

Efficient and rapid solvent-free synthesis of 1,8-dioxo-octahydroxanthenes and 2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) under microwave irradiation condition

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Abstract : Efficient and rapid solvent-free methods have been developed for synthesis of 1,8-dioxo-octahydroxanthenes by microwave irradiation of cyclohexane-1,3-diones with aromatic aldehydes in presence of either amberlyst-15 or benzoic acid as catalyst. 2,2'-(Phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) could be obtained from the same starting materials by microwave irradiation either over neutral alumina or directly. All these methods are eco-friendly.

Keywords : 1,8-Dioxo-octahydroxanthenes, 2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones), microwave irradiation, cyclohexane-1,3-diones, amberlyst-15, neutral alumina.

Introduction

Xanthenes and their derivatives belong to an important class of organic compounds possessing a wide range of biological and pharmaceutical properties such as antiviral¹, antibacterial², anti-inflammatory³, antinociceptive⁴, antidepressant and antimalarial⁵ activities. They constitute a structural unit in a number of natural products⁶, and santalin pigments occurring in a number of plant species are major sources for xanthenes⁷. Furthermore, they find important applications in industries, viz. as leuco-dyes⁸, as pH sensitive fluorescent materials for the visualization of biomolecular assemblies⁹, in laser technology¹⁰, and in photodynamic therapy¹¹. Another important application of xanthenes is in the construction of new chiral bidentate phosphine ligands having potential to be used in catalytic processes¹². 1,8-Dioxo-octahydroxanthenes are very common synthetic compounds and the classical methods for their synthesis involve condensation of cyclohexane-1,3-diones with aldehydes using dif-

ferent acid catalysts¹³. Recently, use of some bases for effecting this condensation has also been reported¹⁴. The last five years have witnessed the development of a very good number of methods for synthesis of 1,8-dioxo-octahydroxanthenes and continuation of research in this area is in full vigor¹⁴⁻⁴⁰. These are mainly with a view to developing more and more rapid and eco-friendly methods. Our requirement for several 1,8-dioxo-octahydroxanthenes (4) in connection with some other research problems along with the current trend in developing environmentally benign methods for their synthesis encouraged us to undertake the present work.

Results and discussion

In order to get some 1,8-dioxo-octahydroxanthenes (4) we first undertook their synthesis by carrying out the reaction of dimedone (1a) and benzaldehydes under the condition recently reported by Das *et al.*^{13d}. As the quality of acetonitrile (the solvent used in the reaction by the

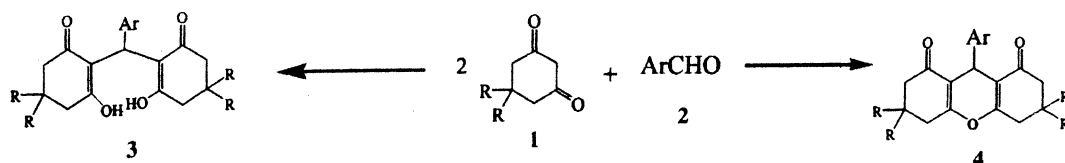
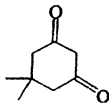
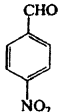
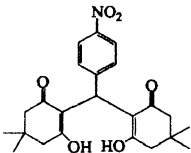
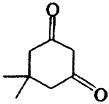
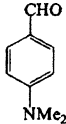
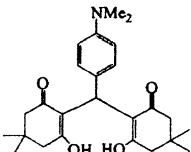


Table 1. Synthesis of 2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) (2)

Reaction condition : ^aReflux in ordinary distilled acetonitrile with added amberlyst-15; ^bMicrowave irradiation over neutral alumina;
^cMicrowave irradiation of only the mixture of the reactants

Entry	Cyclic 1,3-diketone	Aromatic aldehyde	Reaction time	Product (3)	Isolated Yield (%)	M.p. (°C) [lit. value]
1			4 h ^a 90 s ^b 90 s ^c	 3a	83 ^a 91 ^b 92 ^c	193–194 [194–195] ⁴¹
2			4 h ^a 90 s ^b 90 s ^c	 3b	77 ^a 81 ^b 80 ^c	262–263 [262–264] ^{14a}
3			4 h ^a 90 s ^b 90 s ^c	 3c	78 ^a 90 ^b 89 ^c	145–146 [144–146] ⁴¹
4			4 h ^a 90 s ^b 90 s ^c	 3d	76 ^a 91 ^b 93 ^c	172–173 [172–173] ⁴¹
5			5 h ^a 90 s ^b 90 s ^c	 3e	83 ^a 86 ^b 89 ^c	184–185 [183–185] ⁴¹
6			5 h ^a 90 s ^b 90 s ^c	 3f	82 ^a 85 ^b 88 ^c	205–206 [204–206] ^{14a}
7			5 h ^a 90 s ^b 90 s ^c	 3g	86 ^a 89 ^b 91 ^c	196–197 [196–198] ⁴¹

Table-1 (contd.)

