gt;2&lt;/sub&gt;−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>40</td>
<td>82</td>
</tr>
<tr>
<td>3p</td>
<td>3,4-(MeO)&lt;sub&gt;2&lt;/sub&gt;−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>55</td>
<td>86</td>
</tr>
<tr>
<td>3q</td>
<td>3,4,5-(MeO)&lt;sub&gt;3&lt;/sub&gt;−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;−</td>
<td>55</td>
<td>83</td>
</tr>
<tr>
<td>3r</td>
<td>2-HO−C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;−</td>
<td>50</td>
<td>84</td>
</tr>
<tr>
<td>3s</td>
<td>2-Furyl−</td>
<td>30</td>
<td>89</td>
</tr>
<tr>
<td>3t</td>
<td>2-Thienyl−</td>
<td>45</td>
<td>92</td>
</tr>
<tr>
<td>3u</td>
<td>2-Pyridyl−</td>
<td>50</td>
<td>90</td>
</tr>
</tbody>
</table>

<sup>a</sup>All the reactions were run till the completion as indicated by TLC

<sup>b</sup>Yield after crystallization

All the reactions were monitored by TLC and taken to completion. The time taken for the complete conversion and the isolated yields are recorded in Table 4.4c.2. All the synthesized xanthenes were homogeneous on TLC and pure enough for the further practical purpose. However, all the compounds were crystallized from hot ethanol. All the synthesized compounds were
Chapter 4

characterized by melting point, $^1$H NMR, $^{13}$C NMR and DEPT-135 spectral techniques. Additional confirmation for the structures is also obtained by IR and mass spectrometric studies for some representative samples from the series. All the data were in agreement with the cited literature.

4.4c.1.4. Mechanism
The IL [cmmim][BF$_4$] promotes the reaction due to its inherent Brønsted acidity. The -COOH proton of [cmmim][BF$_4$] is capable of bonding with the carbonyl oxygen of aldehyde as well as dimedone. The bonding between IL and substrate may push the reaction into forward direction. The mechanistic pathway follows the same path as shown in section 4.4a.1.4.

4.4c.2. CONCLUSION
The sonochemical reaction provided an easy route to synthesize 1,8-dioxo-octahydroxanthene in very excellent isolated yields. The beneficial features of the reaction, such as mild condition, absence of added catalyst and reusability of ionic liquid puts it on advantage over conventional acid/base catalyzed reaction.

4.4c.3. EXPERIMENTAL
All the chemicals were of research grade and used as obtained without any further purification. The reactions were performed in D-compact ultrasonic cleaner with a frequency of 50 kHz and power 250 W.

4.4c.3.1. General procedure for the synthesis of 1,8-dioxo-octahydroxanthene under ultrasonic irradiation
A mixture of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), aldehyde (1 mmol) and [cmmim][BF$_4$] (200 mg) was charged into a 25 mL flask. The mixture was stirred gently with a spatula for a few seconds to ensure a homogeneous mixing of reactants with ionic liquid. Add 1 mL methanol to it. Then, the reaction mixture was subjected to ultrasonic bath at ambient temperature for appropriate time shown in Table 4.4c.2. Reactant mixture was suspended at the center of the bath, slight below the water level. After
completion of reaction (as indicated by TLC), the reaction mixture was poured onto crushed ice (~20 gm) and stirred well. The solid separated was washed with ice cold water and then crystallized from hot ethanol to afford pure 1,8-dioxo-octahydroxanthenes. The aqueous filtrate was subjected to vacuo at 80 °C under reduced pressure (10 mmHg) for 4 h to leave behind the IL in near complete recovery, pure enough to recycle. The recovered ionic liquid was found to be equally effective for at least six cycles in the synthesis of 3a.

4.4c.3.2. Recyclability of ionic liquid
The recycled ionic liquid was checked for its efficiency by using it at least six times in model reaction of benzaldehyde and dimedone under ultrasonic irradiations (Figure 4.4c.1).

![Graph showing recyclability](image-url)

**Figure 4.4c.1** Recyclibility of [cmim][BF₄] in model reaction of benzaldehyde and dimedone under ultrasonication.
Synthesis of 1,8-dioxo-octahydroxanthene by Solar Irradiation

Section 4d
4.4d.1. RESULTS AND DISCUSSION

4.4d.1.1. Scheme

Solar thermal energy induced synthesis of 1,8-dioxo-octahydroxanthene 3 has been carried out by one-pot condensation of aromatic/heterocyclic aldehydes 1 with dimedone 2 (Scheme 4.4d.1) in presence of [cmmim][BF₄] under solar irradiations. The reaction proceed under mild condition with minimal or no waste. The optimum reaction condition and the role of ionic liquid to accelerate the reaction is discussed in detail in this section.

