



## Cupric Nitrate Catalyzed Efficient and Facile Synthesis of 1,8-Dioxo-octahydroxanthene Derivatives

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An efficient and convenient approach to the synthesis of 1,8-dioxo-octahydroxanthene derivatives by using catalytic amount (10 mol %) of cupric nitrate  $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$  in acetonitrile and the yields obtained are in good to excellent (75-96 %). The reaction is highly chemo selective and applicable to aldehydes only.

**Key Words:** 1,8-Dioxo-octahydroxanthene Derivatives, Acetonitrile, Cupric nitrate, Aldehydes.

### INTRODUCTION

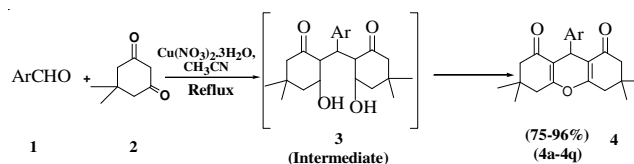
Xanthene derivatives have attracted considerable interest in recent years because of their promising activity as positive allosteric modulators of metabotropic (mGlu) receptors<sup>1</sup> and potent nonpeptidic inhibitors of recombinant human calpain I<sup>2</sup>. These have been used as rigid carbon skeletons for the construction of new chiral bidentate phosphine ligands with potential applications in catalytic processes<sup>3</sup>. In particular, xanthenediones constitute a structural unit in a number of natural products<sup>4</sup> and have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring<sup>5</sup> as well as synthetic derivatives and occupy a prominent position in medicinal chemistry<sup>6</sup>.

The synthesis of xanthenediones usually condenses appropriate active methylene carbonyl compounds with aldehydes catalyzed by sulfuric acid or hydrochloric acid<sup>7</sup>. Vranken *et al.*<sup>8</sup> described two-step synthesis of 9-aryl-6-hydroxy-3*H*-xanthen-3-one fluorophores by condensation of aryl aldehydes and fluoroescorcinol. Singh *et al.*<sup>9</sup> reported a new method for the preparation of xanthenediones through carbon transfer reactions of 1,3-oxazinanes and oxazolidines with carbon nucleophiles.

According to the availability and the economic viability of starting materials, various catalysts such as tetra butyl ammonium hexatungstate  $[\text{TBA}]_2[\text{W}_6\text{O}_{19}]$ <sup>10</sup>, tetrabutyl ammonium hydrogen sulphate<sup>11</sup>, samarium chloride<sup>12</sup>, calcium chloride in DMSO<sup>13</sup>,  $\text{H}_2\text{SO}_4$  in water<sup>14</sup>, MontK10<sup>15</sup>,  $\beta$ -cyclodextrin<sup>16</sup>, DOWEX-50W<sup>17</sup>, amino alcohol<sup>18</sup>, saccharin sulphonic acid<sup>19</sup>, diethyl ethoxymethylene malonate<sup>20</sup>, Silica supported sodium hydrogen sulphate<sup>21</sup>, *N*-bromosuccinimide<sup>22</sup>, benzyltriethyl

ammonium chloride<sup>23</sup>, *p*-dodecyl benzenesulfonic acid<sup>24</sup>,  $\text{InCl}_3$ / ionic liquid<sup>25</sup> and  $\text{Fe}^{3+}$ -mont<sup>26</sup>, have been reported for the synthesis of xanthenedione derivatives. In which some of them often involves the use of expensive reagents, hazard organic solvents and tedious workup.

However, due to their great importance, there still needs to be development of novel methods for the preparation of xanthenediones. With the increasing environmental concerns and the regulatory constraints faced in the chemical and pharmaceutical industries, development of environmentally friendly benign organic reactions has become a crucial and demanding research area in modern organic chemical research<sup>27</sup>. In continuation of our interest in the area of clean synthesis<sup>28</sup> herein, the synthesis of xanthenediones catalyzed by cupric nitrate in acetonitrile is reported (**Scheme-I**).



