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RESEARCH ARTICLE

Ultrasound-Promoted Synthesis of 9-Aryl-l,8-dioxo-octahydroxanthenes Using TiO_2 as a Cheap and Reusable Catalyst

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Abstract: Reaction of aromatic aldehydes and dimedone was efficiently promoted by the TiO_2 as a catalyst in acetonitrile at room temperature under ultrasonic irradiation to afford the corresponding 9-aryl-1,8-dioxo-octahydroxanthene in excellent yields within minutes. However, the same reaction, without catalyst, yielded the corresponding 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cycloexene-1-one). Study with various aldehydes and dimedone reveals that ultrasound and TiO_2 plays a key role in the synthesis of 9-aryl-1,8-dioxo-octahydroxanthene.

Keywords: Aldehydes, Dimedone, Ultrasound, Xanthene derivatives, TiO_2

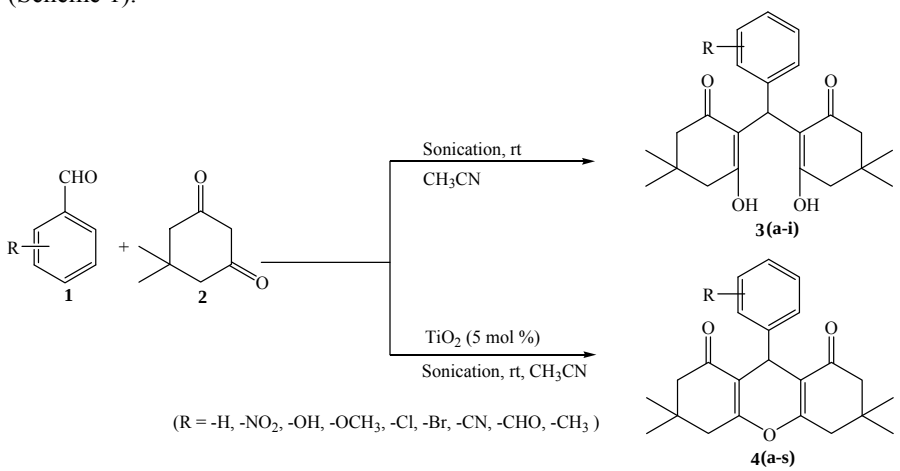
Introduction

In recent years sonochemistry has been widely used in organic syntheses as it offers a versatile and facile pathway for a bewildering range of organic reactions[1]. Sonochemistry involves the use of ultrasound technique to promote organic reactions. A large number of ultrasonic reactions can be carried out in higher yield, shorter reaction time or under milder conditions[2]. Ultrasound irradiation has been demonstrated as an alternative energy source for organic reactions which can be ordinarily accomplished by heating[3]. Due to the thermal effect of ultrasound wave, larger amount of molecules can meet the demand for the active energy in a given reaction, leading to the apparent improvement of the reaction efficiency with increased rates and reduced reaction time. It is also observed that reactions performed under ultrasound irradiation are commonly easier to work-up as compared to the conventional reactions[4]. In recent time, the use of TiO_2 as catalyst has received a considerable attention in organic synthesis due to its environmental compatibility, ease of handling, non-toxic nature, low cost, chemical stability even under irradiation[5], ease of separation from the reaction mixture and above all its reusability protocol[6]. TiO_2 finds diverse industrial applications such as whitener in paint[7], UV absorbers in sunscreen lotions and additives in food[8]. Besides these industrial applications, commercially available TiO_2

has invoked an interest as a green, inexpensive, mild and recyclable heterogeneous Lewis acid catalyst in numerous organic transformations such as Biginelli condensation[9]. Friedal-Crafts acylation[10], Beckmann rearrangement[11] and also in the synthesis of dihydropyrazines[12].

Xanthene derivatives are parent compounds of a large number of naturally occurring as well as synthetic derivatives and occupy a prominent position in medicinal chemistry, such as antiviral, antibacterial, antiflammatory agents, novel CCR1 receptor antagonists, anticancer agents and antinociceptive[13]. Xanthene derivatives are also used as dyes, fluorescent materials and in laser technologies, due to their useful properties[14].

