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Solvent-free and One-pot Facile Synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-one Derivatives Promoted by Manganese (IV) oxide as Efficient Catalyst

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Abstract

One-pot three-condensation synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-one derivatives catalyzed by Manganese (IV) oxide as an efficient, mild and inexpensive catalyst under solvent-free conditions was studied. The method presented is a safe and eco-friendly approach for the multi-component synthesis of xanthene derivatives with many merits in comparison with other reported results including short reaction times, solvent-free conditions, good to high yields, facile reaction profiles and easy work up.

Keywords: Manganese (IV) oxide; One-pot procedure; 12-aryl-tetrahydrobenzo[α] xanthene-11-one derivatives; Solvent-free conditions; Simple work up

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Introduction

Multi-component reactions (MCRs) [1-4] play an important role in combinatorial chemistry with high atom economy due to their ability to synthesize biologically active heterocyclic compounds. Xanthene derivatives possess a variety of pharmaceutical and biological activities. The compounds with xanthene derivatives ring systems are reported as antiplasmodial [5], antiviral [6], anti-inflammatory [7]. Besides, these heterocyclic molecules have been widely used as pH sensitive fluorescent materials for visualization of biomolecules [8,9], laser technology [10,11] and luminescent dyes [12].

In recent decades, a number of methodologies for preparation of these compounds have been reported that is including various catalysts [13-22]. Some of these methodologies have limitations such as difficult work-up, toxic and expensive catalysts, low yields, use of strongly acidic conditions and long-time reactions. Therefore, the development of facile method for the synthesis of xanthene derivatives is of great importance. In continuation of our research work on the synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones, herein we wish to report commercially available Manganese (IV) oxide (MnO_2) as inexpensive, readily and mild catalyst, for the one-pot synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-one derivatives by means of three-component domino reaction of *β*-naphthol, aryl aldehyde derivatives and dimedone. Efficient, readily and low-cost catalyst, good to high yields and short reaction times that makes our protocol alternative in comparison to some of the earlier reported methods. Furthermore, one of the source of environmental pollutions is the usage of organic solvents under reflux conditions and the need for column chromatography to purity the products. In this present work, the products were obtained through simple filtering with no need column chromatographic separation.

Experimental Methods

Melting points of all compounds were determined using an Electro thermal 9100 apparatus. Also, nuclear magnetic resonance, ^1H NMR spectra were recorded on a Bruker DRX-400 Avance instruments with $CdCl_3$ as solvents **(Figure 1)**. In this article, all reagents and solvents were purchased from Merck, Fluka and Acros chemical companies were used without further purification.

General procedure for preparation of 12-aryl-tetrahydrobenzo[α]xanthene-11-one derivatives (4a-o)

A mixture of *β*-naphthol (**1**, 1.0 mmol), aromatic aldehyde derivatives (**2**, 1.0 mmol), dimedone (**3**, 1.0 mmol) and MnO_2 (20

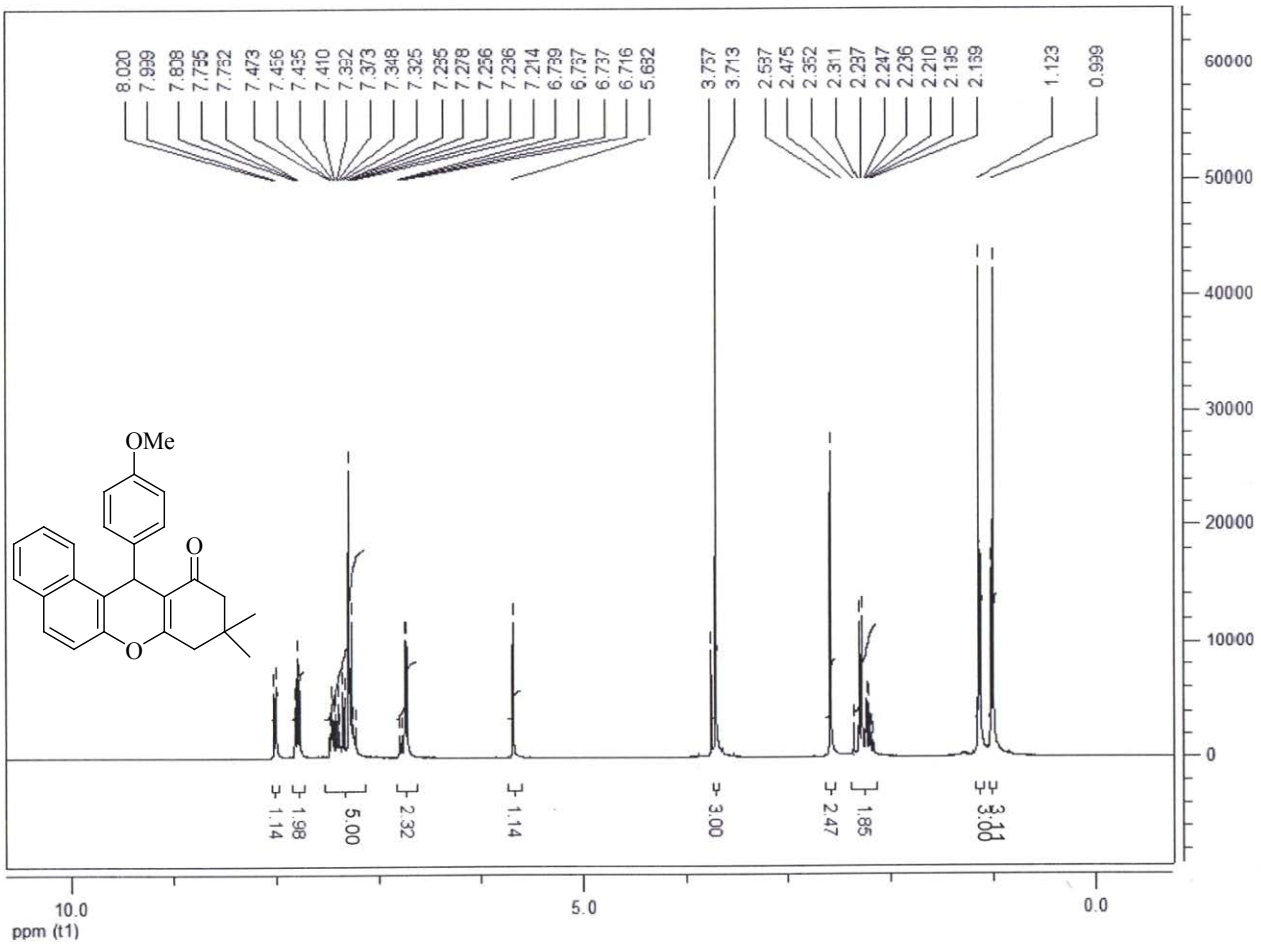
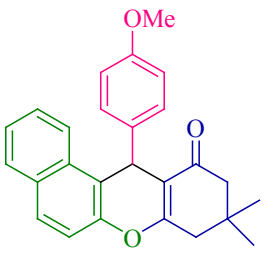


