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Original Resarch Article

Application of nano-CeO_2 catalyst as a suitable and useful catalyst in the synthesis of 1,8-dioxooctahydroxanthenes

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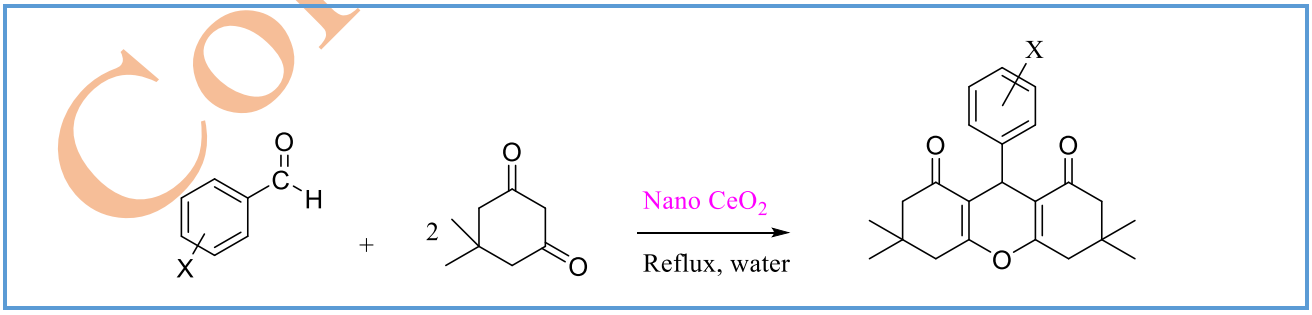
ABSTRACT

Xanthene and their derivatives are an important class of broad-spectrum heterocyclic compounds used as fluorescent dyes to visualize biomolecules and lasers. They have been reported to be antiviral for photodynamic treatment, bactericidal activity in agriculture. In this research, a simple method for the synthesis of high-efficiency 1,8-dioxooctahydroxanthenes through the reaction from aromatic aldehyde and dimedon derivatives in the presence of nano-CeO_2 catalyst in water under the reflux conditions. The results revealed that this synthetic reaction is very simple and 1,8-dioxooctahydroxanthene derivatives produced with good yields compared to other articles. The advantages of this method include catalyst recovery, high efficiency and easy operation method. As shown in Table 5, the highest efficiency (95%) in a short time (1 h) was obtained in this study, which is very important compared to other previous methods presented.

Graphical Abstract



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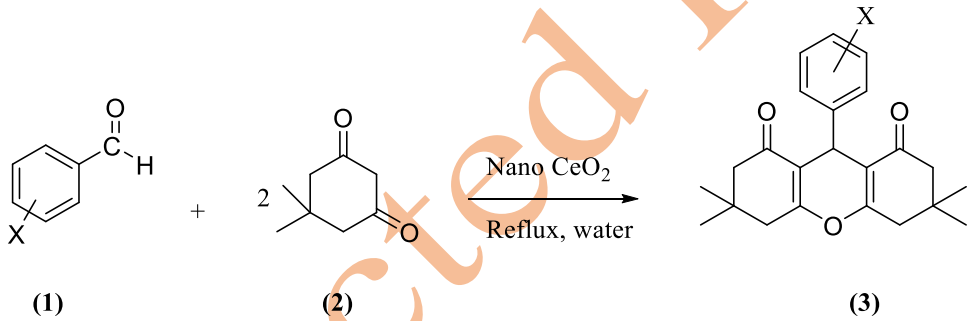
Introduction

Xanthene and its derivatives are important heterocyclic compounds that have been considered for industrial, biological and pharmaceutical applications [1] and have important medicinal properties such as antibacterial, anti-tumor, anti-viral and anti-inflammatory agents, as well as biological properties including useful spectroscopy, laser technology and fluorescent materials [2].

