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Simple and cost effective acid catalysts for efficient synthesis of 9-aryl-1,8-dioxooctahydroxanthene

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ABSTRACT

$CaCl_2$ (20 mol %) dispersion in DMSO or aq HBr (10 mol %) is developed as an efficient and cost effective acid catalyst for the simple one-pot synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives. Reaction of aromatic aldehyde (1 equiv) and dimedone (2 equiv) in the presence of $CaCl_2$ (20 mol %) in $CHCl_3$ at room temperature gave the open chain analogue of 1,8-dioxooctahydroxanthene. Similarly, aq HBr (10 mol %) in water at reflux temperature gave a high yield of 9-aryl-1,8-dioxooctahydroxanthene derivatives. The use of inexpensive, eco-friendly and readily available catalysts, easy work-up, and isolation of the products makes these procedures a convenient method for the synthesis of either of the products.

Natural products with a xanthene heterocylic motif show a variety of important biological activities.[1] 9-Aryl-1,8-dioxooctahydroxa-nthenes contain an inherently reactive pyran ring system and find application in the field of medicinal chemistry as antibacterial, antiviral, anti-inflammatory agents, novel CCR1 receptor antagonists, and anticancer agents.[2] In the field of material science it is used as dyes,[3] luminescent sensors,[4] and fluorescent markers for the visualization of bio-molecules,[5] and photostable laser dyes.[6] Interestingly, this structurally complex molecule can be synthesized by a simple one pot tandem reaction between an aldehyde (1 equiv) and dimedone (2 equiv) or cyclohexane-1,3-dione in the presence of a catalyst. However, in the absence of a catalyst[7] the reaction stops just after Knoevenagel type adduct formation,[7] to give an open chain intermediate, 2,2′-aryl/alkyl methylene-bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one). Thus, value of a synthetic method for this important class of heterocycles depends mainly on identifying a simple, cost effective, and eco-friendly catalyst and a simple work-up procedure.

Majority of the catalysts used are acids which includes Lewis acids,[8–12] modified sulfonic acids,[13–16] acidic clay[17–19] silica based catalysts,[20] organocatalysts, and ionic liguids.[21] However, many of these reagents have their own disadvantages, such as high cost and catalyst loading and low yield in many cases. There remains scope for the identification of new cost effective catalysts. ‘Cheap metals for noble tasks’ is the current trend in the development of metal based catalysts.[22] Calcium, the fifth most frequent element in the earth’s crust (3.4 wt%) fits very well into this. This group 2 metal is biocompatible and it shows a significant dose of metal Lewis-acidity typical for group 3 reagents. Calcium reagents are less exploited in organic synthesis and are beginning to gain momentum.[22] $CaCl_2$, one of the best known dehydrating agents and a green Lewis acid catalyst was used in organic transformations only in a few instances, for example in the synthesis of hexanoic acid 2-(diethylamino)ethyl ester,[23] Mannich bases,[24] synthesis of aminophosphonic esters,[25,26] Biginelli reaction[27], and aldol reaction.[28] Taking into account that xanthenediones are important biologically active compounds, we considered $CaCl_2$, a FDA approved, biocompatible food additive and cost-effective Lewis acid[29] as the catalyst for its synthesis.

Recently, there is a growing interest in the use of protic acids such as HCl, H_2SO_4, $HClO_4$, and its salts as catalysts for the synthesis of 9-aryl-1,8-dioxooctahydroxanthene. HBr, a strong mineral acid than HCl is used for several organic transformations such as the direct conversion of methane to higher hydrocarbons,[30] asymmetric hydrogenation,[31] highly selective cross-cyclodimerization,[32] oxidation of alkynes to diketones,[33] oxidation of benzyl alcohols to benzaldehydes,[34] and the bromination of ketones with H_2O_2–HBr,[35] etc.

This literature background shows that $CaCl_2$ and HBr were used as catalysts, only to a limited extent in organic synthesis and there remains large scope for its further application. In continuation of our interest[8] toward the development of efficient acid catalysts

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for the synthesis of 1,8-dioxooctahydroxanthene derivatives, we found that $CaCl_2$ (20 mol %) dispersed in DMSO and aq HBr (10 mol %) could be used as cheap and efficient catalysts. Herein we present our results.