Figure 1 The ^{1}H NMR spectra of one of the products clearly indicated the formation of 9,9-dimethyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4m) in the presence of Manganese (IV) oxide.

mol%) was heated at 90°C for appropriate time. After completion of the reaction (by thin layer chromatography TLC) the mixture was cooled to r.t. and ethanol was added and the precipitated was separated with filtration and solid was recrystallized from ethanol to afford the pure products (**4a-o**).The products have been characterized by melting points and ^{1}H NMR spectroscopy. Spectra data of selected and known product are represented below:

9,9-dimethyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydrobenzo[a] xanthen-11-one(4m):



White solid; Yield: 82%; Melting point (Mp): 201-203°C.

^{1}HNMR (400 MHz, $CdCl_3$): 0.99 (3H, s, CH_3), 1.12 (3H, s, CH_3), 2.16-2.35 (2H, m, CH_2), 2.58 (2H, s, CH_2), 3.71 (3H, s,OCH_3), 5.68 (^{1}H, s, CHAr), 6.72 (2H, d, *J*=8.4 Hz, ArH), 7.21-7.47 (5H, m, ArH), 7.85 (2H, t, *J*=9.2 Hz, ArH), 8.01 (1H, d, *J*=8.4 Hz, ArH).

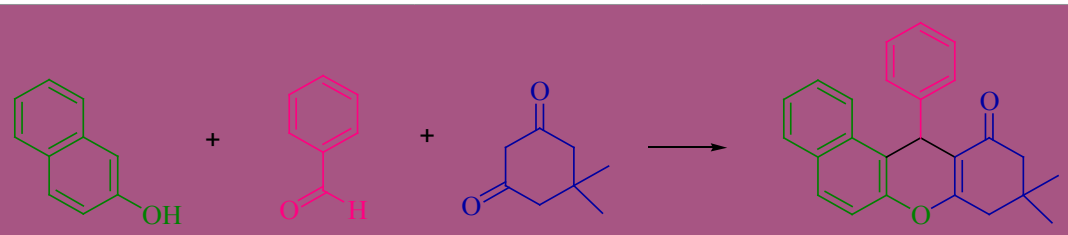
Results and Discussion

Recognizing the solvent free-based processes as eco-friendly methodology for the synthesis of organic compounds, we conceived the preparation of 12-aryl-tetrahydrobenzo[α] xanthene-11-one derivatives from the reaction between *β*-naphthol (**1**), aryl aldehyde derivatives (**2**) and dimedone (**3**) catalyzed by Manganese (IV) oxide (MnO_2) (Scheme 1). In order to determine the optimal reaction conditions, we screened different amounts of MnO_2 (5-25 mol%) at range of rt-100°C in the absence of solvent **(Table 1)** using *β*-naphthol, benzaldehyde and dimedone as a model reaction. When the amount of MnO_2 was increased from 5 to 20 mol%, the yield of product was improved from 32 to 86% **(Table 1, entries 2-5).** However, when the amount of MnO_2 was increased to 25 mol%, a remarkable increase in the yield of the product was not observed **(Table 1, entry 12)**. Consequently, the amount of 20 mol% for MnO_2 was selected as the optimized amount of the catalyst for this procedure. The reasonable results were observed when the reaction was performed at 90°C **(Table 1, entry 5).** The Increment of the temperature up to 100°C **(Table**