8			5 h ^a 90 s ^b 90 s ^c		86 ^a 89 ^b 91 ^c	190–191 [190–191] ⁴³
9			8 h ^a 120 s ^b 120 s ^c		76 ^a 82 ^b 86 ^c	193–194 [193–194] ⁴³

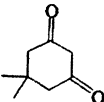
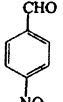
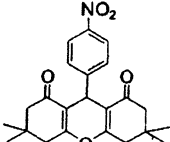
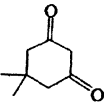
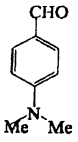
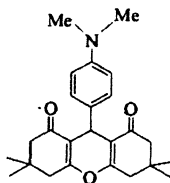
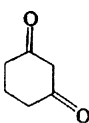
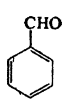
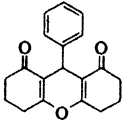
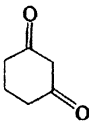
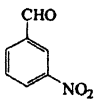
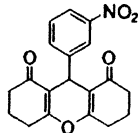
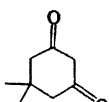
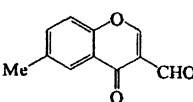
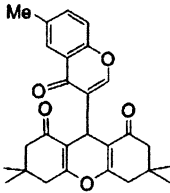
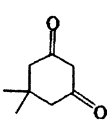
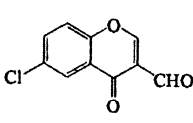
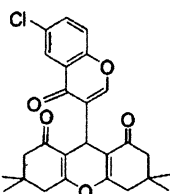
said group) was not specifically mentioned, initially ordinary distilled acetonitrile was used by us. By refluxing a mixture of dimedone and an aromatic aldehyde (mole ratio 2 : 1) in the said solvent with added amberlyst-15 for 4–5 h, instead of 1,8-dioxo-octahydroxanthenes (**4**), 2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) (**3**) were obtained. The results of nine such experiments are presented in Table 1. Repetition of the experiments by using P₂O₅-dried acetonitrile as the solvent, however, gave 1,8-dioxo-octa-hydroxanthenediones (**4**) as products in yields comparable to that reported by Das *et al.*^{13d}. We then endeavored to carry out this reaction using the same catalyst but avoiding any solvent. Thus, when a mixture of an aromatic aldehyde and dimedone or cyclohexane-1,3-dione (mole ratio 1 : 2) was subjected to microwave irradiation on neutral alumina supported amberlyst-15, 1,8-dioxo-octahydroxanthenes (**4**) were obtained in very good to excellent yield (Table 2). In our study neutral alumina was used as support for the catalyst amberlyst-15. But there is a possibility that the former is also playing some role in this condensation process. We therefore, performed the reaction of several aldehydes with dimedone over neutral alumina alone under microwave irradiation condition, when 2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) (**3**) were obtained in very good yield. We then studied the condensation of **1** and **2** under the influence of microwave without using any added catalyst or solid support. In this case also the correspond-

ing 2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) (**3**) were obtained. Thus, we report herein three methods for synthesizing **3**, all of which are good additions to the methods currently appearing in the literature^{36,41–45}. The yields of **3** in the methods developed by us are given in Table 1. One interesting observation in this connection was that for the combination **1a** and **2a** the 1,8-dioxo-octahydroxanthene **4a** was found to be formed either solely or partially when benzaldehyde distilled few days back was used, giving an indication that possibly benzoic acid present as contaminant in this sample of benzaldehyde has been functioning as a catalyst for dehydration in this case. This interested us to investigate the applicability of benzoic acid as an organocatalyst for direct synthesis of **4**. The result of this study is presented in Table 2, which shows that benzoic acid can act as organocatalyst, though a somewhat greater proportion of it (*ca.* 20–80 mole %) becomes necessary. Trifluoroacetic acid, a much stronger organic acid, was found to give somewhat better yield of **4a** (92%, 300 s irradiation) and **4b** (94%, 300 s irradiation) when it was added as catalyst in lower proportions (10 mole %). However, considering the corrosive and toxic nature of this acid, we did not proceed further with it. Regarding recycling of solid catalyst systems (i) amberlyst-15 over neutral alumina (for synthesis of **4**) or (ii) neutral alumina (for synthesis of **3**), it was observed that both of them can be recycled at least for three times without much decrease of the yield of the products.