Reaction between 4-nitrobenzaldehyde (**1d**) and 5,5-dimethyl-1,3-cyclohexanedione (**2**) was used to check and identify one of the cheap and efficient catalysts among some of the unexplored acids and standardization of reaction conditions (Table 1). $LnCl_3·7H_2O$, a hard but mild Lewis acid, in DCM or in water at reflux temperature gave only the open chain compound **3d** as the major product (entries 1 and 2) which was confirmed by the presence of two singlet peaks at 11.87 ppm, and 5.57 ppm, corresponding to –OH and methyne proton respectively in the ^1H NMR spectrum. Similarly a singlet peak at 4.82 ppm, characteristic of the methyne proton was observed for the cyclized compound **4d**. $BaCl_2$ in DCM, $CuSO_4$ in DCM, and clay catalysts KSF or bentonite in toluene at reflux temperature, gave only the uncyclized product **3d**. Similar is the case with $CaCl_2$ (20 mol %) in $CHCl_3$ at room temperature (rt) or at reflux temperature (entry 4). Without $CaCl_2$ no reaction was observed in $CHCl_3$. Even after increasing the quantity of $CaCl_2$ to 100 mol % and heating at 140–150°C without a solvent, complete conversion of uncyclized product **3d** did not take place (entry 5). However, after homogenizing the reaction mixture containing $CaCl_2$ (20 mol %) with DMSO or CH_3CN-DMF (4:1) the cyclized product **4d** was obtained in very good yield in just 5 h. Interestingly, the cyclized product **4d** was obtained within the same time (5 h) when the quantity of DMSO (0.5 mL for 17 mg or 0.1545 mmol of $CaCl_2$) was decreased just to maintain a dispersion. Using such a small quantity of DMSO is as good as using no solvent and just quenching the reaction mixture with water gave the desired product, **4d**, in high yield (87%).

Next, the use of a protic acid, aq HBr (48%, 10 mol %) was examined. At rt and reflux temperature the uncyclized product **3d** and cyclized product **4d** respectively were obtained in very high yield. The yield did not change after decreasing the quantity of the catalyst from 100 mol % to 10 mol %. Based on these results it was concluded that the use of $CaCl_2$ (20 mol %) in $CHCl_3$ at rt as the condition for the formation of uncyclized product **3d** and $CaCl_2$ (20 mol %) dispersed in DMSO (0.5 mL for 17 mg or 0.1545 mmol of $CaCl_2$) at 85–90 °C or aq HBr (48%, 10 mol %) in water at reflux temperature as the condition for the formation of cyclized product **4d**.

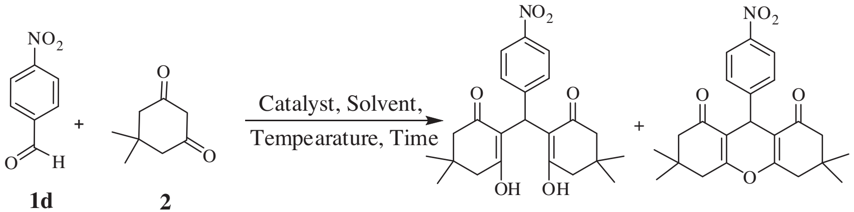
To illustrate the versatility of this method a series of aromatic and heteroaroamtic aldehydes were studied under the standardized reaction condition and the results are summarized in Table 2. Substituted aldehydes (1 equiv) such as **1k–1m**, containing more than one electron donating substituents in $CHCl_3$ at rt, gave the open chain compounds **3k–3m** at faster reaction rate. Almost all other substrates, containing electron donating or electron withdrawing substituents reacted slowly at nearly the same time (15 h). This infers that, unless there is a strong electron donating substituent, $CaCl_2$ will not be able to discriminate the reactivity of the aldehydes. The reaction condition was tolerant to ether, phenolic –OH, furfuryl ring and cinnamoyl groups.

A wide difference in the reaction rate could be observed, when $CaCl_2$ (20 mol %) dispersed in DMSO, was used as the catalyst at 85–90°C for the formation of cyclized products **4a**–**4m**. When the electron withdrawing group or no substituent group is present at the para position the reaction was very fast (Table 2, entries 1 and 4) whereas inverse was the case with the electron donating group present at the para position (Table 2, entries 8 and 9,). Presence of an electron withdrawing group at sterically hindered ortho position (Table 2, entry 2, **1b**, 11 h) and deactivating meta position (Table 2, entry 3, **1c**, 10 h) slowed down the reaction. The expected cyclized products **4n** and **4o** were not formed in the case of furfuraldehyde (**1n**) and cinnamaldehyde (**1o**). Polymerisable nature of the starting material may be the reason.