![Scheme 4.4d.1](image)

4.4d.1.2. Reaction optimization

Table 4.4d.1 Synthesis of 3a under various conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>IL/co-solvent</th>
<th>Max. Temp. reached during reaction (°C)</th>
<th>Yielda (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No IL/5ml methanol</td>
<td>56</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>200 mg [cmmim][BF₄]/no co-solvent</td>
<td>44 (intermediate)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>200 mg [cmmim][BF₄]/5 ml methanol</td>
<td>52</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>200 mg [cmmim][BF₄]/5 ml methanol</td>
<td>-b</td>
<td>Trace</td>
</tr>
</tbody>
</table>

aIsolated yield, breaction carried out under simple stirring at ambient temperature

A model reaction involving benzaldehyde and dimedone to afford the 1,8-dioxo-octahydroxanthene 3a under various reaction conditions was performed for an appropriate time. The results are recorded in Table 4.4d.1. In the beginning, the reaction was carried out in absence of ionic liquid under solar irradiation using 5 mL methanol as the only solvent (Entry 1). After the long time of reaction, starting materials recovered back. On the
contrary, when the reaction was carried out by taking 200 mg IL in absence of co-solvent (i.e. methanol) (Entry 2), surprisingly the formation of only uncyclized intermediate took place. The reaction was run for 6 h but the intermediate did not get cyclized to give targeted xanthene. It was observed that in absence of methanol, reaction mass remained non-homogeneous even after through mixing using a spatula. This is mainly due to the inability of IL in dissolving dimerone at this temperature. Due to the solubility problem, we tried for IL along with co-solvent as a reaction media (Entry 3). To our pleasure, the [cmmim][BF$_4$] gave the formation of xanthene from uncyclized intermediate in presence of methanol under solar irradiation. Unfortunately, it took longer time period and completed with moderate yield as compared to reactions in presence of other energy sources. No significant formation of product 3a was observed, when the reaction was conducted under simple stirring at ambient condition in presence of IL and co-solvent (Entry 4). From these experiments the synthesis of 3a using IL with co-solvent found to be the most optimum condition. All the reactions were carried out under this condition for the appropriate time as shown in Table 4.4d.2. All the reactions were monitored by TLC and carried forward to maximum atom utilization. All the compounds were characterized by melting point, $^1$H NMR, $^{13}$C NMR and DEPT-135 techniques. Additional confirmation was obtained by IR and mass spectrometry. All the data were in agreement with the cited literature. It was noticed that the aldehydes having electron donating/withdrawing substituent reacted within 5-7 h of reaction time to afford the 1,8-dioxo-octahydroxanthene in moderately good isolated yields (62-78%).

4.4d.1.3. Characteristic data showing the synthesis of 1,8-dioxo-octahydroxanthene under solar irradiations

All the aromatic/heterocyclic aldehydes have reacted smoothly under solar irradiations to afford 1,8-dioxo-octahydroxanthene in moderately good isolated yields. Solar induced protocol has the ability to tolerate variations in aldehydes containing both electron donating and electron withdrawing
substituents. Characteristic data for all the synthesized compounds are given in Table 4.4d.2.

**Table 4.4d.2 Characteristic data for all synthesized 1,8-dioxooctahydroxanthenes under solar irradiation**

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Reaction Time&lt;sup&gt;a&lt;/sup&gt; (h)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Ph-</td>
<td>6.0</td>
<td>74</td>
</tr>
<tr>
<td>3b</td>
<td>4- O&lt;sub&gt;2&lt;/sub&gt;N-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.0</td>
<td>68</td>
</tr>
<tr>
<td>3c</td>
<td>2-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>6.5</td>
<td>71</td>
</tr>
<tr>
<td>3d</td>
<td>3-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.5</td>
<td>64</td>
</tr>
<tr>
<td>3e</td>
<td>4-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.5</td>
<td>66</td>
</tr>
<tr>
<td>3f</td>
<td>2- O&lt;sub&gt;2&lt;/sub&gt;N-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>6.0</td>
<td>61</td>
</tr>
<tr>
<td>3g</td>
<td>3- O&lt;sub&gt;2&lt;/sub&gt;N-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>6.0</td>
<td>72</td>
</tr>
<tr>
<td>3h</td>
<td>4-H&lt;sub&gt;2&lt;/sub&gt;C-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.5</td>
<td>62</td>
</tr>
<tr>
<td>3i</td>
<td>4-MeO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>6.5</td>
<td>65</td>
</tr>
<tr>
<td>3j</td>
<td>4-HO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>6.0</td>
<td>63</td>
</tr>
<tr>
<td>3k</td>
<td>4-HO,3-MeO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;-</td>
<td>6.5</td>
<td>71</td>
</tr>
<tr>
<td>3l</td>
<td>2-Br-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.5</td>
<td>67</td>
</tr>
<tr>
<td>3m</td>
<td>3-Br-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.5</td>
<td>69</td>
</tr>
<tr>
<td>3n</td>
<td>4-F-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.0</td>
<td>76</td>
</tr>
<tr>
<td>3o</td>
<td>2,5-(MeO)&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;-</td>
<td>7.0</td>
<td>78</td>
</tr>
<tr>
<td>3p</td>
<td>3,4-(MeO)&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;-</td>
<td>6.5</td>
<td>74</td>
</tr>
<tr>
<td>3q</td>
<td>3,4,5-(MeO)&lt;sub&gt;3&lt;/sub&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>6.5</td>
<td>68</td>
</tr>
<tr>
<td>3r</td>
<td>2-HO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>5.5</td>
<td>73</td>
</tr>
<tr>
<td>3s</td>
<td>2-Furyl-</td>
<td>6.0</td>
<td>75</td>
</tr>
<tr>
<td>3t</td>
<td>2-Thienyl</td>
<td>6.0</td>
<td>70</td>
</tr>
<tr>
<td>3u</td>
<td>2-Pyridyl</td>
<td>5.5</td>
<td>66</td>
</tr>
</tbody>
</table>