Table 2. Synthesis of 1,8-dioxo-octahydroxanthenediones (3) by microwave irradiation under solvent-free condition

Entry	Cyclic 1,3-diketone (1)	Aromatic aldehyde (2)	Reaction		Product (4)	Isolated yield (%)	M.p. (°C) [lit. value]
			irradiation time (s)	[Mole % of benzoic acid w.r.t. aldehyde]			
1			50 ^a 360 ^b [36]			86 ^a 84 ^b	200–201 [198–200] ²³
2			50 ^a 360 ^b [36]			88 ^a 82 ^b	212–213 [212–214] ²³
3			50 ^a 360 ^b [36]			89 ^a 86 ^b	231–232 [230–232] ²³
4			50 ^a 360 ^b [36]			86 ^a 86 ^b	232–233 [231–233] ²³
5			50 ^a 360 ^b [45]			87 ^a 81 ^b	248–249 [248–250] ²³
6			50 ^a 360 ^b [45]			86 ^a 81 ^b	221–222 [221–222] ²⁴
7			50 ^a 360 ^b [30]			89 ^a 87 ^b	169–170 [170–171] ²⁴

Table-2 (contd.)

8			50 ^a 360 ^b [30]	 4h	95 ^a 91 ^b	221–222 [221–223] ²³
9			50 ^a 360 ^b [36]	 4i	86 ^a 86 ^b	225–226 [224–226] ²⁴
10			50 ^a 360 ^b [20]	 4j	86 ^a 86 ^b	269–270 [267–269] ²³
11			50 ^a 360 ^b [20]	 4k	89 ^a 86 ^b	286–287 [285–287] ²³
12			50 ^a 360 ^b [75]	 4l	82 ^a 79 ^b	Above 320
13			50 ^a 360 ^b [80]	 4m	83 ^a 78 ^b	Above 320

Most of the 1,8-dioxo-octahydroxanthenes (4) synthesized by us were known compounds, and they were characterized from their physical and spectral data.

Conclusion :

We have developed an efficient solvent-free methodology for synthesis of 1,8-dioxo-octahydroxanthenes (4) by amberlyst-15 catalyzed condensation of cyclohexane-

1,3-diones (1) and aromatic aldehydes under microwave irradiation condition. For effecting this conversion in acetonitrile using the same catalyst, perfectly dry solvent is necessary, otherwise 2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) (3) result due to non-occurrence of the final dehydration process. One more methodology for synthesizing 4 and two more for 3, as mentioned above, have been developed.

Experimental

All melting points were recorded on a K f ler block and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer (Spectrum BX II) in KBr pellets. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker AV-300 (300 MHz) spectrometer using TMS as internal standard. Analytical samples were routinely dried *in vacuo* at room temperature. Microanalytical data were recorded on a Perkin-Elmer 2400 Series II C, H, N analyzer. Mass spectrum (FAB-MS) was measured with a Jeol the M Station JMS.700 spectrometer. Column chromatography was performed with silica gel (100–200 mesh) and TLC with silica gel G made of SRL Pvt. Ltd. Petroleum ether had the boiling range 60–80 $^\circ\text{C}$. Amberlyst-15 used was made of Fluka Chemika. An unmodified domestic household microwave oven (LG, DMO, Model No. 556P, 900 watt) equipped with inverter technology, which provides a realistic control of the microwave power to the desired level (20–100%) was used for microwave heating. The MW oven was operated at reduced MW-power level of 60% (540 watt), and total power level 100% (900 watt).

General procedure for synthesis of 2,2'-(phenyl-methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-ones) (3) from aromatic aldehydes and dimedone under microwave irradiation condition :

(a) Over neutral alumina :

In a typical procedure, a solution of a mixture of dimedone (2 mmol), aromatic aldehyde (1 mmol) in DCM was added to neutral alumina (5 g), the solvent was removed by evaporation, and the resulting solid was irradiated with microwave for the time period mentioned in Table 1. After cooling, the solid was extracted with acetone and the concentrate of the extract was crystallized from acetone-petroleum ether to get pure product.