**Scheme-I:** Synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in acetonitrile

### EXPERIMENTAL

Chemicals were purchased from Fluka and S.D. Fine chemicals and directly used for the synthesis. Thin layer chromatography (TLC): precoated silica gel plates (60 F<sub>254</sub>, 0.2 mm layer; E. Merck). <sup>1</sup>H NMR (Avance 300 MHz) spectra were recorded in  $\text{CDCl}_3$  using TMS as internal standard.

Chemical shifts ( $\delta$ ) are reported in ppm, Melting points (m.p.) were determined on a Fischer-Johns melting point apparatus. IR and MS were recorded on a Thermo Nicolet Nexus 670 FT-IR Spectrometer and Finnegan MAT 1020 Mass spectrometer operating at 70 eV.

**General procedure:** To the stirred solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in acetonitrile (5 mL) were added successively 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (2 mM) and benzaldehyde (1 mM) and refluxed for the time specified in (Table-3). After completion of the reaction as indicated by TLC, the reaction mixture was washed with water and extracted into ether dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum, the obtained crude product was further purified by column chromatography using EtOAc/hexane (1:9) to afford the white solid of 3,3,6,6-tetramethyl-9-benzene-1,8-dioxo-octahydroxanthene is obtained in 96 % yield. All the compounds are known and gave satisfactory spectroscopic data in accordance to the reported data<sup>11,21-26</sup>.

## RESULTS AND DISCUSSION

In continuation of our interest in the development of a highly expedient methodology for the synthesis of fine chemicals like xanthenediones, which constitutes a structural unit in natural products and used as synthons because of the inbuilt pyran ring, we report here for the first time synthesis of 1,8 di-oxo-octahydroxanthene derivatives **4** from the conjugate addition of various aldehydes **1** and dimedone (5,5-dimethyl-1,3-cyclohexanedione) **2** in the presence of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in acetonitrile at reflux, as an efficient catalyst (**Scheme-I**).

Initially we have studied the efficacy of several metal nitrates chosen (10 mol % as standard) for the model reaction using dimedone (2 mmol) and benzaldehyde (1 mmol) in acetonitrile (5 mL) being refluxed for 7 h to afford the corresponding 3,3,6,6-tetramethyl-9-aryll,8-dioxo-octahydroxanthene derivatives and the results are presented in (Table-1). While comparing the effect of catalysts, we found that  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was more effective than other nitrates tested, in terms of isolated yield (96 %) (Table-1, Entry 7). We choose  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  as the suitable catalyst for further reactions due to its easy availability, cost effectiveness, easy handling, intrigued by these observations, we have then tested the efficacy of several copper salts available such as  $\text{Cu}(\text{OAc})_2$ ,  $\text{H}_2\text{O}$ ,  $\text{Cu}(\text{Cl}, \text{Br}, \text{I})$  along with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  for the model reaction and among the copper salts screened  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was found to be the best both in terms of reaction time and yields.

To examine the influence of effect of various solvents for the model reaction, we also carried out the model reaction in different organic solvents results are shown in (Table-2) and among screened, acetonitrile (96 %) (Entry 5) was found to be the best choice of solvent. An optimum amount of 10 mol % of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in acetonitrile is sufficient to carry forward the reaction. In the presence of catalyst at room temperature for 24 h did not yield the product. Encouraged by these results obtained for benzaldehyde we generalized the reaction scope for a number of other structurally divergent aromatic aldehyde and ketones. The reaction with aliphatic and aromatic ketones such as cyclohexanone and acetophenone were found to be

TABLE-1  
SCREENING OF VARIOUS METAL NITRATES  
FOR THE MODEL REACTION

Entry	Catalyst	Yield (%)
1	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	50
2	$\text{AgNO}_3$	NR
3	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	76
4	$\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	65
5	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	70
6	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	85
7	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	96
8	$\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$	40
9	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	NR
10	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	NR
11	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	45

<sup>a</sup>Isolated yields, NR = No reaction.