<sup>a</sup>All the reactions were run till the completion as indicated by TLC

<sup>b</sup>Yield after crystallization

It is more important to confirm whether the reaction is thermal or photochemical transformation. To investigate exact cause of reaction, model MCR of benzaldehyde and dimedone was carried out in the dark for the same
reaction time and same maximum temperature, reached during solar exposure. Reaction proceeds smoothly and afforded the desired product. The same model MCR was carried out at room temperature under the influence of artificial visible light (60 W Bulb). There was no considerable formation of product observed even after a long time period. This ruled out the possibility of photochemical reaction. Thus it becomes evident that ionic liquid [cmmim][BF$_4$] and solar energy makes this process widely applicable and eco-friendly.

4.4d.1.4. Mechanism
The mechanistic pathway for the reaction is same as given in section 4.4a.1.4 of this chapter.

4.4d.2. CONCLUSION
There was a flourishing outcome, in the synthesis of 1,8-dioxooctahydroxanthene in presence of [cmmim][BF$_4$] under solar irradiations. The use of solar irradiation as an energy source made the process more eco-friendly than conventional acid/base catalyzed process. The reactions proceeded with less consumption of energy and without generating waste. The combine use of ionic liquid and solar energy made the procedure more benign for the environment.

4.4d.3. EXPERIMENTAL
All the chemicals were of research grade and used as obtained without any further purification. The reactions were performed in 25 mL stoppered round bottom flask.

4.4d.3.1. General procedure for the synthesis of DHPMs
A mixture of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), aldehyde (1 mmol) and [cmmim][BF$_4$] (200 mg) was charged into a 25mL flask containing 5 mL methanol. The reaction mixture was stirred gently with a spatula for a few seconds to ensure homogeneous mixing of reactants with ionic liquid. Then, reaction mixture was exposed to direct sunlight during...
10.00 a.m. to 5.00 p.m. on a day having full bright sun in the month of April-May, 2010. After direct irradiation for appropriate time solid product started to form gradually which was completed after the time shown in Table 4.4d.2. At completion of the reaction (as indicated by TLC), a solid product was poured into crushed ice (20 g) and stirred for 15-20 min. The solid separated was filtered through a sintered funnel under suction, washed with ice-cold water (15 mL) and then crystallized from hot ethanol to afford pure xanthenes. The aqueous filtrate was subjected to vacuo at 80 °C under reduced pressure (10 mmHg) for 4 h to leave behind the IL in near complete recovery, pure enough for next run. The recovered ionic liquid was found to be equally effective for at least six cycles in the synthesis of 3a.

4.4d.3.2. Recyclability of ionic liquid

The ionic liquid recycled for six times by charging the same reactants in reaction. The ionic liquid was found to be equally effective in all runs with retention in its activity. The retention in its activity is shown in Figure 4.4d.1.

\[ \begin{array}{ccccccc}
74 & 74 & 72 & 76 & 72 & 71 \\
\end{array} \]

\[ \begin{array}{ccccccc}
\% \text{ Yield} & 100 & 80 & 60 & 40 & 20 & 0 \\
\end{array} \]

\[ \begin{array}{ccccccc}
1 & 2 & 3 & 4 & 5 & 6 \\
\end{array} \]

\begin{center}
Reaction Cycles
\end{center}

**Figure 4.4d.1** Recyclibility of [cmmim][BF₄] in model reaction of benzaldehyde and dimedone under solar irradiations.
Spectroscopic Characterization of 1,8-dioxo-octahydroxanthene

Section - 4e
4.4e.1. CHARACTERIZATION

All the synthesized xanthenediones were characterized by $^1$H NMR, $^{13}$C NMR and DEPT-135 techniques. Additional confirmation was obtained by IR and mass spectrometry analysis of some representative compounds. $^1$H NMR, $^{13}$C NMR and DEPT-135 spectra were recorded on BRUKER AVANCE 400 MHz instrument using CDC$_3$ as the solvent. LC-MS data were recorded on AB APPLIED BIOSYSTEMS IMDS SCIEX. API-2000 LC/MS/MS. FT IR spectra were recorded on Shimadzu FT-IR-S8401 and FT-IR-8400 spectrophotometer using KBr. The representative spectra are included at the end of the section for perusal. $^1$H NMR spectra for compounds 3a, 3b and 3c are given in Figures 4.4e.1, 4.4e.6 and 4.4e.11 respectively. $^{13}$C NMR spectra for the same compounds are described in Figures 4.4e.2, 4.4e.7 and 4.4e.12 respectively. The spectra recorded in DEPT-135 experiments on $^{13}$C NMR spectrophotometer are put on view in Figures 4.4e.3, 4.4e.8 and 4.4e.13 respectively for the same compounds. The infrared spectra of these compounds are given in Figures 4.4e.4, 4.4e.9 and 4.4e.14 respectively. The other parameters like solubility and melting points were checked by the standard methods and compared with the reported one if available from the literature. The $^1$H NMR data is interpreted in terms of number of protons, splitting pattern and their relative $\delta$ values. $^{13}$C NMR data is also given for all synthesized compounds. The DEPT-135 experiments are also conducted for additional confirmation of the structures. Additional confirmation for the structures is also obtained by mass spectrometric and by infrared spectroscopic studies for the representative samples from the series. The molecular structures and characterization data for all synthesized xanthenediones are given below in tabular form.
**3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione**

