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An efficient solvent-free synthesis of 1,8-dioxo-octahydroxanthenes using $Fe_2(SO_4)_3.7H_2O$ as catalyst

Reyhaneh Khoeiniha[a], Ali Ezabadi[a,*], Abolfazl Olyaei[b]

[a]*Department of Chemistry, Faculty of Sciences, Central Tehran Branch, Islamic Azad University, P.O. BOX 14676-86831,Tehran, Iran*

[b]*Department of Chemistry, Payame Noor University, P.O. BOX 19395-3697, Tehran, Iran*

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Abstract

A facile and efficient protocol for the synthesis of 1,8-dioxo-octahydroxanthenes has been developed by one-pot Knoevenagel condensation, Michael addition and cyclodehydration reaction of dimedone (active methylene carbonyl compound) with aromatic aldehydes in the presence of Iron (III) sulfate hydrate as a solid acidic catalyst under solvent-free conditions. Various aromatic aldehydes were utilized in the reaction and in all situations the desired product were synthesized successfully. The present methodology is cost-effective in addition to other advantages like high yields of products in shorter reaction time and simple workup procedure. The non toxicity and easy availability of the catalyst makes this protocol efficient and environmentally benign.

Keywords: Xanthene; iron (III) sulfate hydrate; dimedone; aromatic aldehyde.

Introduction

Xanthenes and their substituted derivatives are useful targets for chemical synthesis as they have been associated with a diverse range of therapeutic and pharmacological properties such as antiviral [1] and antibacterialactivity [2]. Apart from these applications, they are used in photodynamic therapy [3], as dyes in laser technology and as a pH sensitive fluorescent material for the

*Corresponding author: Ali Ezabadi
Tel: +98 (912) 3712768, Fax: +98 (21) 88385798
E-mail: aliezabadi@yahoo.com

visualization of biomolecular assemblies [4-8]. Naturally occurring, santalin pigment isolated from a number of plant species is among the major sources of xanthenes [9-11]. In the literature, several methods have been reported for the preparation of xanthenes and xanthene substitutes, which include cyclodehydrations [12-13], trapping of benzynes by phenols [14-15], cyclocondensations between 2-hydroxy aromatic aldehydes, 2-tetralone [16] and SmI_2-HMPA mediated phenyl-carbonyl coupling reactions [17]. There are several reports on the synthesis of 1,8-dioxo-octahydroxanthene derivatives employing aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione, catalyzed by various acidic catalysts such as *ρ*-dodecylbenzene sulfonic acid [18], amberlyst-15 [19], Fe^{3+}-montmorillonite [20], $NaHSO_4$-SiO_2 or silica chloride [21], PMA-SiO_2 [22], SiO_2-R-SO_3H [23], DABCO-bromine in aqueous media [24], (SO_4^{-2}/ xFe-Zr-O) [25] and VSA NRs [26]. Each of these methods has its advantages and disadvantages such as prolonged reaction time, tedious work-up processes, low yield, the use of toxic organic solvents and harsh reaction conditions. Hence, the development of clean, high-yielding and environmentally benign approaches is still desirable and much in demand. Design of solvent-free catalytic reaction has received tremendous attention in recent years in the area of green synthesis [27].

$Fe_2(SO_4)_3.xH_2O$ is an inexpensive, non-toxic, and commercially available compound that is used as a Lewis acid catalyst for various organic transformations [28]. We report herein a straightforward one-pot method for the synthesis of xanthenedione derivatives by the condensation of various aldehydes with dimedone under solvent-free conditions. To the best of our knowledge, this is the first report for the synthesis of 1,8-dioxo-octahydroxanthenes using $Fe_2(SO_4)_3.7H_2O$ as a solid acidic catalyst.

Experimental

All commercially available chemicals and reagents were used without further purification. Melting points were determined with an Electrothermal model 9100 apparatus and are uncorrected. IR spectra were recorded on a Jasco 410 spectrophotometer. The ^1H NMR spectra were recorded in

$CDCl_3$ on Bruker DRX-300 AVANCE spectrometer. Chemical shifts (δ) are reported in ppm and are referenced to the NMR solvent.