Benzo-xanthene derivatives play an important role in therapeutic photodynamics (a well-known method in the control of concentrated tumors) as sensitizers [3]. They are also used as luminescence sensors and fluorescent materials to observe biomolecules [4]. Other uses of xanthines include their activity in preventing the paralytic effect of zoxazolamine [5]. Different methods are utilized for the synthesis of xanthines and their derivatives, the most important of which are: dewatering with cycling [6] trapping benzyne with phenol [7] reaction of aldehydes with 2 naphthol and dimedone [9].

Different catalysts are used for the synthesis of xanthine derivatives [10–14], such as the use of p-toluensulfonic acid [15], p-dodecyl benzosulfonic acid [16], polyaniline p-sulfoneate [17], heterogeneous catalysts [18].

In this study, we used nano-CeO_2 catalyst to synthesize xanthine derivatives and the reaction was performed with high efficiency and in a short time (Scheme 1).



Scheme 1. Synthesis of xanthene derivatives

Experimental

Materials and methods

Chemicals were purchased from the Merck (Darmstadt, Germany) and Sigma-Aldrich chemical Co. All products were characterized using spectra and physical data. Characterizations were carried out using the Melting points (Electrothermal 9100), ^{1}H-NMR (Bruker 500 MHz), TEM (HRTEM, TF 20 Tecnai G2 200 kV FEI), Fourier transform infrared (model Nexus-870, Nicolet Instrument), thin layer chromatography (TLC) on commercial aluminum-backed plates of silica gel.

Preparation of nano-CeO_2

The cerium oxide catalyst was prepared using a precipitation method of cerium chloride ($CeCl_3 \cdot 7H_2O$) and ammonia. First, cerium chloride is dissolved in water and stirred for half an hour. Then ammonia solution (0.5 M) was added to give a gel with a pH of about 8.5. The gel is then washed with distilled boiling water and placed at 80 °C for 24 h. It is then calcined in an oven at 300 °C for 2 h. The dimensions of nanoparticles were determined by TEM (Figure 1) [19].

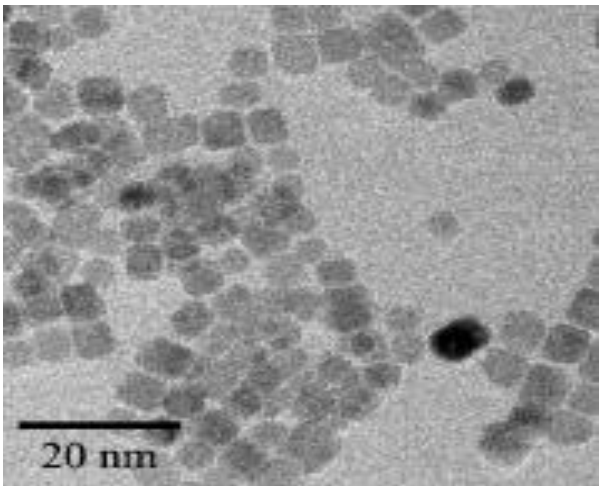


Figure 1. TEM image of nano-CeO_2

General procedure for synthesis of xanthenes

A mixture of dimedone (2 mmol), aldehyde (1 mmol) and nano-CeO_2 (0.05 g) in water (5 mL) was refluxed. With the help of TLC paper, we track the progress of the reaction. After the reaction is complete, the reaction mixture is cooled and the precipitate is filtrated. The precipitate was recrystallized in ethanol.

3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3a): FT-IR (KBr) cm^{-1}: 3103, 2956, 1680, 1599 and 1210. ^1H NMR (400 MHz, $CDCl_3$): δ 0.896 (s, 3 H), 1.036 (s, 3 H), 2.055 (4 H, dd), 2.6 (4H, dd), 4.51 (S. 1 H), 7.07-7.23 (m, 5 HAr).