Aq HBr (48%, 10 mol %), in water at reflux temperature as a catalyst worked efficiently with differently substituted benzaldehydes (Table 2). Aldehydes with strong electron donating groups, especially **1k** and **1p** underwent faster reaction. Aldehyde **1q** with strong electron donating dimethylamino substituent underwent reaction at room temperature itself. HBr is a metal-free catalyst and known to be used as a green brominating agent in water.[35] Since HBr is used only in catalytic quantity and as a dilute solution in water, it is likely to make lower impact on the environment.

Table 1

Effect of different acid catalysts and solvents on the reaction of 4-nitrobenzaldehyde with 5,5-dimethyl-1,3-cyclohexanedione[a]



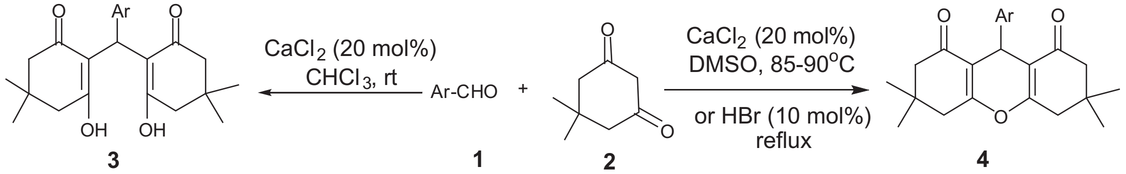
1d **2** **3d** **4d**

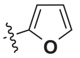
Sl. no.	Catalyst (mol %)	Solvet	Temp (°C)	Time (h)	Yield[b] (%)	
					Product **3**	Product **4**
1	$LnCl_3·7H_2O$ (100)	DCM	Reflux	12	76	Nil
2	$LnCl_3·7H_2O$ (100)	Water	Reflux	13	70	25
3	$BaCl_2$ (100)	DCM	Reflux	14	85	Trace
4	$CaCl_2$ (20)	$CHCl_3$	Reflux (or) rt	15	87	Nil
5	$CaCl_2$ (100)	Neat	140–150	24	10	80
6	$CaCl_2$ (20)	DMSO	85–90	05	Nil	87
7	$CaCl_2$ (20)	Cat. DMSO	85–90	05	Nil	87
8	Anhyd.$CuSO_4$ (100)	DCM	Reflux	14	77	Nil
9	KSF clay (10, w/w)	Toluene	Reflux	15	80	Nil
10	Bentonite (10, w/w)	Toluene	Reflux	16	80	20
11	Aq HBr (48%, 10)	Water	rt	14	76	Nil
12	Aq HBr (48%, 10)	Water	Reflux	14	Nil	99

[a] All reactions were performed using 4-nitrobenzaldehyde (1 mmol), dimedone (2 mmol).

[b] Isolated yield.

Table 2
Acid catalyzed synthesis of 2,2′ arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) and 3,3,6,6-tetramethyl-9-aryl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione derivatives