General procedure for the preparation of 1,8-dioxo-octahydroxanthenes 3

A mixture of dimedone (2 mmol), aldehyde (1mmol) and $Fe_2(SO_4)_3.7H_2O$ (10 mol %) was stirred at 120 °C for the appropriate times as indicated in Table 2. The progress of the reaction was monitored by TLC. After completion, 10 mL hot water was added to the mixture to dissolve the catalyst. The resulting solid product was collected by filtration. The residue was crystallized by ethanol to obtain pure 9-aryl-1,8-dioxo-octahydroxanthene **3** as crystalline solid.

9-Phenyl-1,8-dioxo octahydroxanthene (3a)

Yield 86%, IR (KBr) (υmax, cm^{-1}): 3042, 2954, 1663, 1459, 1365, 1198; ^1H NMR (300 MHz, $CDCl_3$); 0.98 (s, 6H, 2×CH_3), 1.10 (s, 6H, 2×CH_3), 2.19 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.46 (s, 4H, 2×CH_2), 4.74 (s, 1H, CH), 7.07-7.29 (m, 5H, Ar-H).

9-(4-Bromophenyl)-dioxo-octahydroxanthene (3b)

Yield 86%, IR (KBr) (υmax, cm^{-1}): 3051, 2955, 1663, 1477, 1364, 1195; ^1H NMR (300 MHz, $CDCl_3$); 0.97 (s, 6H, 2×CH_3), 1.09 (s, 6H, 2×CH_3), 2.18 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.45 (s, 4H, 2×CH_2), 4.69 (s, 1H, CH), 7.17 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-H), 7.31 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-H).

9-(4-Cholorophenyl)-dioxo-octahydroxanthene (3c)

Yield 93%, IR (KBr) (υmax, cm^{-1}): 3069, 2957, 1663, 1479, 1365, 1197; ^1H NMR (300 MHz, $CDCl_3$); 0.98 (s, 6H, 2×CH_3), 1.10 (s, 6H, 2×CH_3), 2.19 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.46 (s, 4H, 2×CH_2), 4.71 (s, 1H, CH), 7.16-7.21 (m, 4H, Ar-H).

9-(3-Chlorophenyl)-dioxo-octahydroxanthene (3d)

Yield 80%, IR (KBr) (υmax, cm^{-1}): 3073, 2959, 1665, 1465, 1424, 1364, 1198, 1159; ^1H NMR (300 MHz, $CDCl_3$); 1.00 (s, 6H, 2×CH_3), 1.11 (s, 6H, 2×CH_3), 2.21 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2); 2.48 (s, 4H, 2×CH_2), 4.73 (s, 1H, CH), 7.09-7.20 (m, 4H, Ar-H).

9-(4-Hydroxyphenyl)-dioxo-octahydroxanthene (3e)

Yield 92%, IR (KBr) (υmax, cm^{-1}): 3405, 2960, 1657, 1613, 1457, 1365, 1198; ^1H NMR (300 MHz, $CDCl_3$); 0.99 (s, 6H, 2×CH_3), 1.09 (s, 6H,

2×CH_3), 2.20 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.45 (s, 4H, 2×CH_2), 4.66 (s, 1H, CH), 6.57 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-H), 7.09 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-H).

9-(3-Hydroxyphenyl)-dioxo-octahydroxanthene (3f)

Yield 82%, IR (KBr) (υmax, cm^{-1}): 3364, 3069, 2959, 1661, 1599, 1457, 1362, 1256, 1198, 1150; ^{1}H NMR (300 MHz, $CDCl_3$); 1.00 (s, 6H, 2×CH_3), 1.10 (s, 6H, 2×CH_3), 2.22 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.47 (s, 4H, 2×CH_2), 4.74 (s, 1H, CH), 6.58-7.05 (m, 4H, Ar-H).

9-(4-Nitrophenyl)-dioxo-octahydroxanthene (3g)

Yield 80%, IR (KBr) (υmax, cm^{-1}): 3071, 2956, 1660, 1518, 1353, 1199; ^{1}H NMR (300 MHz, $CDCl_3$); 0.97 (s, 6H, 2×CH_3), 1.10 (s, 6H, 2×CH_3), 2.21 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.50 (s, 4H, 2×CH_2), 4.83 (s, 1H, CH), 7.46 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-H), 8.07 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-H).

