



Research Article

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Microwave Assisted Rapid Synthesis of 1, 8-Dioxo-Octahydroxanthenes Using Lignin Sulphonic Acid

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ABSTRACT

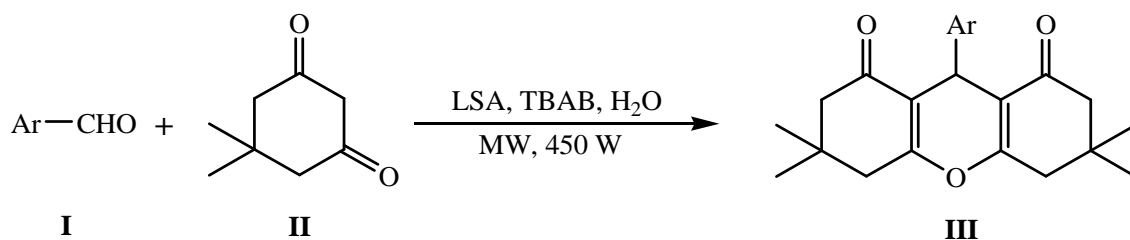
Lignin sulphonic acid was found to be a recyclable solid acid catalyst for the synthesis of 1, 8-dioxo-octahydroxanthenes in excellent yields by irradiation to microwave. The important features of new procedure are rapid rates of reaction with cleaner conversions, and simple work-up.

Keywords: MWI, Lignin sulphonic acid, 1, 8-dioxo-octahydroxanthenes.

INTRODUCTION

Xanthene derivatives are mostly used in laser technology because of its spectroscopic properties. These are also used as dyes fluorescent materials for visualization of biomolecules [1, 2]. Xanthenes are having agricultural bactericidal activity [3], photodynamic therapy (PDT) [4], anti-inflammatory effect [5], and antiviral activity [6]. Xanthenes are well-known heterocycles utilized as antagonists for paralyzing zoxazolamine [7]. This wide range of applications tends to give attention towards inventing different methods for their synthesis. There are numerous methods available for the preparation of xanthenes derivatives, such as synthesis by cyclisation of polycyclic aryl triflate esters [8]. Intramolecular trapping of benzyne by phenols [9]. Reaction of aryloxy magnesium halides with triethyl orthoformate [10].

Now a day's heterogeneous solid acid catalysts are playing an important role for the synthesis of organic compounds due to its handle, no toxicity and recyclability [11]. Chemical industries are forced to consider environmental aspects; therefore it becomes necessary to replace liquid acid with solid acid [12-13]. Use of naturally occurring polymers such as silica, starch, cellulose, is attractive candidates to explore for supported catalysis. Silica sulphuric acid [14], silica supported NaHSO_4 [15], cellulose sulphonic acid [16], starch sulphuric acids [17] are used as solid catalyst for various organic transformations. This prompted us to investigate the lignin sulphonic acid (LSA) as an alternative catalyst for the synthesis of 1, 8-dioxo-octahydroxanthenes. In continuation of our work [18-21], we are reporting the clean synthesis of 1, 8-dioxo-octahydroxanthenes (III) from the reaction of aromatic aldehydes (I) with 5, 5-dimethyl-1, 3-cyclohexanedione (dimedone) (II) in water using lignin sulphonic acid as heterogeneous solid acid catalyst by microwave irradiation (MWI) at 450 W (**Scheme 1**).



Scheme 1: Synthesis of 1,8-Dioxo-octahydroxanthenes

EXPERIMENTAL SECTION

Chemicals and Materials

All chemicals and were purchased from Merck, Mumbai and used with or without purification.

Instrumentation

IR spectra were obtained using a Shimadzu FT-IR spectrophotometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument. ^1H NMR spectra were recorded on a Bruker Advance Dpx-250. Melting points were observed in open capillary.

General Procedure

A mixture of aromatic aldehyde (1 mmol), dimedone (2 mmol), and LSA (5 wt %) as catalyst were taken in a 50 mL beaker containing TBAB (2 wt %) dissolved in water (5 mL). The contents of the beaker were irradiated under microwave (450 W) for appropriate time as shown in **Table 1**. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, water was added and solid product obtained. It was filtered off and was purified by recrystallization from ethanol. All Products were characterized by comparison with authentic samples, physical data and spectral analysis.

