International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)
Journal Home page: www.iscientific.org/Journal.html

Efficient and reusable heterogeneous nano sized CeO_2 catalyst for the synthesis of 1, 8-dioxo-octahydroxanthenes

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Abstract

Effective heterogeneous CeO_2 nano catalyst was used for preparation of 1, 8-dioxo-octahydroxanthene derivatives in high yields, simple methodology and easy work-up. The catalyst is easily accessible, reusable and efficient under the reaction conditions.

Key words: 1,8-Dioxo-octahydroxanthene, 5,5-Dimethyl-1,3-cyclohexanedione, Solvent free, Nano sized Cerium oxide

Full length article Received: 04-05-2014 Revised: 23-07-2014 Accepted: 23-07-2014 Available online: 31-07-2014
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1. Introduction

Secondary metabolites are important natural products with many applications in medicine and technology [1]. Among the natural heterocyclic compounds, xanthene derivatives have an extensive range of biological and pharmaceutical applications as antiviral, antibacterial and anti-inflammatory activities [2-4]. Also, their importance as dyes in laser technology, pH-sensitive fluorescent and versatile synthons caused to obtain a considerable interest in researches [5-6]. The synthesis of 1,8-dioxo-octahydroxoxanthene derivatives with the same reagents using $InCl_3.4H_2O$ in ionic liquids, solid state condensation, aqueous media containing NH_2SO_3 and micro wave media [7-9] were studied but these methodologies have some defects like low yield, prolonged reaction time and using of toxic organic solvents. Recently some research groups reported some efficient methodologies using catalysts such as ferric-montmorilonite [10], nano sized TiO_2 [11], sodium hydrogen sulfate supported on silica chloride [12], magnetite-silver nanoparticles [13-14], amberlyst-15 [15], polyaniline-p-toluenesulfonate salt [16] and TMSCl [17] for removing or lowering disadvantages in synthesis of xanthenedione derivatives.

Nowadays nano catalysts showed very valuable role in organic synthesis because of obtaining high yield, simple preparation and isolation, low expense, high recovery, reusability and green properties, therefore, a lot of interest in various chemical transformations using catalysts under heterogeneous conditions has been increased [18-23]. For unusual physico chemical properties of nano sized metal oxides, they can exist with numerous surface sites and enhanced surface reactivity such as crystal corners, edges or ion vacancies [24-26]. The small size and large specific surface area of nano sized CeO_2 allow for certain unique and unusual physico chemical properties [27-28]. Cerium oxide is a prominent material for various kinds of industrial applications related to catalysis [29-30].

Through our further studies on the heterocycles [2, 31-33], we investigated the effect of catalytic activity of nano sized CeO_2 for preparation of 1,8-dioxo-octahydroxanthenes using various aromatic aldehydes (Figure. 1).

2. Material and Methods

Nano powder CeO_2 with particle size of 25 nm was purchased of sigma Aldrich company. ^{13}C NMR and ^{1}H NMR spectra were recorded on Brucker, 100 and 250 MHz using TMS as an internal standard. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. IR spectra were recorded on a Shimadzu 470 spectrophotometer. TLC was performed on Merck-precoated silica gel 60-F254 plates.

2.1. General Procedure for the synthesis of 1,8-dioxo-dodecahydroxanthenes

The synthesis of 1,8-dioxo-dodecahydroxanthenes was according to method reported in literature with some modifications [2]. A mixture of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), aldehyde (1 mmol) and Nano CeO_2 (0.15 g) was heated at 110 ^{o}C for 12 h. After cooling the reaction mixture, it washed with $CHCl_3$ (10 ml). The solvent was evaporated and the crude product was recrystallized from EtOH to obtain the pure product. All products were known and characterized by comparison of their physical data with those reported in literatures [2, 13]. The spectral data of some representative 1,8-dioxo-dodecahydroxanthenes are given:

3,3,6,6-Tetramethyl-9-(4-N,N-dimethylphenyl)-1,8-dioxooctahydroxanthene (3f)

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (6H, s), 1.11 (6H, s), 2.15-2.28 (4H, J = 16.3 Hz, q), 2.47 (4H, s), 2.89 (6H, s), 4.68 (1H, s), 6.64-7.15 (4H, m).

3,3,6,6-Tetramethyl-9-(3,4-dimetoxyphenyl)-1,8-dioxooctahydroxanthene (3i)

IR (KBr): 3008, 2959, 1665, 1464, 1361, 1199, 1167, 856 cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.93 (6H, s), 1.03 (6H, s), 2.13 (4H, s), 2.39 (4H, s), 3.71 (3H, s), 3.77 (3H, s), 4.62 (1H, s), 6.66-6.82 (3H, m). Anal. Calcd for $C_{25}H_{29}O_5$: C, 73.33; H, 7.14. Found: C, 73.40; H, 7.18.