9-(3-Nitrophenyl)-dioxo-octahydroxanthene (3h)

Yield 94%, IR (KBr) (υmax, cm^{-1}): 3019, 2961, 1666, 1595, 1529, 1351, 1197, 1003; ^{1}H NMR (300 MHz, $CDCl_3$); 0.99 (s, 6H, 2×CH_3), 1.11 (s, 6H, 2×CH_3), 2.20 (ABq, $^2J_{HH}$ = 5.6 Hz, 4H, 2×CH_2), 2.48 (s, 4H, 2×CH_2), 5.25 (s, 1H, CH), 7.39-7.99 (m, 4H, Ar-H).

9-(2-Nitrophenyl)-dioxo-octahydroxanthene (3i)

Yield 85%, IR (KBr) (υmax, cm^{-1}): 3037, 2959, 1671, 1528, 1355, 1203, 1158, 1013; ^{1}H NMR (300 MHz, $CDCl_3$); 1.00 (s, 6H, 2×CH_3), 1.09 (s, 6H, 2×CH_3), 2.18 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.46 (s, 4H, 2×CH_2), 5.51 (s, 1H, CH), 6.99-7.76 (m, 4H, Ar-H).

9-(2-Bromophenyl)-dioxo-octahydroxanthene (3j)

Yield 78%, IR (KBr) (υmax, cm^{-1}): 3070, 2950, 1615, 1520, 1353, 1200, 1152, 1102; ^{1}H NMR (300 MHz, $CDCl_3$); 1.00 (s, 6H, 2×CH_3), 1.08 (s, 6H, 2×CH_3), 2.18 (ABq, $^2J_{HH}$ = 12.4 Hz, 4H, 2×CH_2), 2.45 (s, 4H, 2×CH_2), 5.02 (s, 1H, CH), 6.95 (t, 1H, $^3J_{HH}$ = 6.4 Hz, Ar-H), 7.17 (t, 1H, $^3J_{HH}$ = 6.8 Hz, Ar-H), 7.32 (s, 1H, Ar-H), 7.42 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Ar-H).

9-(4-Flurophenyl)-dioxo-octahydroxanthene (3k)

Yield 75%, IR (KBr) (υmax, cm^{-1}): 3052, 2956, 1661, 1520, 1345, 1190; ^{1}H NMR (300 MHz, $CDCl_3$); 0.91 (s, 6H, 2×CH_3), 1.04 (s, 6H, 2×CH_3), 2.06 (ABq, $^2J_{HH}$ = 16.0 Hz, 4H, 2×CH_2), 2.39 (s, 4H, 2×CH_2), 4.65 (s, 1H, CH),

6.83-6.80 (m, 2H, Ar-H), 7.16-7.18 (m, 2H, Ar-H).

9-(4-*N,N*-Dimethylaminophenyl)-dioxo-octahydroxanthene (3l)

Yield 77%, IR (KBr) (υmax, cm^{-1}): 3045, 2957, 1663, 1613, 1517, 1464, 1362, 1197; ^1H NMR (300 MHz, $CDCl_3$); 0.99 (s, 6H, 2×CH_3), 1.09 (s, 6H, 2×CH_3), 2.20 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.46 (s, 4H, 2×CH_2), 2.89 (s, 6H, NMe_2), 4.66 (s, 1H, CH), 6.68- 7.16 (m, 2H, Ar-H), 7.16- 7.18 (m, 2H, Ar-H).

9-(3-Metoxyphenyl)-dioxo-octahydroxanthene (3m)

Yield 71%, IR (KBr) (υmax, cm^{-1}): 3041, 2956, 1665, 1457, 1363, 1270, 1199, 1047; ^1H NMR (300 MHz, $CDCl_3$); 1.00 (s, 6H, 2×CH_3), 1.09 (s, 6H, 2×CH_3), 2.21 (ABq, $^2J_{HH}$ = 16.2 Hz, 4H, 2×CH_2), 2.45 (s, 4H, 2×CH_2), 3.76 (s, 3H, OCH_3); 4.73 (s, 1H, CH), 6.63-6.66 (m, 1H, Ar-H); 6.58-6.88 (m, 2H, Ar-H), 7.10-7.15 (m, 1H, Ar-H).