RESULTS AND DISCUSSION

The condensation of dimedone and aromatic aldehydes with LSA as a catalyst and TBAB as phase transfer catalyst afforded the corresponding 1,8-dioxooctahydroxanthene derivatives under the microwave conditions.

LSA was prepared by using procedure reported in Literature [16]. To optimize the required amounts and catalysts ratio, LSA/TBAB, condensation of *p*-nitrobenzaldehyde (1 mmol) as a model substrate with dimedone (2 mmol) to the corresponding derivative, 3,3,6,6-tetramethyl-9-nitrophenyl-2,4,5,7-tetrahydro(2H)-9-hydro(1H)xanthene-1,8-dione was carried out under conventional heating using different amounts and combinations of LSA, and TBAB. We found that 5 wt % of LSA, and 2 wt % of TBAB in 5 mL of water gave product in higher yields but requires longer duration for completion of reaction. Therefore to enhance the rate of reaction, we have performed the reaction using microwave irradiation technique. There to find out the desired power of microwave irradiation, we have performed the above reaction under microwave at different powers of microwave irradiation. We found that 450W is good enough power to carry out transformation. All other derivatizations were carried out under the optimized conditions and results are summarized in **Table 1**.

Aromatic aldehydes having both electron donating or withdrawing groups reacted readily with dimedone to give the corresponding products in good yields (**Table 1**). As can be seen from the table, it was possible to carry out the reaction within shorter times in good yields. The functionalities present in aryl aldehydes such as chloro, nitro, methoxy, methyl and hydroxyl groups tolerated the reaction conditions in short time.

Spectral data of selected compounds.

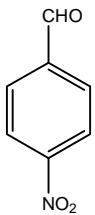
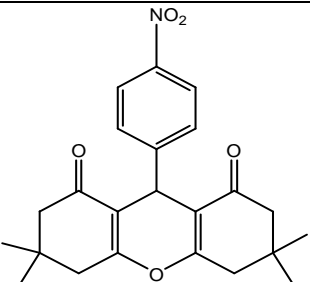
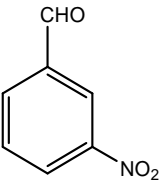
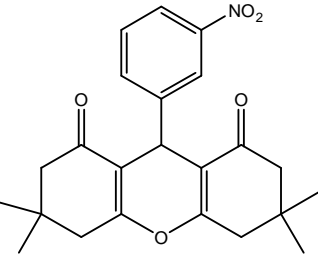
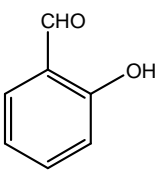
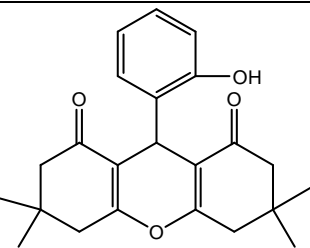
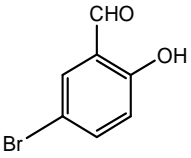
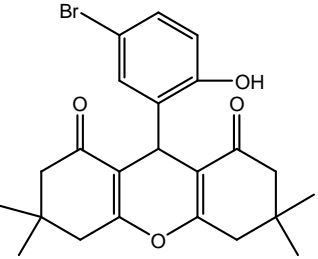
Entry 1: 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-nitrophenyl)-2H-xanthene-1,8- (5H,9H)-Dione