3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3c): FT-IR (KBr) cm^{-1}: 3112, 2968, 1681, 1609, 1546, 1367 and 1217. ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (s, 3 H), 1.06 (s, 3 H), 2.07 (4 H, dd), 2.62 (4H, dd), 4.65 (S. 1 H), 7.13-7.76 (m, 4 HAr).

Reusability of nano-CeO_2

After the reaction, 10 mL of ethyl acetate was added to the compounds on filter paper containing catalyst. The mixture was stirred at room temperature for 5 min using a magnetic stirrer. The reaction mixture was filtered, and the catalyst remained on filter paper due to its insolubility in ethyl acetate solvent. Then, in order to reuse the catalyst, the filter material was washed several times with acetone. After drying, the reaction was repeated to check the potency of the catalyst (Table 2). As seen in the Table 4, the reaction can be performed up to five times with good efficiency by the recycled catalyst.

Result and Discussion

We have established a one-pot reaction of various aldehydes with dimedone in water in the presence of nano-CeO_2 as available, green and inexpensive catalyst in good yields for the preparation of 1,8-dioxooctahydroxanthenes (Table 1).

We tested the synthesis of compound **3a** in the presence of different solvents to compare the effects of the solvent on the reaction. As you can see in the Table 2, the best efficiency and the shortest time were obtained in water (Table 3).

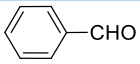
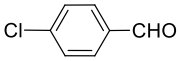
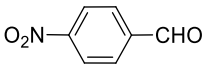
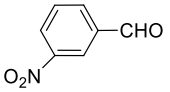
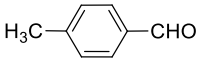
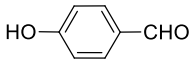
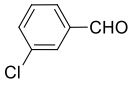
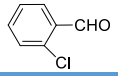
The reaction was investigated with different amounts of nano-CeO_2. In all cases, with 0.05 g catalyst, the maximum yield of products was

obtained and Using more catalysts has no effect on the reaction efficiency (Table 4).

By comparing the reaction results with other methods, we find that the nano-CeO_2 catalyst performs the reaction in shorter time and with higher efficiency (Table 5).

To reach the appropriate temperature conditions, the model reaction was performed at different temperatures and reflux. As indicated, the highest efficiency was observed in reflux conditions (Table 6).

Table 1. Preparation of 1,8-dioxo-octahydroxanthene derivatives using nano-CeO_2

Entry	Aldehyde	Product	Time (h)	Yield (%)[a]	m.p. (°C)	
					Found	Reported
1		**3a**	1	95	204	204-205 [20]
2		**3b**	1	97	231	228-230 [9]
3		**3c**	1	98	230	226-228 [9]
4		**3d**	1	97	167	168-170 [9]
5		**3e**	1	95	216	217-218 [9]
6		**3f**	1	93	242	241-243 [20]
7		**3g**	1	95	248	246 [20]
8		**3h**	1	96	233	230-232 [9]
9		**3i**	1	97	231	228-230 [9]

[a]Yields refer to isolated products

Table 2. Reuse of the nano-CeO_2 for synthesis of (**3a**)

Entry	Time (h)	Yield (%)[a]
1	1	95
2	1	94
3	1	92
4	1	85
5	1	80

[a]Isolated yields

Table 3. Synthesis of xanthenes using various solvents

Entry	Solvent	Time (hour)	Yield (%)
1	Water	1	95
2	Acetonitrile	1	89
3	dichloromethane	1	77
4	Methanol	1	88
5	Ethanol	1	92
6	Slvent free	1	90

Table 4. Comparison of amount of catalysts for the synthesis of **3a**

Entry	Amount of catalysts (g)	Yield (%)[a]
1	0.02 g	66
2	0.03 g	80
3	0.05 g	94
4	0.08 g	95
5	0.1 g	95