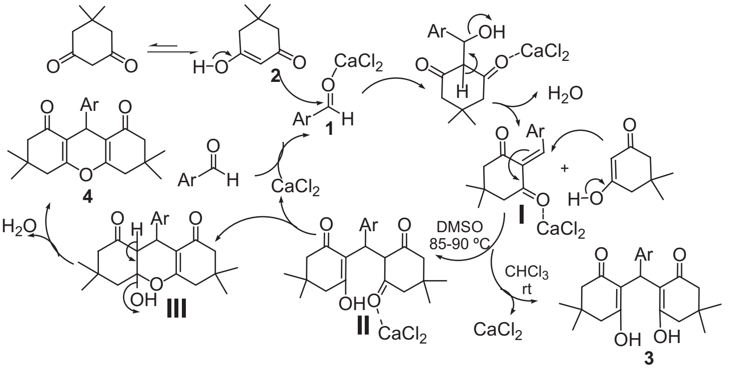


Entry	Ar	Product	Time (h) **3/4/4***	Yield (%) **3/4/4***	Melting Point °C (**3**)		Melting Point °C (**4**)	
					Found	Reported	Found	Reported
1	C_6H_5–(**1a**)	**3a/4a**	13/4/14	69/85/84	186–188	192–194[36]	203–205	204–206[9]
2	2-NO_2–C_6H_4–(**1b**)	**3b/4b**	14/11/14	85/85/71	244–246	248–252[37]	246–248	248–249[9]
3	3-NO_2–C_6H_4–(**1c**)	**3c/4c**	15/10/12	80/80/94	201–203	201–203[36]	171–173	170–172[9]
4	4-NO_2–C_6H_4–(**1d**)	**3d/4d**	15/5/12	87/87/99	194–196	195–197[36]	225–226	221–223[9]
5	2-Br–C_6H_4–(**1e**)	**3e/4e**	14/10/12	90/88/80	238–240	241–243[38]	226–229	226-229 [39]
6	2-Cl–C_6H_4–(**1f**)	**3f/4f**	14/11/14	86/88/80	200–202	202–204[36]	230–232	225–227[9]
7	4-Cl–C_6H_4–(**1g**)	**3g/4g**	14/8/15	79/83/81	142–144	145–147[36]	230–233	229–230[9]
8	4-CH_3–C_6H_4–(**1h**)	**3h/4h**	15/14/14	91/86/79	139–141	141–143[36]	212–214	210–211[9]
9	4-OCH_3–C_6H_4–(**1i**)	**3i/4i**	15/12/12	85/86/81	146–148	146–148[36]	242–245	242–243[40]
10	4-OH–C_6H_4–(**1j**)	**3j/4j**	15/11/12	89/87/94	188–190	201–203[36]	244–246	247–248[9]
11	4-OH,3-OCH_3–C_6H_3–(**1k**)	**3k/4k**	10/8/4	92/92/91	193–195	193–195[36]	227–228	224–225[40]
12	3,4–OCH_3–C_6H_3–(**1l**)	**3l/4l**	13/8/11	94/93/80	178–180	187–189[36]	179–181	170–172[40]
13	3,4,5–OCH_3–C_6H_2–(**1m**)	**3m/4m**	10/9/10	88/87/90	203–205	205–208[12]	186–188	182–183[9]
14	 **(1n)**	**3n/4n**	13/–/–	95/–/–	139–141	142–144[38]	–	–
15	$C_6H_5CH{=}CH$–(**1o**)	**3o/4o**	14/–/12	96/–/50	213–215	215–216[7b]	174–176	175–177[41]
16	3-CH_3–4-OCH_3–C_6H_4–(**1p**)	**3p/4p**	–/–/10	–/–/91	–	–	194–196	–
17	4-$N(CH_3)_2$–C_6H_5–(**1q**)	**3q/4q**	–/–/5	–/–/79	–	–	221–223	225–226[12]

3/4/4* the reaction was carried out using $CaCl_2$ (20 mol %) in $CHCl_3$ at rt /$CaCl_2$ (20 mol %) dispersed in DMSO at 85–90 °C/aq HBr (48%, 10 mol %) in water at reflux temperature.

Based on the observations mentioned, a possible mechanism is proposed for the catalytic activity of $CaCl_2$ as shown in the Scheme 1. Knoevenagel type adduct **I** formed under the influence of $CaCl_2$ is expected to undergo Michael addition with another molecule of dimedone to form intermediate **II**. It is likely that the hetereogeneous nature of the reaction in $CHCl_3$ does not facilitate complex formation between highly polar intermediate **II** and $CaCl_2$, hence only product **3** was obtained, whereas homogenization with DMSO helps better complexation and the formation of compound **4**.

In conclusion, we have identified $CaCl_2$ (20 mol %), a mild Lewis acid, and a conventional dehydrating agent, and aq. HBr (48%, 10 mol %), a protic acid, as new, simple, and efficient catalysts for the synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives and its open chain analogues. This simple procedure is applicable to a wide variety of aromatic and heterocyclic aldehydes with electron donating as well as electron withdrawing substituents. A spectacular solvent effect was observed in $CaCl_2$ catalyzed reaction on changing the solvent from $CHCl_3$ to DMSO. This study further exemplifies that calcium, a bio-compatible and cheap metal in the form of $CaCl_2$ could be used for noble tasks inorganic synthesis. Water, a safe benign, cheap and environmental friendly solvent was used in HBr catalyzed reactions. The procedures said above offer several advantages such as, a simple water work-up, no purification step, high yield, inexpensive catalyst, and minimal environmental impact, thus making it one of the attractive and practical protocols for the synthesis of xanthenediones. Further studies on the use of xanthenediones as visible light sensitizers and as better excited state electron donors to TiO_2 for application in dye sensitized solar cells are in progress.



Scheme 1. Proposed mechanism for the $CaCl_2$ catalyzed synthesis of 9-aryl-1,8-dioxooctahydroxanthene and its open chain form.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.11.058.

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