Molecular Formula \( \text{C}_{23}\text{H}_{26}\text{O}_3 \)

Molecular Weight (gm·mol⁻¹) 350.5

Melting Point (°C) 198-200

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.29 (m, 2H), 7.23 (m, 2H), 7.11 (m, 1H), 4.77 (s, 1H), 2.48 (s, 4H), 2.21 (dd, 4H, \( j=16.4 \) Hz), 1.12 (s, 6H), 1.01 (s, 6H)

\(^{13}\)C NMR: \( \delta \) 27.34, 29.26, 31.84, 32.19, 40.90, 50.76, 115.70, 126.36, 128.04, 128.38, 144.10, 162.22, 196.32

DEPT-135: Up Peaks: \( \delta \) 27.34, 29.26, 31.84, 126.36, 128.04, 128.38

Down Peaks: \( \delta \) 40.89, 50.75

IR (KBr): 3030, 2955, 1662, 1624, 1361, 1197, 1163 cm⁻¹

LC-MS: 351.0 \([\text{M}^++1]\)

---

**3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-nitrophenyl)-2H-xanthene-1,8(5H,9H)-dione**

Molecular Formula \( \text{C}_{23}\text{H}_{25}\text{NO}_5 \)

Molecular Weight (gm·mol⁻¹) 395.4

Melting Point (°C) 222-224

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 8.10 (m, 2H), 7.49 (m, 2H), 4.84 (s, 1H), 2.51 (s, 4H), 2.22 (dd, 4H, \( j=16.4 \) Hz), 1.13 (s, 6H), 1.00 (s, 6H)

\(^{13}\)C NMR: \( \delta \) 27.28, 29.23, 32.22, 32.37, 40.58, 50.61, 114.54, 123.42, 129.36, 146.50, 151.51, 162.95, 196.23

DEPT-135: Up Peaks: \( \delta \) 27.27, 29.23, 32.37, 123.42, 129.36

Down Peaks: \( \delta \) 40.84, 50.60

IR (KBr): 3020, 2956, 1660, 1516, 1361, 1199, 1004 cm⁻¹

LC-MS: 396.0 \([\text{M}^++1]\)

---

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

Molecular Formula \( \text{C}_{23}\text{H}_{25}\text{ClO}_3 \)

Molecular Weight (gm·mol⁻¹) 384.9

Melting Point (°C) 226-228

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.45 (m, 1H), 7.20 (m, 2H), 7.08 (m, 1H), 5.01 (s, 1H), 2.46 (s, 4H), 2.20 (dd, 4H, \( j=16.0 \) Hz), 1.12 (s, 6H), 1.03 (s, 6H)

\(^{13}\)C NMR: \( \delta \) 27.39, 29.26, 31.92, 32.01, 40.84, 50.72, 113.70, 126.33, 127.80, 130.16, 133.0, 133.45, 139.84, 162.95, 196.44

DEPT-135: Up Peaks: \( \delta \) 27.38, 29.28, 31.89, 126.33, 127.80, 130.16, 133.00

Down Peaks: \( \delta \) 40.83, 50.71

IR (KBr): 3347, 3072, 2949, 2311, 1794, 1663, 1468, 1353, 1201 cm⁻¹

LC-MS: 386.2 \([\text{M}^++2]\)
3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(3'-chlorophenyl)-2H-xanthene-1,8(5H,9H)-dione

**Molecular Formula:** \(C_{23}H_{25}ClO_3\)

**Molecular Weight (gm-mol\(^{-1}\))** 384.9

**Melting Point (°C)** 184-186

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.35 \text{ (m, } 1\text{H}), 7.20 \text{ (m, } 1\text{H}), 7.06 \text{ (m, } 1\text{H}), 6.92 \text{ (m, } 1\text{H}), 4.93 \text{ (s, } 1\text{H}), 2.51 \text{ (s, } 4\text{H}), 2.15 \text{ (dd, } 4\text{H, } J=16.3 \text{ Hz}), 1.10 \text{ (s, } 6\text{H}), 1.02 \text{ (s, } 6\text{H})\)

\(^13\)C NMR: \(\delta 27.35, 29.22, 32.02, 32.10, 41.04, 50.32, 113.20, 125.33, 125.50, 127.16, 130.0, 134.45, 144.84, 162.95, 196.49\)