Results and discussion

The exploration of an appropriate reaction condition is of crucial importance for the targeted synthesis. In this work, initially, the condensation reaction of benzaldehyde and dimedone as a simple model substrate was investigated to establish the feasibility of the strategy and to optimize the reaction conditions.

In the beginning, the model reaction was carried out in the absence of catalyst at 120 ^oC under solvent-free conditions. The trace product **3a** was obtained after running the reaction for 1.5 h (Table 1, Entry 8). To improve the yield, $Fe_2(SO_4)_3.7H_2O$ (10 mol %) as a solid acidic catalyst was tested at 25-120 ^oC. The results showed that 120 ^oC was the best temperature for occurring cyclization as indicated in Table 1. Performing the reaction with a higher catalyst loading 20 mol % had no significant effect on yield. However, if the amount of the catalyst was reduced to 5 mol %, the product yield was reduced to 45 % (Table 1, Entry 7). With $Fe_2(SO_4)_3.7H_2O$ (10 mol %) as catalyst, the condensation reaction was tested in different solvents such as H_2O, CH_2Cl_2, EtOH, EtOAc, $CHCl_3$, CH_3CN and CH_3COCH_3 under reflux conditions (Table 1). The results showed clearly low product yield. However, solvent-free condition is an effective method for this three-component condensation reaction in the presence of iron (III) sulfate hydrate. To our delight, the reaction worked very well under solvent-free conditions at 120 ^oC under

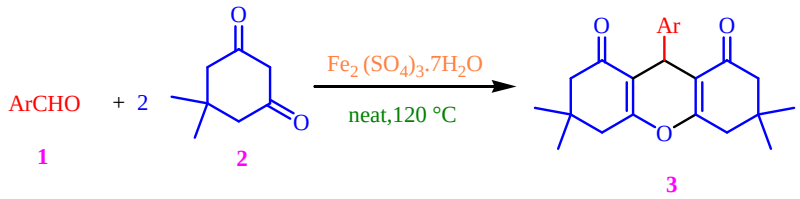
the catalysis of 10 mol % $Fe_2(SO_4)_3.7H_2O$ to give 1,8-dioxo-octahydroxanthene (**3a**) in 86% yield. With these encouraging results in hand, we turned to explore the scope of the reaction using different aromatic aldehydes as substrate under the optimized reaction conditions (Scheme 1). It was observed that the aromatic aldehydes with electron donating as well as electron withdrawing groups reacted successfully to furnish the final product in high yields (Table 2).

Table1. Optimization for the synthesis of **3a**[a]

Entry	Solvent	$Fe_2(SO_4)_3.7H_2O$ (mol %)	Temperature (°C)	Time (h)	Yield[b]
1	-	10	25	7	trace
2	-	10	60	7	trace
3	-	10	80	7	trace
4	-	10	100	2	43
5	-	10	120	1.5	86
6	-	20	120	1.5	86
7	-	5	120	1.5	45
8	-	-	120	1.5	trace
9	H_2O	10	reflux	8	trace
10	CH_2Cl_2	10	reflux	8	46
11	EtOH	10	reflux	8	49
12	EtOAc	10	reflux	8	49
13	$CHCl_3$	10	reflux	8	54
14	CH_3CN	10	reflux	8	57
15	CH_3COCH_3	10	reflux	8	78

[a]Reaction conditions: benzaldehyed (1 mmol), dimedone (2 mmol).

[b]Isolated yield



Scheme 1. Synthesis of 1,8-dioxo-octahydroxanthene catalyzed by $Fe_2(SO_4)_3.7H_2O$