(b) By direct irradiation of a mixture of the reactants :

In a typical procedure, an intimate mixture of dimedone (2 mmol) and aromatic aldehyde (1 mmol) was irradiated with microwave for the time period mentioned in Table 1 and the resulting mass was crystallized from acetone-petroleum ether, which gave pure product.

Selected spectral data :

Compound **3c** : IR ν_{max} (KBr) : 3448 (OH), 2964,

1680 (C=O), 1661 (C=O), 1361, 1198, 1166, 1140, 1089, 852, 844 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 1.10 (6H, s, $2 \times -\text{CH}_3$), 1.21 (6H, s, $2 \times -\text{CH}_3$), 2.27–2.49 (8H, m, $4 \times \text{CH}_2$), 5.47 (1H, s, Ar-CH<), 7.01 (2H, d, J 8.9 Hz), 7.22 (2H, d, J 8.9 Hz), 11.86 (1H, s, OH); ^{13}C NMR (75 MHz, CDCl_3) : δ 27.3, 29.5, 31.3, 32.3, 46.4, 47.0, 115.3, 128.1, 128.3, 131.5, 136.6, 189.4, 190.6.

Compound **3d** : IR ν_{max} (KBr) : 3447 (OH), 2952, 1678 (C=O), 1661 (C=O), 1361, 1198, 1166, 1140, 1009, 852 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 1.10 (6H, s, $2 \times -\text{CH}_3$), 1.21 (6H, s, $2 \times -\text{CH}_3$), 2.27–2.49 (8H, m, $4 \times \text{CH}_2$), 5.45 (1H, s, Ar-CH<), 6.95 (2H, d, J 7.9 Hz), 7.37 (2H, d, J 8.5 Hz), 11.87 (1H, s, OH); ^{13}C NMR (75 MHz, CDCl_3) : δ 27.4, 29.5, 31.4, 32.5, 46.4, 47.0, 115.2, 119.6, 128.6, 131.3, 137.3, 189.4, 190.6.

General procedure for synthesis of 1,8-dioxo-octa-hydroxanthenes (4) by amberlyst-15 catalyzed condensation of aromatic aldehydes (2) with cyclohexane-1,3-diones (1) under microwave irradiation condition :

In a typical procedure, a mixture of a cyclic 1,3-diketone (2 mmol), aromatic aldehyde/chromone-3-aldehyde (1 mmol) in DCM was added to neutral alumina (5 g), the solvent was removed by evaporation, amberlyst-15 (100 mg) was added and thoroughly mixed. The whole mixture was taken in a Pyrex beaker (20 mL) and irradiated in the microwave oven for an appropriate time. After irradiation the mixture was cooled, shaken with acetone (10 mL) and filtered. The filtrate was concentrated and subjected to rapid column chromatography over silica gel using petroleum ether-ethyl acetate (6 : 4) as eluent to obtain the crystalline pure product. Majority of the products were known compounds (referred in Table 2). The products were characterized from their physical, analytical and spectral (IR and ^1H and ^{13}C NMR) data. The spectral data of some of the compounds (vide Table 2) are given below :

Compound **4b** : IR ν_{max} (KBr) : 2959, 1679, 1665, 1624, 1358, 1199, 1166, 1138, 1000, 824 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 0.99 (6H, s, $2 \times -\text{CH}_3$), 1.09 (6H, s, $2 \times -\text{CH}_3$), 2.15 (2H, d, J 16.1 Hz), 2.23 (2H, d, J 16.1 Hz), 2.23 (3H, s, Ar-CH₃), 2.45 (4H, s, $2 \times -\text{CO}-\text{CH}_2$), 4.70 (1H, s, Ar-CH<), 7.01 (2H, d, J 8.7 Hz, H-

3',5'), 7.16 (2H, d, *J* 8.7 Hz, H-2',6').

Compound **4e** : IR ν_{\max} (KBr) : 2958, 1679, 1667, 1608, 1511, 1370, 1261, 1235, 1195, 1165, 1138, 1034, 999, 824 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 0.99 (6H, s, $2 \times -\text{CH}_3$), 1.09 (6H, s, $2 \times -\text{CH}_3$), 2.15 (2H, d, *J* 16.3 Hz), 2.23 (2H, d, *J* 16.3 Hz), 2.45 (4H, s, $2 \times -\text{CO}-\text{CH}_2$), 3.73 (3H, s, Ar-OCH₃), 4.69 (1H, s, Ar-CH<), 6.75 (2H, d, *J* 7.8 Hz, H-3',5'), 7.14 (2H, d, *J* 7.8 Hz, H-2',6').