DEPT-135: Up Peaks: \(\delta 27.35, 29.22, 32.10, 125.33, 125.50, 127.16, 130.0, 134.45\)

Down Peaks: \(\delta 41.04, 50.32\)

---

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

**Molecular Formula:** \(C_{23}H_{25}ClO_3\)

**Molecular Weight (gm-mol\(^{-1}\))** 384.9

**Melting Point (°C)** 230-232

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.24 \text{ (m, } 2\text{H}), 7.02 \text{ (m, } 2\text{H}), 4.59 \text{ (s, } 1\text{H}), 2.54 \text{ (s, } 4\text{H}), 2.17 \text{ (dd, } 4\text{H, } J=16.0 \text{ Hz}), 1.11 \text{ (s, } 6\text{H}), 1.02 \text{ (s, } 6\text{H})\)

\(^13\)C NMR: \(\delta 27.25, 29.30, 31.91, 32.10, 41.34, 50.24, 113.14, 124.08, 128.84, 135.34, 141.94, 162.23, 196.21\)

DEPT-135: Up Peaks: \(\delta 27.25, 29.30, 32.10, 124.08, 128.84, 135.34\)

Down Peaks: \(\delta 41.34, 50.24\)

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3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2'-nitrophenyl)-2H-xanthene-1,8(5H,9H)-dione

**Molecular Formula:** \(C_{23}H_{25}NO_5\)

**Molecular Weight (gm-mol\(^{-1}\))** 395.45

**Melting Point (°C)** 258-260

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.65 \text{ (m, } 1\text{H}), 7.24-7.45 \text{ (m, } 3\text{H}), 5.25 \text{ (s, } 1\text{H}), 2.53 \text{ (s, } 4\text{H}), 2.22 \text{ (dd, } 4\text{H, } J=16.4 \text{ Hz}), 1.10 \text{ (s, } 6\text{H}), 1.02 \text{ (s, } 6\text{H})\)

\(^13\)C NMR: \(\delta 27.21, 29.34, 32.08, 32.14, 41.36, 51.04, 114.52, 123.06, 128.61, 130.42, 131.94, 141.96, 145.79, 164.89, 196.03\)

DEPT-135: Up Peaks: \(\delta 27.21, 29.34, 32.14, 123.06, 128.61, 130.42, 131.94\)

Down Peaks: \(\delta 41.36, 51.04\)
3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(3-nitrophenyl)-2H-xanthene-1,8(5H,9H)-dione

**Molecular Formula**: $C_{23}H_{25}NO_5$

**Molecular Weight (gm·mol⁻¹)**: 395.45

**Melting Point (°C)**: 166-168

**¹H NMR** (400 MHz, CDCl₃): $\delta$ 8.06-7.93 (m, 2H), 7.42 (m, 1H), 7.31 (m, 1H), 5.15 (s, 1H), 2.50 (s, 4H), 2.20 (dd, 4H, $J=16.0$ Hz), 1.13 (s, 6H), 1.01 (s, 6H)

**¹³C NMR**: $\delta$ 27.27, 29.34, 32.09, 32.15, 41.65, 51.05, 113.49, 122.58, 123.02, 129.11, 133.06, 147.05, 148.32, 162.89, 195.63

**DEPT-135**: Up Peaks: $\delta$ 27.27, 29.34, 32.15, 122.58, 123.02, 129.11, 133.06

**Down Peaks**: $\delta$ 41.65, 51.05

**IR (KBr)**: 3020, 2960, 1664, 1595, 1354, 1194 cm⁻¹

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

**Molecular Formula**: $C_{24}H_{26}O_3$

**Molecular Weight (gm·mol⁻¹)**: 364.48

**Melting Point (°C)**: 216-218

**¹H NMR** (400 MHz, CDCl₃): $\delta$ 7.02 (m, 2H), 6.82 (m, 2H), 4.92 (s, 1H), 2.51 (s, 4H), 2.29 (s, 3H), 2.19 (dd, 4H, $J=16.3$ Hz), 1.09 (s, 6H), 1.00 (s, 6H)

**¹³C NMR**: $\delta$ 21.20, 27.23, 29.24, 31.95, 32.18, 42.06, 50.09, 112.11, 125.23, 129.25, 135.26, 141.50, 162.54, 195.83

**DEPT-135**: Up Peaks: $\delta$ 21.20, 27.23, 29.24, 125.23, 129.25

**Down Peaks**: $\delta$ 42.06, 50.09

**IR (KBr)**: 3135, 2954, 1720, 1592, 1378, 1191, 1081 cm⁻¹

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

**Molecular Formula**: $C_{24}H_{28}O_4$

**Molecular Weight (gm·mol⁻¹)**: 380.48

**Melting Point (°C)**: 240-242

**¹H NMR** (400 MHz, CDCl₃): $\delta$ 6.92 (m, 2H), 6.86 (m, 2H), 4.91 (s, 1H), 3.71 (s, 3H), 2.53 (s, 4H), 2.21 (dd, 4H, $J=16.0$ Hz), 1.11 (s, 6H), 1.00 (s, 6H)