Table 2. Synthetic results of 1,8-dioxo-octahydroxanthenes **3a-l**

Entry	Ar	Products	Time (h)	Yield (%)	Mp (°C)	
					Found	Reported [Lit]
1	C_6H_5	**3a**	1.5	86	203-205	203-204 [29]
2	4-BrC_6H_4	**3b**	1	86	230-232	229-232 [24]
3	4-ClC_6H_4	**3c**	1.3	93	231-233	230-233 [20]
4	3-ClC_6H_4	**3d**	4.5	80	190-191	190-192 [30]
5	4-OHC_6H_4	**3e**	3.2	92	245-246	245-247 [31]
6	3-OHC_6H_4	**3f**	3.2	82	217-219	215-218 [30]
7	4-$NO_2C_6H_4$	**3g**	1.3	80	222-223	221-223 [24]
8	3-$NO_2C_6H_4$	**3h**	2.4	94	168-170	167-170 [24]
9	2-$NO_2C_6H_4$	**3i**	3.5	85	259-260	258-262 [30]
10	2-BrC_6H_4	**3j**	4.5	78	227-229	226-228 [32]
11	4-FC_6H_4	**3k**	2	75	223-225	224-225 [33]
12	4-$(NMe_2)C_6H_4$	**3l**	4.5	77	220-222	221-223 [34]
13	3-$(MeO)C_6H_4$	**3m**	4.2	71	164-166	162-165 [30]

In order to demonstrate the merites of the present method in comparision with other reported methods in the synthesis of xanthenediones with 4-chlorobenzaldehyde, we have tabulated some of the results in Table 3. The results show the promising feature of this method in terms of reaction rate and the yield of the product with those reported in the literature. Additionally, the present catalyst seems to be more beneficial from the economical and accessibility point of view (Entry 7).

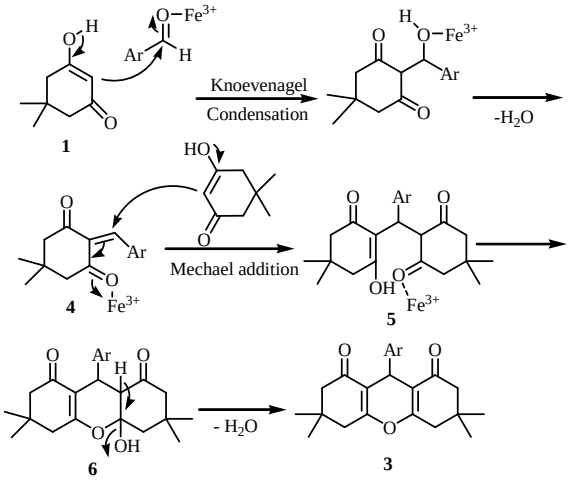
Table 3. Studying efficiency of the presence method over some reported catalysts

Entry	Catalyst	Conditions	Time (h)	Yield (%)	Ref.
1	Fe^{3+}-montmorillonite	EtOH/reflux	6	88	[20]
2	DABCO-bromine	H_2O/reflux	2.5	80	[24]
3	$HClO_4$-SiO_2	Neat/140 °C	3	30.8	[30]
4	PPA-SiO_2	Neat/140 °C	0.5	84.6	[30]
5	TBAHS	1,4-dioxane + H_2O/reflux	3	92	[34]
6	30 wt.% HPWA/MCM-41	EtOH/ 90 °C	5	84	[35]
7	$Fe_2(SO_4)_3.7H_2O$	Neat/ 120 °C	1.3	93	Present work

A possible mechanism for this reaction is shown in Scheme 2. The catalyst initially acts as a Lewis acid to activate aldehyde. Subsequently, the reaction proceeds through the nucleophilic addition of dimedone to aldehyde *via* Knoevenagel condensation and intermediate **4** was obtained by dehydration. Then, Michael addition of dimedone to activated intermediate **4** followed by cyclization through the intramolecular nucleophilic addition of hydroxy to carbonyl in intermediate **5** provides intermediate **6** which on dehydration afforded the product **3**.

Conclusion

In conclusion, we have reported herein iron (III) sulfate hydrate catalyzed highly efficient, one-pot Knoevenagel condensation, Michael addition and cyclodehydration synthesis of 1,8-dioxo-octahydroxanthene derivatives (**3a**–**m)** by the condensation of aromatic aldehydes and dimedone under solvent-free conditions in high to excellent yields. The remarkable catalytic activity exhibited that our method is convincingly superior to the other recently reported catalytic methods with respect to the reaction time, amount of catalyst and the pure products were obtained by simple crystallization. Easy work up, simple experimental procedure, solvent-free reaction conditions, utilization of an inexpensive and readily available catalyst, high to excellent yields of products, make the procedure an attractive alternative to the existing methods for the synthesis of 1,8-dioxo-octahydroxanthenes**.**



Scheme 2. Plausible mechanism for the synthesis of xanthene **3**

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