Compound **4j** : IR ν_{\max} (KBr) : 2961, 2929, 1650, 1592, 1373, 1160, 1060, 842, 774, 690 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 1.98–2.02 (4H, m, $2 \times -\text{CH}_2-$), 2.25–2.40 (4H, m, $2 \times -\text{CH}_2-$), 2.50–2.70 (4H, m, $2 \times -\text{CH}_2-\text{CO}-$), 4.76 (1H, s, Ar-CH<), 7.16–7.25 (5H, m, Ar-H).

Compound **4k** : IR ν_{\max} (KBr) : 2925, 1661, 1520, 1456, 1358, 1177, 1013, 962, 778 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 1.93–2.12 (4H, m, $2 \times -\text{CH}_2-$), 2.26–2.43 (4H, m, $2 \times -\text{CH}_2-$), 2.53–2.75 (4H, m, $2 \times -\text{CH}_2-\text{CO}-$), 4.88 (1H, s, Ar-CH<), 7.40 (1H, t, *J* 7.5 Hz, H-5'), 7.83 (1H, br. d, *J* 7.5 Hz, H-6'), 7.95–7.99 (2H, m, H-2',4').

Compound **4l** : IR ν_{\max} (KBr) : 2957, 1680 (C=O), 1654 (C=O), 1621, 1483, 1363, 1203, 1141, 1002, 817 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 0.97 (6H, s, $2 \times -\text{CH}_3$), 1.08 (6H, s, $2 \times -\text{CH}_3$), 2.15 (2H, d, *J* 16.2 Hz), 2.23 (2H, d, *J* 16.2 Hz), 2.38 (3H, s, CH₃), 2.41 (2H, d, *J* 17.7 Hz), 2.54 (2H, d, *J* 17.7 Hz), 4.49 (1H, s, Ar-CH<), 7.30 (1H, d, *J* 8.4 Hz), 7.39 (1H, dd, *J* 8.4 and 2.7 Hz), 7.85 (1H, d, *J* 2.6 Hz), 8.22 (1H, s, H-2 of chromone moiety); ^{13}C NMR (75 MHz, CDCl_3) : δ 20.9, 26.9, 27.1, 29.3, 32.1, 40.8, 50.9, 111.1, 117.9, 121.4, 124.6, 134.2, 134.6, 154.3, 156.1, 165.0, 176.9, 197.2. FABMS : *m/z* 433.5 (M+H)⁺ (Found : C, 75.11; H, 6.34. Calcd. for C₂₇H₂₈O₅ (432.50) : C, 74.98; H, 6.53%).

Compound **4m** : IR ν_{\max} (KBr) : 2958, 1681 (C=O), 1655 (C=O), 1466, 1440, 1363, 1202, 1142, 1002, 823 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 0.97 (6H, s, $2 \times -\text{CH}_3$), 1.09 (6H, s, $2 \times -\text{CH}_3$), 2.16 (2H, d, *J* 16.3 Hz), 2.39 (2H, d, *J* 16.5 Hz), 2.42 (2H, d, *J* 17.7 Hz), 2.54 (2H, d, *J* 17.7 Hz), 4.49 (1H, s, Ar-CH<), 7.36 (1H, d, *J* 8.9 Hz), 7.52 (1H, dd, *J* 8.9 and 2.5 Hz), 8.03 (1H, d, *J* 2.5 Hz), 8.24 (1H, s, H-2 of chromone moiety); ^{13}C

NMR (75 MHz, CDCl_3) : δ 27.0, 27.1, 29.3, 32.1, 40.8, 50.8, 110.8, 119.9, 121.8, 124.7, 125.7, 130.7, 133.3, 154.4, 156.3, 165.2, 175.7, 197.3.

General procedure for synthesis of 1,8-dioxo-octahydroxanthenes (4) by benzoic acid catalyzed condensation of aromatic aldehydes (2) with cyclohexane-1,3-diones (1) under microwave irradiation condition :

In a typical procedure, an intimate mixture of a cyclic 1,3-diketone (2 mmol), aromatic aldehyde/chromone-3-aldehyde (1 mmol) and benzoic acid (amount given in Table 2) was taken in a Pyrex beaker (20 mL) and irradiated in a microwave oven for an appropriate time. After irradiation the mixture was cooled, dissolved in CH_2Cl_2 (25 mL) and the CH_2Cl_2 layer was washed with saturated NaHCO_3 solution (2×25 mL). The concentrate of the CH_2Cl_2 extract was crystallized from CH_2Cl_2 -petroleum ether to get pure product.

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