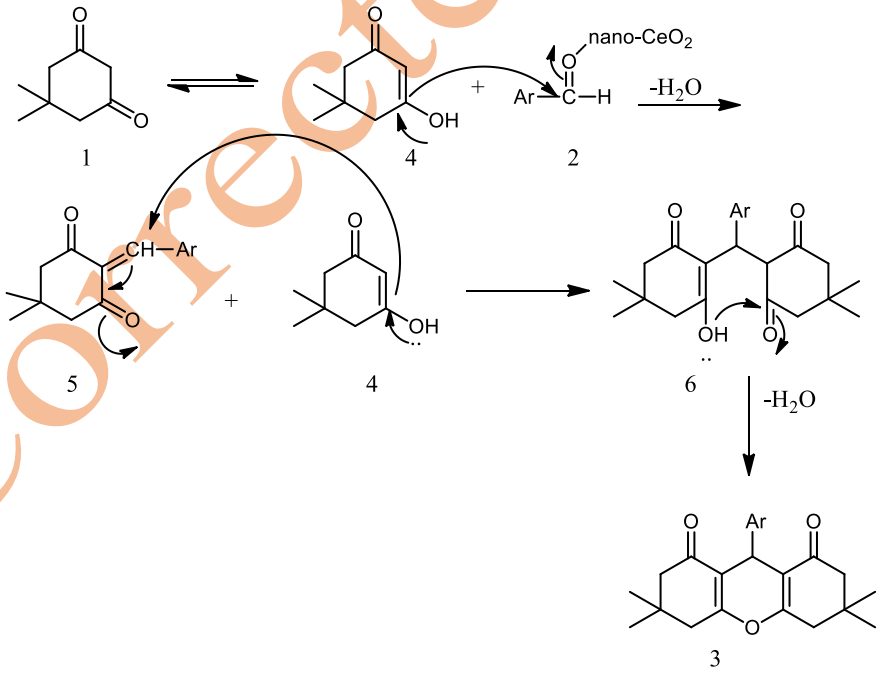
[a]Isolated yields

Table 5. Comparison of various catalysts for the synthesis of **3a**

Entry	Catalyst	Yield (%)	Time (h)	Reference
1	Selecfluor	93	1.5	[21]
2	SaSA	90	1	[22]
3	DABCO–bromine	80	2.5	[23]
4	TCCA	89	1	[24]
7	SiO_2	95	3	[25]
8	Nano CeO_2	95	1	Present study

Table 6. Comparison of various temperature for the synthesis of **3a**

Entry	Time (h)	Temperature (°C)	Yield (%)
1	1	25	66
2	1	50	75
3	1	Reflux	95



Scheme 2. Mechanism for the synthesis of substituted xanthenes

A probable mechanism for this reaction has been suggested in Scheme 2. In first step the dimedone tatumerize and condenses with aldehyde that activated with the catalyst to afford intermediate **5**. Then dimedone tatumerize attach to intermediate **5** and the hydroxy attack after remove water. Finally, the expected products **3** were obtained.

Conclusions

In this work, we discussed a highly efficient green procedure for preparing 1,8-dioxo-octahydroxanthene via a condensation reaction of various aldehydes and dimedone in the presence of nano-CeO_2 as a catalyst in water. The results demonstrated that this synthetic reaction is very simple and 1,8-dioxooctahydroxanthene derivatives produced with good yields in short reaction time compared to other articles. The procedure offers several advantages including high yields, operational simplicity, environmental-friendly solvent, recoverable/reusable catalyst, and low cost; rendering it a useful and attractive industrial process for the synthesis of these compounds**.** In this research study nano-CeO_2 as an efficient catalyst was synthesized and characterized by TEM analysis. According to the data presented in this study, the 1,8-dioxo-octahydroxanthene have been synthesized in the presence of nano-CeO_2 catalyst compared to other articles with high efficiency and in a shorter time. As shown in Table 5, the highest efficiency (95%) in a short time (1 h) was obtained in this study, which is very important compared to other previous methods presented. As shown in Table 3, the best efficiency (95%) was obtained in the presence of water and according to Table 6, the best efficiency was obtained in the reflux condition.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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