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ONE-POT CONDENSATION APPROACH FOR THE SYNTHESIS OF SOME 1,8-DIOXO-OCTAHYDROXANTHENES AND 14-ARYL-14*H*-DIBENZO[*a,j*]XANTHENES USING LACTIC ACID AS AN EFFICIENT AND ECO-FRIENDLY CATALYST

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Abstract: The synthesis of some biologically important xanthenes, by efficient and convenient approach for one-pot condensation reaction of aldehydes and dimedone or β-naphthol in the presence of lactic acid as an efficient, inexpensive and environmental friendliness catalyst under solvent-free conditions, is presented. The merits of this reaction are higher product yields in shorter reaction time and environmentally benign reaction conditions.

***Keywords*:** xanthenes, environmental friendliness, lactic acid, solvent-free.

Introduction

Critical role of heterocycles is distinguished in the design and synthesis of bioactive small molecules. Among the many heteroaromatic

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compounds, xanthenes and benzoxanthenes as one of the important classes of organic compounds have received significant attention for many pharmaceutical and organic researchers essentially due to their vast biological and pharmaceutical potent, such as antiviral,[1] antibacterial,[2] and antimalarial[3]. Xanthenes also have been used as dyes,[4,5] fluorescent materials,[6] and in laser technologies[7]. According to the literature data, various catalysts have been used for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes and 1,8-dioxo-octahydroxanthenes such as Dowex-50W,[8] silica sulfuric acid,[9] $[Et_3N\text{-}SO_3H]Cl$,[10] 1,3,5-trichloro-2,4,6-triazinetrion,[11] *o*-sulfonated poly(4-vinylpyrrolidonium)chloride,[12] acetic acid,[13] and $[n\text{-}Pr_2NH_2][HSO_4]$[14].

In the multi-component reactions (MCRs) protocol, several simple starting substrates are involved in a single reaction vessel to generate molecular complexity which possesses substantial elements of all the reactants.[15] MCRs have demonstrated to be a privileged asset in organic and medicinal chemistry owing to their application in synthesis of multi-functionalized and structurally diverse drug-like chemical entities.[16] These reactions in conjunction with solvent-free conditions as one of the key green chemistry protocols present notable evolutions, such as easier work up, decrease in reaction times, increase in yield, avoiding the use of toxic solvents, and minimizing waste generation.[17]

As a part of our ongoing efforts towards the development of greener catalytic systems for important organic conversions,[18-21] we had recently explored the catalytic potential of lactic acid as an efficient, non toxic, commercially available, high yielding, and inexpensive catalyst for the synthesis of various 1,8-dioxo-octahydroxanthene and 14-aryl-14*H*-

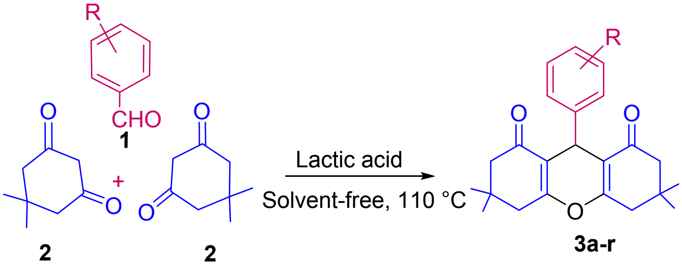
dibenzo[*a,j*]xanthene molecules by one-pot condensation reactions of different benzaldehydes with dimedone or *β*-naphthol.

Results and Discussion

At first, we focused our attention on the synthesis of 1,8-dioxo-octahydroxanthenes (**3a-r**) (scheme 1). The reaction between benzaldehyde (**1**) and dimedone (**2**) in ratio 1:2 was chosen as a simple model substrate, and optimization studies are shown in Table 1. Further evaluation of the solvent-free reaction conditions using of different temperatures accomplished in the presence of lactic acid as catalyst. As it can be seen in Table 1, the shorter times and excellent yields were gained when the reaction was carried out at 110 °C (Table 1, entry 4).

We carried on our endeavors for improvement in the result. So model reactants were allowed to react at a higher or lower catalyst loading (entries 5-8) that the optimum yield of 1,8-dioxo-octahydroxanthene was obtained in the presence of 20 mol % of lactic acid.

After optimized the reaction conditions, we evaluated the reaction scope using a various aryl aldehydes; results are summarized in Table 2. As shown in Table 2, the reaction of aryl aldehydes either with electron-withdrawing groups or electron-donating groups gave the corresponding products with good to excellent yields.



Scheme 1. One-pot synthesis of 1,8-dioxo-octahydroxanthenes using lactic acid as catalyst.