A literature survey indicates that 9-aryl-1,8-dioxo-octahydroxanthene can be synthesized from aromatic aldehydes and dimedone in the presence of a number of catalysts, such as $CaCl_2$,[15] $SbCl_3/SiO_2$,[16] $HClO_4/SiO_2$,[17] $FeCl_3/SiO_2$,[18] silica sulfuric acid[19], Dowex-50w[20]. Amberlyst-15[21], $[Hbim]BF_4$[22] and TMSCl[23], However, many of these reported synthetic protocols suffer from one or more disadvantages, such as long reaction time, moderate yields, the use of expensive catalyst, strongly acidic conditions, tedious work-up and formation of by-products. We herein report the TiO_2 promoted synthesis of 9-aryl-1,8-dioxo-octahydroxanthene from corresponding aldehydes and dimedone in acetonitrile at a room temperature under ultrasound. However, the same reaction, in absence of the catalyst, yielded the corresponding 2,2′-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cycloexene-1-one) (Scheme 1).



Scheme 1. Two-component synthesis of Xanthene derivatives

Experimental

All chemicals were purchased from commercial suppliers, such as Sigma-Aldrich and Merck. Reactions were carried out in a Rivotek (25±1 ^oC) ultrasonic cleaning bath at 50 kHz. The ultrasonic cleaner had an output power of 120W and a power supply of 450W. The tank dimensions were 290: 240:150 mm with a liquid holding capacity of 9.5 L. The reactions were carried out in a RB flask of 10 mL capacity suspended at the center of the cleaning bath, 5 cm below the surface of the liquid. The melting points of the products were recorded on a Bruker instrument and compared with the reported literature values. ^1H and ^{13}C NMR spectra were obtained on a 400 MHz NMR spectrometers Bruker Maldi-TOF. Chemical shifts are indicated in parts per million with respect to TMS. The IR spectra were recorded in the range of 4000-400 cm^{-1} on an FTIR Perkin 2000 Model spectrometer using

KBr disk. Mass spectra were recorded on a High resolution mass spectrometer (UPLCMS) Bruker. Purity of the compounds was checked by TLC on a silica gel alumina sheet using *n*-hexane and ethylacetate as eluent. The visualization was accomplished with UV lamps at 254 nm.

General procedure for the synthesis of the synthesis of 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexane-1-one) ***3(a-i)***

A 10 mL round-bottomed flask containing an aldehyde (1 mmol), dimedone, (2 mmol), in acetonitrile (2 mL) was placed in an ultrasonic bath for 5 to 15 minute at room temperature. After completion, the reaction mixture was analyzed by TLC. The reaction mixture was treated with water, aqueous phase was extracted with ethylacetate (2x10 mL) and the organic layers was washed with water, saturated brine solution and dried over anhydrous Na_2SO_4. The combined organic layers were evaporated under reduced pressure and the resulting crude product was purified by column chromatography with ethylacetate and *n*-hexane. The products were characterized by ^{1}H NMR spectra. The spectroscopic data obtained on the synthesized compounds are given in spectral section.

General procedure for the synthesis of the synthesis of 9-Aryl-1,8-dioxo-octahydr-oxanthene derivatives ***4(a-s)***

A 10 mL round- bottomed flask containing an aldehyde (1 mmol), dimedone, (2 mmol) and 5 mol % of TiO_2 in acetonitrile (2 mL) was placed in an ultrasonic bath for 5 to 15 minute at room temperature. The product was isolated with ethylacetate (3x5 mL) and the combined layer was filtered to separate out TiO_2 and residue washed with ethylacetate. The solid residue of TiO_2 was further washed with acetone (10 mL) and then dried up; this recovered TiO_2 is reusable. After removal of solvent from the combined filtrate under reduced pressure, the organic residue was subjected to column chromatography to obtain pure 9-aryl-1,8-dioxo-octahydroxanthene compound. The identity of the product was confirmed by IR, ^{1}H and ^{13}C{^{1}H} NMR and Mass spectra. The spectroscopic data obtained on the synthesized compounds are given in below.

Spectral data for selected compounds

Compound ***3a***

White solid; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.09 (s, 6H, 2 x CH_3), 1.22 (s, 6H, 2 x CH_3), 2.27-2.47 (m, 8H, 4 x CH_2), 5.53 (s, 1H, CH), 7.07-7.27 (m, 5H, Ar), 11.88 (s, 1H, OH).