**¹³C NMR**: $\delta$ 27.26, 29.84, 32.01, 32.18, 44.12, 51.03, 54.16, 111.03, 112.27, 127.06, 135.02, 154.14, 161.89, 195.83

**DEPT-135**: Up Peaks: $\delta$ 27.26, 29.84, 32.18, 51.03

**Down Peaks**: $\delta$ 44.12, 51.03

**IR (KBr)**: 3014, 2960, 2877, 1890, 1665, 1625, 1510, 1358, 1215 cm⁻¹
3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-hydroxyphenyl)-2H-xanthene-1,8(5H,9H)-dione

Molecular Formula \( C_{23}H_{26}O_4 \)
Molecular Weight \( (\text{gm-mol}^{-1}) \) 366.45
Melting Point \( (^\circ \text{C}) \) 246-248

\(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.10 (s, 1H), 6.91 (m, 2H), 6.63 (m, 2H), 4.76 (s, 1H), 2.45 (s, 4H), 2.20 (dd, 4H, J=16.0 Hz), 1.09 (s, 6H), 0.99 (s, 6H)

\( ^{13}\text{C NMR:} \) \( \delta \) 27.12, 29.56, 31.89, 32.10, 41.21, 51.24, 112.28, 112.96, 127.15, 135.84, 154.91, 163.21, 196.16

DEPT-135: Up Peaks: \( \delta \) 27.12, 29.56, 32.10, 112.96, 127.15
Down Peaks: \( \delta \) 41.21, 51.24

IR (KBr): 3681, 3608, 3019, 2965, 1655, 1512, 1426, 1362, 1215, 1198 cm\(^{-1}\)

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3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-hydroxy-3-methoxyphenyl)-2H-xanthene-1,8(5H,9H)-dione

Molecular Formula \( C_{24}H_{28}O_5 \)
Molecular Weight \( (\text{gm-mol}^{-1}) \) 396.48
Melting Point \( (^\circ \text{C}) \) 226-228

\(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 6.93 (m, 1H), 6.71 (m, 1H), 6.64 (m, 1H), 5.81 (s, 1H), 4.66 (s, 1H), 3.88 (s, 3H), 2.44 (s, 4H), 2.19 (dd, 4H, J=16.3 Hz), 1.10 (s, 6H), 1.01 (s, 6H)

\( ^{13}\text{C NMR:} \) \( \delta \) 27.31, 29.15, 31.98, 32.08, 42.36, 51.13, 55.92, 111.13, 113.16, 117.12, 120.54, 132.31, 145.56, 148.23, 162.21, 196.12

DEPT-135: Up Peaks: \( \delta \) 27.31, 29.15, 32.08, 55.92, 111.13, 117.12, 120.54
Down Peaks: \( \delta \) 42.36, 51.13

IR (KBr): 3692, 3581, 3155, 2964, 2228, 1645, 1509, 1362, 1164 cm\(^{-1}\)

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

Molecular Formula \( C_{23}H_{25}BrO_3 \)
Molecular Weight \( (\text{gm-mol}^{-1}) \) 429.35
Melting Point \( (^\circ \text{C}) \) 226-228

\(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.52-7.13 (m, 4H), 4.96 (s, 1H), 2.53 (s, 4H), 2.22 (dd, 4H, J=16.3 Hz), 1.11 (s, 6H), 1.08 (s, 6H)

\( ^{13}\text{C NMR:} \) \( \delta \) 27.54, 29.56, 32.42, 32.98, 41.66, 51.32, 112.77, 120.13, 124.96, 125.95, 126.43, 131.55, 134.25, 161.85, 195.91

DEPT-135: Up Peaks: \( \delta \) 27.54, 29.56, 32.98, 124.96, 125.95, 126.43, 131.55
Down Peaks: \( \delta \) 41.66, 51.32

IR (KBr): 2959, 273, 1674, 1664, 1622, 1355, 1207 cm\(^{-1}\)
3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(3-bromophenyl)-2H-xanthene-1,8(5H,9H)-dione

Molecular Formula: C_{23}H_{25}BrO_{3}

Molecular Weight (gm·mol⁻¹): 429.35

Melting Point (°C): 192-194

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.42-6.94 (m, 4H), 4.86 (s, 1H), 2.43 (s, 4H), 2.23 (dd, 4H, J=16.0 Hz), 1.21 (s, 6H), 1.10 (s, 6H)

\(^1^3\)C NMR: \(\delta\) 27.31, 29.51, 32.06, 32.51, 42.13, 51.24, 112.65, 122.89, 125.23, 127.21, 130.26, 131.86, 141.92, 162.23, 196.46

DEPT-135: Up Peaks: \(\delta\) 27.31, 29.51, 32.51, 125.23, 127.21, 130.26, 131.86
Down Peaks: \(\delta\) 42.13, 51.24