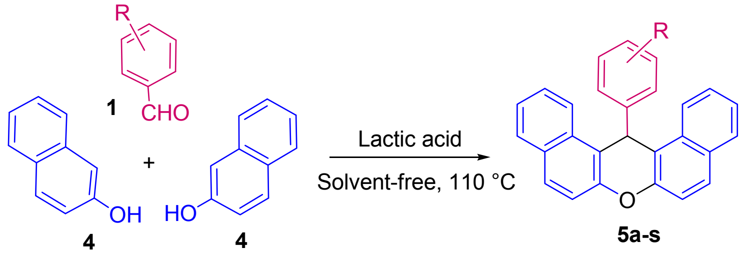
Table 1. Optimization of reaction condition between benzaldehyde (1.0 mmol) and dimedone (2.0 mmol) in the presence of lactic acid under solvent-free conditions.

Entry	Temprature (°C)	Catalyst (mol %)	Time (min)	Yield (%)
1	80	20	90	87
2	90	20	60	85
3	100	20	45	85
4	**110**	**20**	**30**	**95**
5	110	5	30	70
6	110	10	30	84
7	110	15	30	92
8	110	30	30	95

Table 2. 1,8-Dioxo-octahydroxanthene derivatives of pseudo three-component coupling reaction catalysed by lactic acid under solvent-free conditions.

Entry	R	Product	Time (min)	Yield (%)	Mp (°C)	
					Found	Reported Ref
1	H	**3a**	30	95	204-206	203-205[11]
2	2-Cl	**3b**	25	90	226-227	225-227[11]
3	3-Cl	**3c**	30	92	185-187	185-186[14]
4	4-Cl	**3d**	25	95	234-236	233-235[11]
5	2,4- di Cl	**3e**	25	95	179-181	175-177[27]
6	4-F	**3f**	20	95	225-227	226-227[11]
7	3-Br	**3g**	35	85	278-281	281-282[12]
8	4-Br	**3h**	30	95	237-238	235-237[12]
9	2-NO_2	**3i**	25	89	249-251	251-252[12]
10	3-NO_2	**3j**	25	91	170-172	168-170[11]
11	4-NO_2	**3k**	20	95	226-228	226-228[29]
12	3-OH	**3l**	25	93	224-227	220-222[28]
13	4-OH	**3m**	25	95	248-250	250-254[14]
14	3-Me	**3n**	35	85	205-207	205-207[30]
15	4-Me	**3o**	25	91	210-212	215-217[11]
16	3-OMe	**3p**	35	83	298-301	308-310[29]
17	4-OMe	**3q**	20	95	248-249	243-245[28]
18	3,4- di OMe	**3r**	25	82	179-181	175-177[28]

In the next step, lactic acid was used in the condensation of *β*-naphthol (**4**) with aldehydes (**1**) leading to 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (**5a-s**) (scheme 2). Our observations showed that under the same conditions used for the preparation of 1,8-dioxo-octahydroxanthenes, this reaction was completed; the respective results are summarized in Table 3. Evidences indicate that, lactic acid is one of the efficient catalyst for one-pot synthesis of 1,8-dioxo-octahydroxanthenes (**3a-r**) and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (**5a-s**) under solvent-free conditions that confirms the efficiency of this method.



Scheme 2. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes using lactic acid as catalyst.

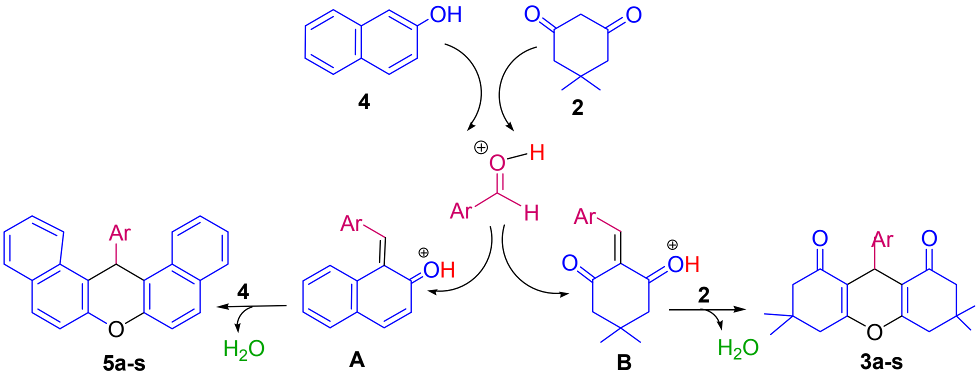
Table 3. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives using lactic acid as catalyst under solvent-free conditions.