TABLE-2  
SCREENING OF VARIOUS SOLVENTS  
FOR THE MODEL REACTION

Entry	Solvent	Yield (%) <sup>a</sup>
1	DCM	NR
2	DMF	75
3	THF	30
4	$\text{H}_2\text{O}$	NR
5	$\text{CH}_3\text{CN}$	96
6	EtOAc	54
7	$\text{CHCl}_3$	50
8	DEA	NR
9	Ethanol	50

<sup>a</sup>Isolated yields, NR = No reaction.

unsuccessful. To study their behaviour under the optimized reaction parameters *i.e.*, 10 mol % of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in acetonitrile at reflux and summarizes the observations.

The nature of substituent's on aromatic ring showed some effect on this conversion. In general, electron rich counter parts such as hydroxy group, methoxy group, methyl group and so forth required less reaction times, than those of electron withdrawing groups such as (nitro group, halide) were employed and reacted well to give the corresponding, 1,8-dioxo-octahydroxanthene derivatives in good to excellent yields, without undergoing polymerization and isomerisation. There were some limitations for the  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  catalyzed reaction, surprisingly reaction with aliphatic aldehyde does not yield the desired product, instead which gives some by products. The possible mechanism to account for the reaction is Knoevenagel addition between aldehyde and dimedone and subsequently, water elimination of intermediate **3** (**Scheme-I**) resulted in the formation of desired product<sup>26</sup>. Hetero-aromatic aldehyde such as pyridine-2-carboxaldehyde survived well without the formation of any side product under the present reaction conditions giving the corresponding 1,8-dioxo-octahydroxanthene derivatives in moderate yields. All the products were well characterized (Table-3).

The efficiency and generality of the present cupric nitrate catalyzed protocol can be realized by comparing our result for the reaction of benzaldehyde with dimedone chosen as model substrate with those of some recently developed procedures by comparing with respect to the reaction times-mol % of the catalyst used and the yields. As it is evident from the previous data, our protocol is comparatively better in terms of

TABLE-3  
SYNTHESIS OF 1,8-DIOXO-OCTAHYDROXANTHENES\* CATALYZED BY  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  IN ACETONITRILE

Entry	Aldehyde	$\tau$ (h)	Product	Yield (%)	m.p. ( $^\circ\text{C}$ )		Ref.
					(Found)	(Reported)	
1	$\text{C}_6\text{H}_5$	7.0	<b>4a</b>	96	203-204	204-205	11 <sup>b</sup>
2	4-ClC <sub>6</sub> H <sub>4</sub>	9.0	<b>4b</b>	89	228-231	230-231	11 <sup>b</sup>
3	4-HOC <sub>6</sub> H <sub>4</sub>	7.0	<b>4c</b>	88	245-247	246-247	11 <sup>b</sup>
4	2-HOC <sub>6</sub> H <sub>4</sub>	7.0	<b>4d</b>	93	203-205	205-206	18
5	3-HOC <sub>6</sub> H <sub>4</sub>	7.0	<b>4e</b>	81	224-226	225-227	26
6	4-HO-3-CH <sub>3</sub> OC <sub>6</sub> H <sub>3</sub>	7.0	<b>4f</b>	90	228-229	226-228	26
7	$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	7.0	<b>4g</b>	90	176	175-177	11 <sup>b</sup>
8	2-ClC <sub>6</sub> H <sub>4</sub>	8.5	<b>4h</b>	94	227	224-226	11 <sup>b</sup>
9	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	9.5	<b>4i</b>	91	169-170	171-172	11 <sup>b</sup>
10	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	9.5	<b>4j</b>	90	221-222	222	11 <sup>b</sup>
11	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	7.0	<b>4k</b>	90	218-219	217-218	11 <sup>b</sup>
12	4-BrC <sub>6</sub> H <sub>4</sub>	9.0	<b>4l</b>	90	233	234-236	18
13	4-FC <sub>6</sub> H <sub>4</sub>	9.0	<b>4m</b>	75	225	224-226	18
14	2-C <sub>5</sub> H <sub>4</sub> N	9.0	<b>4n</b>	80	187-189	188-190	11 <sup>b</sup>
15	3-ClC <sub>6</sub> H <sub>4</sub>	8.0	<b>4o</b>	80	182-183	183-184	11 <sup>b</sup>
16	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	7.0	<b>4p</b>	82	244-245	242-245	18
17	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	7.0	<b>4q</b>	86	186-188	190-191	18

\*All the products are characterized by <sup>1</sup>H NMR, mass and IR spectral analysis.

ready availability, easy handling, cost effectiveness and remarkably low toxicity with most of the recently reported catalysts.