IR (KBr): 3020, 2965, 2886, 1594, 1215 cm⁻¹

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

Molecular Formula: C_{23}H_{25}FO_{3}

Molecular Weight (gm·mol⁻¹): 368.44

Melting Point (°C): 224-226

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.13 (m, 2H), 6.69 (m, 2H), 4.96 (s, 1H), 2.51 (s, 4H), 2.20 (dd, 4H, J=16.4 Hz), 1.10 (s, 6H), 1.01 (s, 6H)

\(^1^3\)C NMR: \(\delta\) 27.15, 29.08, 31.85, 32.02, 40.85, 50.01, 112.45, 116.23, 116.95, 125.45, 125.81, 139.08, 139.15, 157.06, 162.83, 196.42

DEPT-135: Up Peaks: \(\delta\) 27.15, 29.08, 32.02, 116.23, 116.95, 125.45, 125.81
Down Peaks: \(\delta\) 40.85, 50.01

IR (KBr): 3029, 2945, 2875, 1681, 1660, 1265, 1354, 1203 cm⁻¹

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

Molecular Formula: C_{25}H_{30}O_{5}

Molecular Weight (gm·mol⁻¹): 410.50

Melting Point (°C): 172-174

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 6.95 (m, 1H), 6.76-6.80 (m, 2H), 4.83 (s, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.48 (s, 4H), 2.19 (dd, 4H, J=16.4 Hz), 1.90 (s, 6H), 0.98 (s, 6H)

\(^1^3\)C NMR: \(\delta\) 27.18, 29.22, 31.62, 32.05, 42.06, 51.23, 54.21, 54.46, 111.94, 114.17, 114.26, 114.97, 126.24, 146.52, 152.23, 163.21, 195.86

DEPT-135: Up Peaks: \(\delta\) 27.18, 29.22, 32.05, 54.21, 54.46, 111.94, 114.26, 114.97
Down Peaks: \(\delta\) 42.06, 51.23

IR (KBr): 3385, 3025, 2964, 2834, 1719, 1668, 1596, 1467, 1371, 1221 cm⁻¹
3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(3,4-dimethoxyphenyl)-2H-xanthene-1,8(5H,9H)-dione

Molecular Formula: $C_{25}H_{30}O_{5}$
Molecular Weight (gm·mol$^{-1}$): 410.50
Melting Point (°C): 174-176

$^1$H NMR (400 MHz, CDCl$_3$): δ 6.67-6.81 (m, 3H), 4.78 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.51 (s, 4H), 2.18 (dd, 4H, J=16.0 Hz), 1.09 (s, 6H), 0.99 (s, 6H)
$^{13}$C NMR: δ 27.14, 29.34, 31.02, 32.12, 41.26, 51.02, 54.81, 54.96, 111.96, 113.19, 115.13, 116.23, 134.55, 148.48, 151.18, 164.23, 196.25
DEPT-135: Up Peaks: δ 27.14, 29.34, 32.12, 54.81, 54.96, 111.96, 115.13, 116.23 Down Peaks: δ 41.26, 51.02

IR (KBr): 3008, 2956, 2925, 2872, 1664, 1587, 1502, 1378 cm$^{-1}$

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

Molecular Formula: $C_{26}H_{32}O_{6}$
Molecular Weight (gm·mol$^{-1}$): 440.53
Melting Point (°C): 186-188

$^1$H NMR (400 MHz, CDCl$_3$): δ 6.37 (s, 2H), 4.98 (s, 1H), 3.84 (s, 6H), 3.80 (s, 3H), 2.58 (s, 4H), 2.20 (dd, 4H, J=16.0 Hz), 1.10 (s, 6H), 1.00 (s, 6H)
$^{13}$C NMR: δ 27.14, 29.23, 31.85, 32.06, 42.11, 51.08, 55.84, 55.99, 111.82, 112.26, 114.23, 116.12, 132.25, 146.25, 150.36, 162.59, 196.42
DEPT-135: Up Peaks: δ 27.14, 29.23, 32.06, 55.84, 55.99, 111.82, 114.23, 116.12 Down Peaks: δ 42.11, 51.08
IR (KBr): 3008, 2956, 2925, 2872, 1664, 1587, 1502, 1378 cm$^{-1}$

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

Molecular Formula: $C_{23}H_{26}O_{4}$
Molecular Weight (gm·mol$^{-1}$): 366.45
Melting Point (°C): 202-204

$^1$H NMR (400 MHz, CDCl$_3$): δ 6.97-7.02 (m, 3H), 6.78 (m, 1H), 5.92 (s, 1H), 5.18 (s, 1H), 2.52 (s, 4H), 2.21 (dd, 4H, J=16.3 Hz), 1.08 (s, 6H), 1.01 (s, 6H)
$^{13}$C NMR: δ 27.58, 28.94, 31.44, 32.16, 42.16, 50.66, 114.16, 115.94, 121.34, 123.65, 124.72, 127.96, 153.14, 162.31, 194.96
DEPT-135: Up Peaks: δ 27.58, 28.94, 32.16, 115.94, 121.34, 124.72, 127.96 Down Peaks: δ 42.16, 50.66
<table>
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<tr>
<th>Compound</th>
<th>Molecular Formula</th>
<th>Molecular Weight (gm-mol⁻¹)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
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<td>3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-furyl)-2H-xanthene-1,8(5H,9H)-dione</td>
<td>C₂₁H₂₄O₄</td>
<td>340.41</td>
<td>60-62</td>
</tr>
<tr>
<td>3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-thienyl)-2H-xanthene-1,8(5H,9H)-dione</td>
<td>C₂₁H₂₄O₃S</td>
<td>356.48</td>
<td>164-166</td>
</tr>
<tr>
<td>3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-pyridyl)-2H-xanthene-1,8(5H,9H)-dione</td>
<td>C₂₂H₂₅NO₃</td>
<td>351.44</td>
<td>204-206</td>
</tr>
</tbody>
</table>