Entry	**R**	**Product**	**Time (min)**	**Yield (%)**	**Mp (°C)**	
					Found	**Reported**[Ref]
1	H	**5a**	45	85	185-188	184-186[12]
2	2-Cl	**5b**	50	90	214-216	214-216[22]
3	3-Cl	**5c**	45	94	206-209	207-209[23]
4	4-Cl	**5d**	30	95	292-295	290-292[22]
5	2,4- di Cl	**5e**	40	90	225-227	229-230[24]
6	4-F	**5f**	30	90	247-249	250-252[25]
7	3-Br	**5g**	40	84	193-195	190-192[26]
8	4-Br	**5h**	30	95	297-299	297-298[22]
9	2-NO_2	**5i**	25	85	214-216	214-216[11]
10	3-NO_2	**5j**	50	90	226-228	233-234[25]

Table 3. Continued

11	4-NO_2	**5k**	20	90	318-320	313-315[12]
12	3-OH	**5l**	45	82	247-253	250-253[24]
13	4-OH	**5m**	30	85	136-139	135-137[12]
14	2-Me	**5n**	40	80	259-262	258-259[31]
15	3-Me	**5o**	40	80	253-255	250-253[24]
16	4-Me	**5p**	40	80	230-233	230-231[22]
17	3-OMe	**5q**	40	88	171-173	170-171[12]
18	4-OMe	**5r**	30	90	202-205	204-205[22]
19	4-OH-3-OMe	**5s**	40	80	198-200	198-201[25]

A plausible mechanism, illustrating the role of lactic acid in the synthesis of of 1,8-dioxo-octahydroxanthenes (**3a-r**) and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (**5a-s**). Initally, aldehyde is activated by the proton from lactic acid. Next, the carbonyl group aldehyde is attacked by the nucleophilic *β*-naphthol (**4**) or dimeone (**2**) to create the intermediated products (**A, B**). The subsequent addition of (**4**) or (**2**) to these intermediates, gives the acyclic adduct product, which undergoes intramolecular cyclization with elimination of one H_2O molecule to afford the desired xanthene derivatives.



Scheme 3. The proposed mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes and 14-aryl- 14*H*-dibenzo[*a,j*]xanthenes catalysed by lactic acid.

Experimental

General

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a FT-IR-JASCO-460 plus spectrometer, respectively. ^{1}H NMR spectra of known compounds were recorded on a Bruker DRX-400 Avance instrument in $CDCl_3$ operating at 400 MHz. All reagents were purchased from Merck (Darmastadt, Germany) and Fluka (Buchs, Switzerland) and used without further purification.

General procedure for preparation of 1,8-dioxo-octahydroxanthenes and 14-aryl-14H-dibenzo[a,j]xanthenes

A mixture of different aldehydes (**1**) (1.0 mmol) with dimedone (**2**) or *β*-naphthol (**4**) (2.0 mmol) and lactic acid (20 mol %) was stirred at 110 °C under solvent-free conditions. The completion of reactions was monitored through thin layer chromatography (TLC). The reaction mixture was cooled to room temperature, then ethanol (5 mL) was added to the reaction mixture and the precipitate formed was filtered off. The crude products were recrystallized from ethanol to afford the pure xanthene derivatives.

Characterization data of selected compounds

9-(3-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**3l**):White solid; IR (KBr, cm^{-1}): 3364, 3054, 2963, 1671, 1658, 1452, 1359, 1256, 1137; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 6H, $2CH_3$), 1.13 (s, 6H, $2CH_3$), 2.22 (d, J = 16.4 Hz, 2H, $2CH_2$), 2.28 (d, J = 16.4 Hz, 2H, $2CH_2$), 2.49 (s, 4H, $2CH_2$), 4.77 (s, 1H, CH), 6.59-7.10 (m, 4H, Ar-H).

3,3,6,6-tetramethyl-9-(m-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**3n**): White solid; IR (KBr, cm^{-1}): 3098, 2956, 1672, 1662, 1464, 1358, 1233, 1135; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 6H, $2CH_3$), 1.13 (s, 6H, 2CH_3), 2.20 (d, *J* = 16.4 Hz, 2H, 2CH_2), 2.26 (d, *J* = 16.0 Hz, 2H, 2CH_2), 2.31 (s, 3H, CH_3), 2.49 (s, 4H, 2CH_2), 4.74 (s, 1H, CH), 6.92-7.16 (m, 4H, Ar-H).