Compound ***3b***

White solid; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.09 (s, 6H, 2 x CH_3), 1.20 (s, 6H, 2 x CH_3), 2.24-2.47 (m, 8H, 4 x CH_2), 5.52 (s, 1H, CH), 7.06-7.17 (m, 4H, Ar), 11.77 (s, 1H, OH).

Compound ***3d***

White solid; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.05 (s, 6H, 2 x CH_3), 1.19 (s, 6H, 2 x CH_3), 2.20-2.39 (m, 8H, 4 x CH_2), 5.32 (s, 1H, CH), 7.18-7.20 (m, 4H, Ar), 11.71 (s, 1H, OH).

Compound ***3e***

White solid; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.00 (s, 6H, 2 x CH_3), 1.10 (s, 6H, 2 x CH_3), 2.19-2.35 (m, 8H, 4 x CH_2), 5.45 (s, 1H, CH), 6.90-6.97 (m, 4H, Ar), 11.80 (s, 1H, OH).

*Compound **3g***

White solid; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.02 (s, 6H, 2 x CH_3), 1.12 (s, 6H, 2 x CH_3), 2.22-2.43 (m, 8H, 4 x CH_2), 3.45 (s,3H, OCH_3), 5.50 (s, 1H, CH), 6.78-7.84 (2H, Ar), 6.92-7.00 (2H, Ar), 11.79 (s, 1H, OH).

*Compound **3h***

White solid; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.02 (s, 6H, 2 x CH_3), 1.15 (s, 6H, 2 x CH_3), 2.19 (s, 3H, CH_3) 2.36-2.57 (m, 8H, 4 x CH_2), 5.62 (s, 1H, CH), 6.80-6.89 (2H, Ar), 6.90-7.19 (2H, Ar), 11.84 (s, 1H, OH).

*Compound **3i***

White solid; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.04 (s, 6H, 2 x CH_3), 1.15 (s, 6H, 2 x CH_3), 2.27-2.47 (m, 8H, 4 x CH_2), 5.53 (s, 1H, CH), 6.72-7.89 (2H, Ar), 6.90-7.00 (2H, Ar), 11.88 (s, 1H, OH).

*Compound **4a***

White solid; Analytical TLC (silica gel 60) (25% EtOAc in hexane) R_f = 0.25; ^{1}H NMR ($CDCl_3$, 400 MHz): d 0.99 (s, 6H, 2 x CH_3), 1.12 (s, 6H, 2 x CH_3), 2.14-2.47 (m, 8H, 4 x CH_2), 4.53 (s, 1H, CH), 7.07-7.27 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) : δ 27.33, 29.27, 31.83, 32.2, 40.87, 50.74, 115.67, 126.36, 128.04, 128.37, 144.08, 162.24, 196.37.LC–MS: 367 [M+17].

*Compound **4b***

White solid; Analytical TLC (silica gel 60) (25% EtOAc in hexane) R_f = 0.25; IR ($CHCl_3$,cm^{-1}): 3020, 2961, 1720, 1667, 1592, 1530, 1352, 1198, 1000; ^{1}H NMR ($CDCl_3$, 400 MHz): d 01.19 (s, 6H, 2 x CH_3), 1.24 (s, 6H, 2 x CH_3), 2.37-2.57 (m, 8H, 4 x CH_2), 4.86 (s, 1H, CH), 7.27 (d, 2H, Ar), 8.14 (d, 2H,Ar); ^{13}C NMR ($CDCl_3$) : δ 27.14, 29.60, 32.72, 50.16, 56.85, 60.19, 106.20, 115.10, 136.85, 140.78, 153.68, 163.93, 197.17 LC–MS: 412 [M+17].

*Compound **4e***

white solid; Analytical TLC (silica gel 60) (25% EtOAc in hexane) R_f = 0.25; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.08 (s, 6H, 2 x CH_3), 1.20 (s, 6H, 2 x CH_3), 2.27-2.47 (m, 8H, 4 x CH_2), 5.43 (s, 1H, CH), 6.93-6.95 (d, 2H, Ar), 7.35-7.37 (d, 2H,Ar); ^{13}C NMR ($CDCl_3$) : δ 27.43, 29.53, 31.43, 32.48, 46.43, 47.05, 115.26, 119.64, 128.61, 131.26, 137.31, 189.41, 190.64; LC–MS: 445 [M+17].