3,3,6,6-Tetramethyl-9-(2-chloro-6-flourophenyl)-1,8-dioxooctahydroxanthene (3j)

IR (KBr): 3070, 2957, 1703, 1653, 1452, 1376, 1240, 1186, 787 cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.92 (6H, s), 1.04 (6H, s), 2.26 (4H, s), 2.46 (4H, s), 4.85 (1H, s), 6.54-7.19 (3H, m). Anal. Calcd for $C_{23}H_{23}O_3ClF$: C, 68.74; H, 5.77. Found: C, 68.80; H, 5.80.

3. Results and Discussion

Firstly, the optimized amount of nano catalyst was obtained as 0.15 g through the reaction between reactants. To study the effect of catalyst, the reaction of 5,5-dimethyl-1,3-cyclohexanedion (2 mmol) and benzaldehyde (1 mmol) and nano sized CeO_2 (0.15 g) was selected as model reaction under thermal and solvent free conditions, (Figure 1). Also, the aromatic aldehydes containing electron realizing and withdrawing groups were employed and yield was obtained, (Table 1). In all cases the reaction gives the products in good yields and prevents problems associated with solvent utilizing such as toxicity, cost, handling, safety and pollution. Nano Cerium oxide works under heterogeneous conditions. It can easily be handled and removed from the reaction mixture by simple filtration. The recovered catalyst was reused consecutive five times with insignificant loss and a minimum variation in yields of the product (Figure 2).

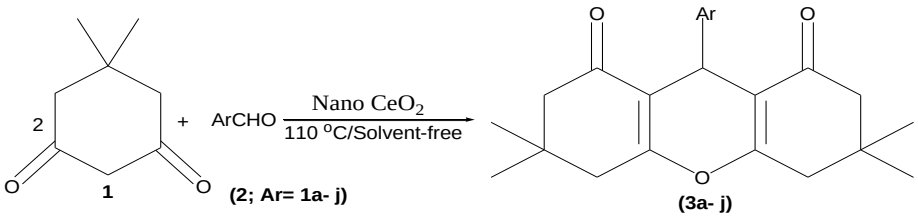

Figure 1. 1,8-dioxo-octahydroxanthenes from different aromatic aldehydes using nano sized CeO_2 as a heterogeneous catalyst

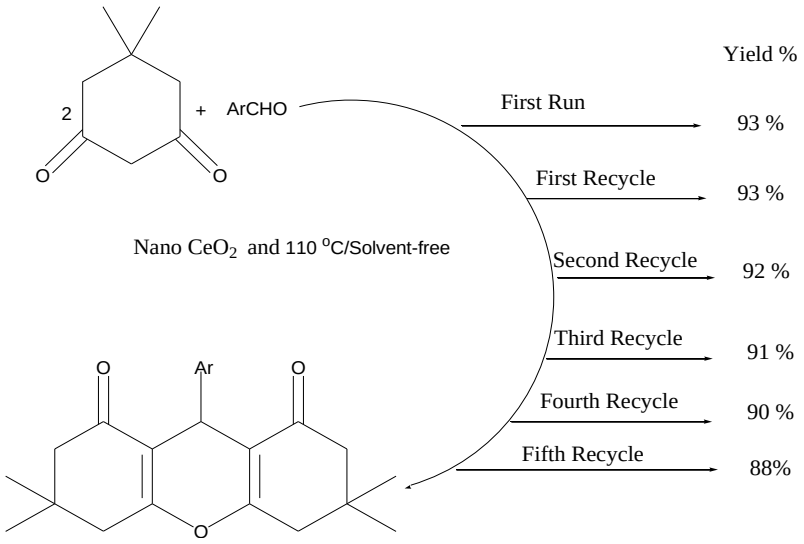

Figure2. Reusability of nano sized CeO_2 as a heterogeneous catalyst for synthesis of 1,8-dioxo-octahydroxanthenes.

Table 1: Synthesis of 9-aryl substituted 1,8-dioxo-octahydroxanthenes using nano CeO_2

Entry	Ar	Product	Yield [%][a]	Mp (^oC)
1	C_6H_5	**3a**	78	203-205
2	2-ClC_6H_4	**3b**	92	225-227
3	2,4-$(Cl)_2C_6H_3$	**3c**	88	253-256
4	3-$NO_2C_6H_4$	**3d**	71	169-171
5	3-BrC_6H_4	**3e**	74	190-192
6	4-$N(Me)_2C_6H_5$	**3f**	83	221-224
7	2-$OCH_3C_6H_4$	**3g**	80	183-185
8	4-$OCH_3C_6H_4$	**3h**	83	240-242
9	3,4-$(OCH_3)_2C_6H_3$	**3i**	87	182-184
10	2-Cl-6-F-C_6H_3	**3j**	90	117-120

[a]Yield refer to the pure isolated products.

4. Conclusion

In conclusion, we described the application of CeO_2 nano sized particles as a reusable and efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes. These compounds were prepared through treatment of dimedone with various aromatic aldehydes under solvent-free and thermal conditions. The simplicity together with the use of inexpensive, non-toxic and environmentally benign catalyst are remarkable features of the procedure**.**

Acknowledgement

We appreciate young researchers club for partial support of this work.

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