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**3o**): White solid; IR (KBr, cm^{-1}): 3039, 2958, 1679, 1664, 1467, 1357, 1198, 1137; ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 6H, 2CH_3), 1.12 (s, 6H, 2CH_3), 2.18 (d, *J* = 16.2 Hz, 2H, 2CH_2), 2.26 (d, *J* = 16.2 Hz, 2H, 2CH_2), 2.26 (s, 3H, CH_3), 2.48 (s, 4H, 2CH_2), 4.73 (s, 1H, CH), 7.04 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.20 (d, *J* = 8.1 Hz, 2H, Ar-H).

9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**3q**): White solid; IR (KBr, cm^{-1}): 3028, 2958, 1678, 1665, 1461, 1358, 1260, 1234, 1164; ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 6H, 2CH_3), 1.12 (s, 6H, 2CH_3), 2.19 (d, *J* = 16.0 Hz, 2H, 2CH_2), 2.26 (d, *J* = 16.4 Hz, 2H, 2CH_2), 2.48 (s, 4H, 2CH_2), 3.75 (s, 3H, OCH_3), 4.72 (s, 1H, CH), 6.78 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.23 (d, *J* = 8.8 Hz, 2H, Ar-H).

9-(3,4-dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**3r**): White solid; IR (KBr, cm^{-1}): 3007, 2957, 1666, 1627, 1465, 1360, 1262, 1228, 1139; ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 6H, 2CH_3), 1.12 (s, 6H, 2CH_3), 2.20 (d, *J* = 16.2 Hz, 2H, 2CH_2), 2.27 (d, *J* = 16.5 Hz, 2H, 2CH_2), 2.48 (s, 4H, 2CH_2), 3.81 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.27 (s, 1H, CH), 6.73 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.78 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.92 (s, 1H, Ar-H).

14-(4-hydroxyphenyl)-14-H-dibenzo[a,j]xanthene (**5m**): White solid; IR (KBr, cm^{-1}): 3414, 3056, 2929, 1622, 1593, 1508, 1428, 1250, 1174, 800, 748; ^1H NMR (400 MHz, $CDCl_3$): δ 6.46 (s, 1H, CH), 6.61 (d, *J* = 8.8 Hz, 2H, ArH), 7.39-7.62 (m, 8H, ArH), 7.80-7.87 (m, 4H, ArH), 8.39 (d, *J* = 8.4Hz, 2H, ArH).

14-(3-methylphenyl)-14-H-dibenzo[a,j]xanthene (**5o**): White solid; IR (KBr, cm^{-1}): 3043, 2918, 1620, 1592, 1514, 1431, 1252, 1172, 808, 747; ^1H NMR ^1H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H, CH_3), 6.48 (s, 1H, CH), 6.83 (d, *J* = 7.2Hz, 2H, ArH), 7.42-7.63 (m, 8H, ArH), 7.81-7.87 (m, 4H, ArH), 8.44 (d, *J* = 8.4 Hz, 2H, ArH).

14-(4-methoxyphenyl)-14-H-dibenzo[a,j]xanthene (**5r**): White solid; IR (KBr, cm^{-1}): 3072, 2927, 1621, 1592, 1509, 1399, 1250, 1177, 808, 742; ^1H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 3H, OCH_3,) 6.48 (s, 1H, CH), 6.70 (d, *J* = 8.0 Hz, 2H, ArH), 7.39-7.62 (m, 8H, ArH), 7.80-7.86 (m, 4H, ArH), 8.39 (d, *J* = 8.0 Hz, 2H, ArH).

14-(4-hydroxy-3-methoxyphenyl)-14-H-dibenzo[a,j]xanthene (**5s**): White solid; IR (KBr, cm^{-1}): 3414, 3056, 2929, 1622, 1593, 1508, 1428, 1250, 1240, 1137, 801, 753; ^1H NMR (400 MHz, $CDCl_3$): δ 3.69 (s, 3H, OCH_3), 6.47 (s, 1H, CH), 6.75 (d, *J* = 8.4 Hz, 1H, ArH), 6.87 (d, *J* = 2.4 Hz, 1H, ArH), 7.18 (dd, *J* = 8.4 Hz, 1H, ArH), 7.43-7.63 (m, 6H, ArH), 7.81-7.87 (m, 4H, ArH), 8.43 (d, *J* = 8.4 Hz, 2H, ArH).

Conclusions

In compendium, we have expanded a very facile and comfortable strategy for one-pot synthesis of biologically 14-aryl-14*H*-dibenzo[*a,j*]xanthenes and 1,8-dioxo-octahydroxanthene derivatives in the presence of lactic acid as a commercially available, and eco-compatibility catalyst via pseudo three-component condensation reaction between aldehydes and dimedone or *β*-naphthol under solvent-free conditions. Good to excellent yields, simplicity of operation, comfortable purification, and high atom-economy are the key advantages of the present method.

Acknowledgements

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