*Compound **4h***

White solid; Analytical TLC (silica gel 60) (25% EtOAc in hexane) R_f = 0.25; IR ($CHCl_3$,cm^{-1}): 3392, 3064, 2960, 2929, 2253,1719, 1667, 1595, 1380,1166; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.08 (s, 6H, 2 x CH_3), 1.20 (s, 6H, 2 x CH_3), 2.27-2.47 (m, 8H, 4 x CH_2), 4.51 (s, 1H, CH), 6.90-7.0 (d, 2H, Ar), 7.22-7.24 (d, 2H,Ar); ^{13}C NMR ($CDCl_3$) : δ 27.70, 29.72, 31.80, 32.60, 41.37, 51.11, 115.60, 128.60, 130.20, 132.40, 143.11, 162.80, 196.70; LC–MS: 401 [M+17].

*Compound **4k***

Colorless solid; Analytical TLC (silica gel 60) (25% EtOAc in hexane) R_f = 0.25; IR ($CHCl_3$, cm^{-1}): 3014, 2958, 2873, 1891, 1667, 1624,1510, 1360,1215; ^{1}H NMR ($CDCl_3$, 400 MHz): d 1.08 (s, 6H, 2 x CH_3), 1.21 (s, 6H, 2 x CH_3), 2.27-2.37 (m, 8H, 4 x CH_2), 4.53 (s, 1H, CH), 6.78-6.80 (d, 2H, Ar), 7.22-7.24 (d, 2H,Ar); ^{13}C NMR ($CDCl_3$) : δ 27.39, 29.27, 31.40, 32.05, 46.47, 47.4, 113.67, 115.02, 127.36, 129.04, 157.37, 189.08, 190.24; LC–MS: 397 [M+17].

*Compound **4n***

White solid; Analytical TLC (silica gel 60) (25% EtOAc in hexane) R_f = 0.25; IR ($CHCl_3$,cm^{-1}): 3148, 2958, 1720, 1590, 1378, 1192,1081; ^1H NMR ($CDCl_3$, 400 MHz): d 0.99 (s, 6H, 2 x CH_3), 1.09 (s, 6H, 2 x CH_3), 2.14-2.20 (d, 4H), 2.24(s, 3H), 2.45(s, 4H), 4.78 (s, 1H, CH), 6.77-7.27 (4H, Ar); LC–MS: 387 [M+17].

Results and Discussion

We investigated theTiO_2 catalyzed, ultrasound promoted two-component synthesis of 9-aryl-1,8-dioxo-octahydroxanthene from various aldehydes and dimedone in acetonitrile at room temperature. Initially, the reaction of 4-nitrobenzaldehyde (1 mmol), dimedone (2 mmol) was chosen as a model reaction to optimize the reaction conditions, with or without catalyst. To our surprise the reaction proceeded efficiently in presence of TiO_2 (5 mol %) as catalyst to the afford the corresponding 9-aryl-1,8-dioxo-octahydroxanthene 4b (95% yields) in dramatically 5 min at room temperature under sonication (Table 1, entry 5). However the same reaction under the, same reaction conditions, but without catalyst, yielded the corresponding open chain analogue of 9-aryl-1,8-dioxo-octahydroxanthene 3b (90%) (Table 1, entry 6).

Table 1. Reaction of 4-nitrobenzaldehyde and dimedone under different reaction conditions

Entry	Condition	Catalyst/ No Catalyst	Solvent	Time	Product 3 Yield[a], %	Product 4 Yield[b], %
1	30 ^oC without sonication	TiO_2	Acetonitrile	24 h	Trace	Trace
2	30 ^oC without sonication	No Catalyst	Acetonitrile	24 h	Trace	Nil
3	30 ^oC without sonication	TiO_2	No solvent	24 h	Nil	Trace
4	30 ^oC without sonication	No Catalyst	No solvent	24 h	Nil	Nil
5	30 ^oC with sonication	TiO_2	Acetonitrile	5 min	Nil	95
6	30 ^oC with sonication	No Catalyst	Acetonitrile	5 min	90	Trace
7	30 ^oC with sonication	TiO_2	No Solvent	5 min	Nil	58
8	30 ^oC with sonication	No Catalyst	No Solvent	5 min	28	Trace
9	Reflux without sonication	TiO_2	Acetonitrile	24 h	10	Trace
10	Reflux without sonication	No Catalyst	Acetonitrile	24 h	Trace	Trace