**1H NMR (400 MHz, CDCl₃):**

- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-furyl)-2H-xanthene-1,8(5H,9H)-dione**
  - δ 6.92-6.98 (m, 2H), 6.28 (m, 1H), 5.20 (s, 1H), 2.50 (s, 4H), 2.24 (dd, 4H, J=16.0 Hz), 1.12 (s, 6H), 1.03 (s, 6H)
- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-thienyl)-2H-xanthene-1,8(5H,9H)-dione**
  - δ 7.82-7.98 (m, 2H), 6.78 (m, 1H), 4.92 (s, 1H), 2.53 (s, 4H), 2.26 (dd, 4H, J=16.0 Hz), 1.13 (s, 6H), 1.01 (s, 6H)
- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-pyridyl)-2H-xanthene-1,8(5H,9H)-dione**
  - δ 8.52 (m, 1H), 6.98-7.23 (m, 3H), 5.42 (s, 1H), 2.51 (s, 4H), 2.22 (dd, 4H, J=16.2 Hz), 1.13 (s, 6H), 0.99 (s, 6H)

**13C NMR:**

- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-furyl)-2H-xanthene-1,8(5H,9H)-dione**
  - δ 27.13, 29.14, 31.20, 34.60, 41.02, 49.36, 97.26, 111.20, 113.54, 142.23, 159.63, 163.05, 196.23
- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-thienyl)-2H-xanthene-1,8(5H,9H)-dione**
  - δ 27.18, 29.33, 31.02, 31.89, 41.06, 49.63, 113.69, 119.39, 124.01, 132.26, 136.25, 161.84, 196.33
- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-pyridyl)-2H-xanthene-1,8(5H,9H)-dione**
  - δ 27.54, 29.11, 32.22, 32.69, 41.36, 50.21, 111.47, 118.63, 122.46, 134.26, 149.26, 155.23, 163.23, 195.32

**DEPT-135:**

- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-furyl)-2H-xanthene-1,8(5H,9H)-dione**
  - Up Peaks: δ 27.13, 29.14, 34.60, 97.26, 113.54, 142.23
  - Down Peaks: δ 41.02, 49.36

- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-thienyl)-2H-xanthene-1,8(5H,9H)-dione**
  - Up Peaks: δ 27.18, 29.33, 31.89, 119.39, 124.01
  - Down Peaks: δ 41.06, 49.63

- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-pyridyl)-2H-xanthene-1,8(5H,9H)-dione**
  - Up Peaks: δ 27.54, 29.11, 32.69, 118.63, 122.46, 134.26, 149.26, 155.23, 163.23, 195.32
  - Down Peaks: δ 41.36, 50.21

**IR (KBr):**

- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-furyl)-2H-xanthene-1,8(5H,9H)-dione**
  - 2958, 2935, 2870, 1685, 1655, 1623, 1203 cm⁻¹
- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-thienyl)-2H-xanthene-1,8(5H,9H)-dione**
  - 2955, 2896, 2871, 1659, 1624, 1371, 1350, 1201 cm⁻¹
- **3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(2-pyridyl)-2H-xanthene-1,8(5H,9H)-dione**
  - 2958, 2935, 2870, 1685, 1655, 1623, 1203 cm⁻¹
Chapter 4

Figure 4.4.e.1 $^1$H NMR spectrum of compound 3a

Figure 4.4.e.2 $^{13}$C NMR spectrum of compound 3a
Figure 4.4e.3 DEPT-135 spectrum of compound 3a

Figure 4.4e.4 IR spectrum of compound 3a
Figure 4.4e.5 Mass spectrum of compound 3a

Figure 4.4e.6 ¹H NMR spectrum of compound 3b
Figure 4.4e.7 $^{13}$C NMR spectrum of compound 3b

Figure 4.4e.8 DEPT-135 spectrum of compound 3b
Figure 4.4e.9 IR spectrum of compound 3b

Figure 4.4e.10 Mass spectrum of compound 3b
Figure 4.4e.11 $^1$H NMR spectrum of compound 3c

Figure 4.4e.12 $^{13}$C NMR spectrum of compound 3c
Figure 4.4.e.13 DEPT-135 spectrum of compound 3c

Figure 4.4.e.14 IR spectrum of compound 3c
Figure 4.4e.15 Mass spectrum of compound 3c
4.4. REFERENCES


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