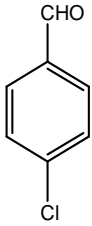
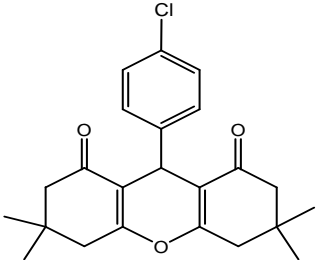
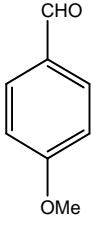
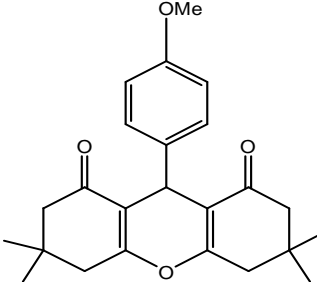
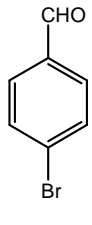
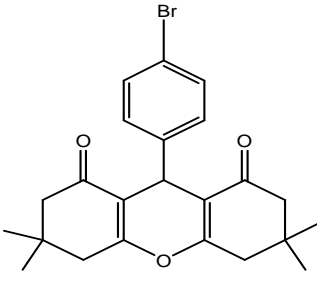
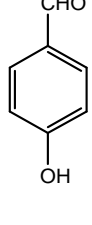
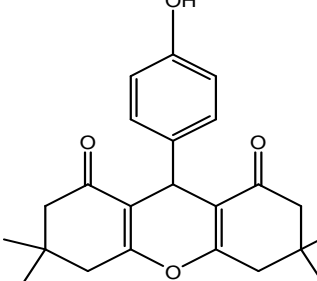
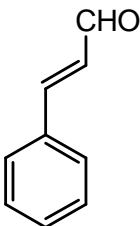
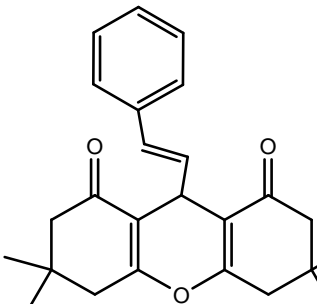
White solid; Yield 95% ; mp: 224°C; IR(KBr, $\lambda_{\text{max}}\text{cm}^{-1}$): 3019, 2961, 1666, 1595, 1530, 1351, 1197, 1003; ^1H NMR: (CDCl_3 , ppm): δ 1.11(s, 6H), 1.23 (s, 6H), 2.29–2.50 (m, 8H), 5.53 (s, 1H), 7.22-7.25(d, $J = 8.6$ Hz, 2H), 8.12-8.14 (d, $J = 8.8$ Hz, 2H); MS (m/z , %): 412.77 (M^+); Elemental analysis calcd. for M.F.- $\text{C}_{23}\text{H}_{25}\text{O}_5\text{N}$ (395.17) C= 69.86%, H= 6.37%, O= 20.23%, N= 3.54% and Found: C= 69.85%, H= 6.35%, O= 20.22%, N= 3.53%.

Entry 5: 3, 4, 6, 7-tetrahydro-3,3,6,6-tetramethyl-9-(4-Chlorophenyl)-2H-xanthene-1, 8-(5H,9H) -dione

White solid; yield 95%; mp: 285°C; IR (KBr, λ_{\max} cm^{-1}): 2961, 2929, 2880, 1666, 1591, 1489, 1351, 1197, 1003; ^1H NMR: (CDCl_3 , 250 MHz, δ ppm): 1.12(s, 6H), 1.24 (s, 6H), 2.37–2.50 (m, 8H), 5.53 (s, 1H), 7.23(d, $J = 8.6$ Hz, 2H), 8.12 (d, $J = 8.8$ Hz, 2H); MS (m/z , %): 403 (M^+) Elemental analysis calcd. for M.F.- $\text{C}_{23}\text{H}_{25}\text{O}_3\text{Cl}$ (384.90): C= 71.77%, H= 6.55%, O= 12.47%, Cl= 9.21% and Found: C= 71.75%, H= 6.53%, O= 12.43%, Cl= 9.20%.

Table 1: Synthesis of 1, 8-Dioxo-octahydroxanthene

Sr. No.	Aldehyde	Product ^a	Time (min)	Yield (%) ^b	M.P. (°C) (Obs.)	M.P. (°C) [Lit.]
1			3	95	224	(226-228) ¹⁸
2			3	89	168	(186-188) ¹⁶
3			1	90	200	(203-204)
4			3	88	220	(220-222)

5			5	95	285	(287-288) ¹⁸
6			3	96	240	(241-243) ¹⁸
7			3	90	210	(222-224) ¹⁶
8			3	90	243	(246-248) ¹⁸
9			3	89	175	(177-179) ¹⁸

Reaction conditions:

Aldehyde 1 (eq.), Dimedone (2 eq.), LSA (5 wt %), TBAB (2 wt %), Solvent free, MWI 450 W.

^aProducts were confirmed by physical and spectral analysis, ^bIsolated yield.

CONCLUSION

In conclusion, a series of 1, 8-dioxooctahydroxanthenes were synthesized using LSA as an efficient catalyst by the condensation of aldehydes and dimedone in good yields. All the reactions were conducted in water as a green solvent under microwave irradiation.

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