[a,b]*Isolated yield*

When the reaction was carried out with and without solvents at room temperature without ultrasonic radiations, merely traces of the product were observed even after 24 h. (Table1, entry 1–4). Only traces of product were obtained when the reaction was carried out at elevated temperature in the absence of ultrasound radiations (Table1, entry 9-10). The mechanism of the reaction between aldehyde and dimedone has been described in literature[24]. First, intermediate **3** was formed through Knoevenagel addition between dimedone and aldehyde and subsequently, water elimination from intermediate **3** resulted in the formation of desired **4**. In these processes, TiO_2 plays a crucial role in accelerating the reaction, especially for water elimination of intermediate **3**. It can be verified by the fact that the reaction under catalyst-free condition only yielded the product **3**. Ultrasonic effect also plays an important role in accelerating the reaction, presumably by cavitations[25].

In addition to TiO_2, the reaction was also carried out in the presence of other catalyst, *i.e.* ZnO, CuO and SiO_2 and the results are summarized in Table 2. As evident from Table 2, TiO_2 proved to be the best catalyst for the reaction of 4-nitrobenzaldehyde and dimedone under ultrasonic irradiation, in acetonitrile at room temperature (Table 2, entry 1).

Table 2. Scanning of catalysts, using reaction between 4-nitrobenzaldehyde and dimedone under ultrasonication

Entry	Catalyst, 5 mol %	Time, min	Product 4, %,Yield[a]
1	TiO_2	5	95
2	ZnO	5	45
3	CuO	5	36
4	SiO_2	5	52

[a]*Isolated yield*

With the best catalyst in hand, we moved to study the effect of catalyst loading on the model reaction and the result was listed in Table 3.

Table 3. Effect of catalyst loading on the reaction of 4-nitrobenzaldehyde and dimedone under ultrasonication

Entry	TiO_2 mol %	Time min	Product 4 %, Yield[a]
1	1	5	63
2	5	5	95
3	10	5	95
4	20	5	95

[a]*Isolated yield*

After optimization of the catalyst loading, the reaction was also performed in various solvents such as, water, ethanol, methanol, dichloromethane, ethyl acetate, toluene and acetonitrile for the both type of reaction (with/ without catalyst). As evident from Table 4, the acetonitrile was found to be the best solvent for the reaction (Table 4, entry 1-6).

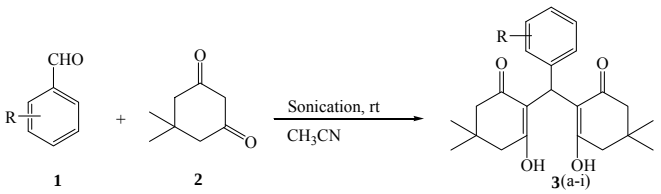
Table 4. Effect of solvents on the reaction of 4-nitrobenzaldehyde, and dimedone under ultrasonication

Entry	Solvent	Time min	Product 3 %, Yield[a]	Product 4 %, Yield[b]
1	Dichloromethane	5	82	89
2	Acetonitrile	5	90	95
3	Water	5	80	66
4	Ethanol	5	65	71
5	Methanol	5	54	79
6	Toluene	5	61	76

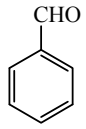
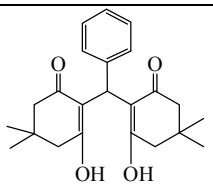
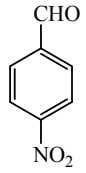
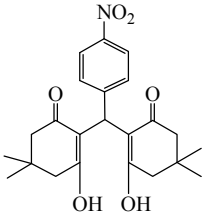
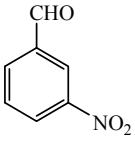
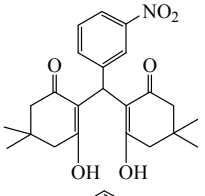
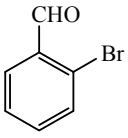
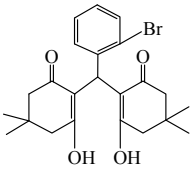
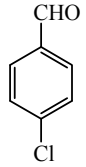
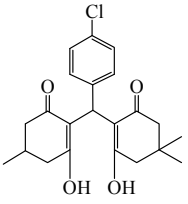
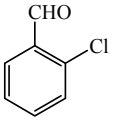
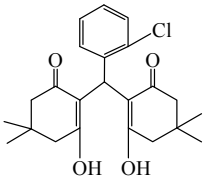
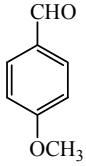
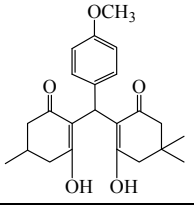
[a,b]*Isolated yield*