1, entry 11) didn't significantly improve the reaction results. The efficiency of this protocol was examined by the reaction of a variety of aryl aldehydes with electron-donating and electron-withdrawing groups with *β*-naphthol and dimedone and the results are summarized in **Table 2 (4a-o).**

Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-one derivatives are shown in **Table 3**. This study reveals that MnO_2 has shown its extraordinary potential to be an alternative inexpensive, readily and efficient catalyst for the one-pot

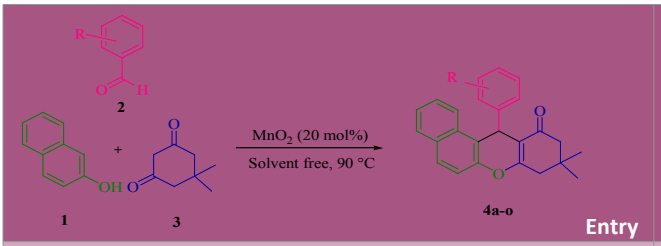
Table 1 Optimization of the reaction condition for the synthesis of **4a**[a].



Entry	MnO_2 (mol%)		Time (min)	Isolated Yields (%)
1	Catalyst free	90	360	trace
2	5	90	65	32
3	10	90	35	55
4	15	90	20	74
5	**20**	**90**	**15**	**86**
6	20	rt	360	trace
7	20	40	90	26
8	20	60	65	43
9	20	70	40	65
10	20	80	20	71
11	20	100	15	87
12	25	90	15	88

[a]Reaction conditions: *β*-naphthol (1.0 mmol); benzaldehyde (1.0 mmol); dimedone (1.0 mmol) and MnO_2 was heated under various temperatures for the appropriate time.

Table 2 MnO_2 catalyzed synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones.



Entry	R	Product	Time (min)	Isolated Yields (%)	Mp (°C)	Literature Mp (°C)
1	C_6H_5	**4a**	15	86	147-149	148-150 [17]
2	4-F- C_6H_4	**4b**	15	89	182-184	184-185 [13]
3	4-O_2N-C_6H_4	**4c**	15	87	176-178	175-178 [19]
4	3-O_2N-C_6H_4	**4d**	10	85	168-170	167-169 [13]
5	4-Br- C_6H_4	**4e**	25	77	183-186	184-186 [17]
6	3-Br- C_6H_4	**4f**	25	81	164-166	161-164 [19]
7	4-Me- C_6H_4	**4g**	15	88	170-172	171-173 [17]
8	3-Me- C_6H_4	**4h**	15	91	180-181	178-180 [16]
9	4- Cl-C_6H_4	**4i**	25	79	178-180	176-178 [17]
10	3- Cl-C_6H_4	**4j**	25	81	179-181	178-180 [22]
11	2- Cl-C_6H_4	**4k**	20	83	177-179	179-180 [20]
12	2, 4- Cl_2-C_6H_3	**4l**	30	76	184-186	183-184 [22]
13	4-OMe- C_6H_4	**4m**	20	82	201-203	202-204 [17]
14	2-OMe- C_6H_4	**4n**	15	89	167-169	165-167 [22]
15	4-OH- C_6H_4	**4o**	25	78	220-222	222-223 [17]

Table 3 Comparison of catalytic ability some of catalysts reported in the literature for synthesis of 12- aryl-tetrahydrobenzo[α]xanthene-11-ones*a*.

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Fe3O4@SiO2-SO3H	Solvent-free, 110°C	30 min/95	[13]
2	NaHSO4/SiO2	CH2Cl2, Reflux	300 min/91	[14]
3	NO2-FePc/C	EtOH, Reflux	30 min/91%	[15]
4	DSIMHS	Solvent-free, 55°C	20 min/93	[17]
5	CAN	Microwave irradiation, 120°C	120 min/85	[18]
6	Sr(OTf)2	1,2-Dichloroethane, 80°C	300 min/85	[21]
7	MnO2	Solvent-free, 90°C	15 min/86	This work

*a*Based on the three-component reaction of *β*-naphthol (1.0 mmol); benzaldehyde (1.0 mmol) and dimedone (1.0 mmol).

synthesis of these biologically active heterocyclic compounds, in addition good to high yields and short reaction times under solvent-free conditions are the notable advantages this present methodology.

Conclusion

Extremely facile and efficient procedure have been developed for the synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-one derivatives. One-pot three-component reaction of *β*-naphthol, aromatic aldehyde derivatives and dimedone in the presence of Manganese (IV) oxide (MnO_2) as efficient, readily and inexpensive catalyst under solvent-free conditions provides these biologically active heterocyclic compounds. Operational simplicity, inexpensive catalyst, enhanced rates, short reaction times and good to high isolated yields of the pure products are notable advantages of this eco-friendly protocol.

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