#### Spectral data for selected compounds

**3,3,6,6-Tetramethyl-9-benzene-1,8-dioxo-octahydroxanthene (4a):** IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3154, 1668, 1356, 1274, 1201, 1198, 1138, 867. <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 0.98 (s, 6H, 2CH<sub>3</sub>), 1.12 (s, 6H, 2CH<sub>3</sub>), 2.20 (dd, 4H, 2CH<sub>2</sub>), 2.43 (s, 4H, 2CH<sub>2</sub>), 4.70 (s, 1H, CH), 6.74 (m, 2H, ArH), 6.95(m,3H, ArH); EI MS (m/z): 350 (M<sup>+</sup>).

**3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene (4b):** IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3086, 2989, 1689, 1664, 1640, 1617, 1497, 1366, 1194, 1142, 1121, 1094, 1021, 846. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 0.88 (s, 6H, 2CH<sub>3</sub>), 1.01 (s, 6H, 2CH<sub>3</sub>), 2.19 (dd, 4H, 2CH<sub>2</sub>), 2.51 (dd, 4H, 2CH<sub>2</sub>), 4.72 (s, 1H, CH), 7.52-8.10 (m, 4H, ArH); EI MS (m/z): 385 (M + 1).

**3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene (4j):** IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3081, 2957, 1666, 1641, 1542, 1492, 1368, 1219, 1170, 1145, 1121, 822, 748. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm) 0.96 (s, 6H, 2CH<sub>3</sub>), 1.09 (s, 6H, 2CH<sub>3</sub>), 2.15 (dd, 4H, 2CH<sub>2</sub>), 2.59 (s, 4H, 2CH<sub>2</sub>), 4.48 (s, 1H, CH), 7.16-7.26 (m, 4H, ArH); EI MS (m/z): 396 (M + 1).

**3,3,6,6-Tetramethyl-9-(4-bromophenyl)-1,8-dioxo-octahydroxanthene (4l):** IR(KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3442, 2932, 1660, 1585, 1362, 1274, 1201, 1138, 1047, 694, 572. <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm), 0.99 (s, 6H, 2CH<sub>3</sub>); 1.11 (s, 6H, 2CH<sub>3</sub>); 2.10-2.23 (q, 4H, 2CH<sub>2</sub>); 2.42 (s, 4H, 2CH<sub>2</sub>); 4.63 (s, 1H, CH); 7.12-7.23 (m, 4H, Ar); EI MS (m/z): 429 (M<sup>+</sup>).

**3,3,6,6-Tetramethyl-9-(pyridine-2yl)-1,8-dioxo-octahydroxanthene (4n):** IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3305, 1685, 1543, 1011, 874. <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 0.96 (s, 6H, 2CH<sub>3</sub>) 1.12 (s, 6H, 2CH<sub>3</sub>), 2.25 (dd, 4H, 2CH<sub>2</sub>) 2.54 (s, 4H, 2CH<sub>2</sub>), 4.71 (s, 1H, CH) 7.35-7.92 (m, 4H, Py); EI MS (m/z): 352 (M + 1).

#### Conclusion

A practical and new procedure is developed for the synthesis of 1,8-dioxo-octahydroxanthene derivatives using  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  as catalyst. The present protocol has several advantages, mild reaction conditions, readily available, inexpensive catalyst, easy handling, excellent yields, greater selectivity, operational and experimental simplicity. Study of wide range of structurally divergent aldehydes we believe that,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  catalyzed methodology will definitely be a valuable addition to the existing process in the field of synthesis of 1,8-dioxo-octahydroxanthene derivatives.

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