After the optimization of catalyst and other reactions conditions, we investigated the reaction of other benzaldehydes having electron-donating and electron-withdrawing group with dimedone under ultrasonic conditions. The results are given in Table 5 and Table 6 which shows that all the reactions preceded clean, to give the corresponding 2,2′-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cycloexene-1-one) **3** and 9-aryl-1,8-dioxo-octahydroxanthene **4** respectively.

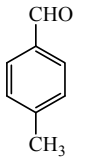
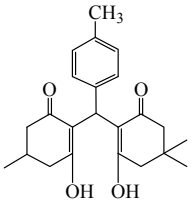
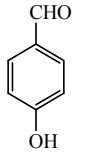
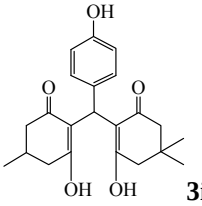
Table 5. Synthesis of 2,2′-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexane-1-one) derivatives



1 **2** **3**(a-i)

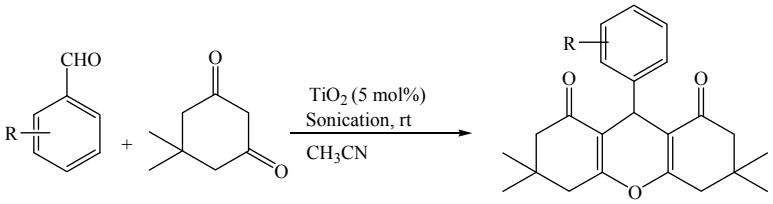
Entry	Aldehyde	Product[a]	Time, min	%,Yield[b]	m.p. °C	m.p.[lit] °C
1		 **3a**	6	88	190-191	192-194[22]
2		 **3b**	5	90	194-197	195-197[22]
3		 **3c**	8	86	200-202	201-203[22]
4		 **3d**	8	73	236-238	241-243[22]
5		 **3e**	13	85	141-144	145-147[22]
6		 **3f**	14	79	199-201	202-204[22]
7		 **3g**	10	84	148-149	146-148[22]

Contd…

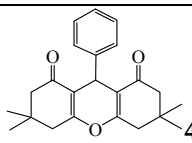
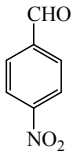
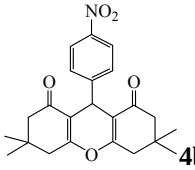
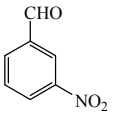
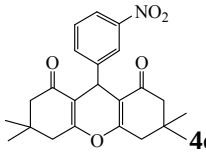
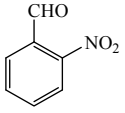
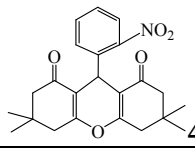
8		 **3h**	11	89	140-142	141-143[22]
9		 **3i**	9	84	200-202	201-203[22]

[a]Purity determined by TLC &[1]H NMR. [b]Isolated yield

Table 6. Synthesis of 9-aryl-1,8-dioxo-octahydroxanthene derivatives



1 **2** **4**(a-s)

Entry	Aldehyde	Product[a]	Time min	%,Yield[b]	m.p. °C	m.p.[lit] °C
1		 **4a**	6	90	204-206	205[24]
2		 **4b**	5	95	221-223	222-224[24]
3		 **4c**	8	93	164-166	165-166[24]
4		 **4d**	7	87	250-252	252-254[24]

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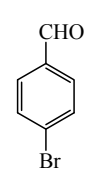
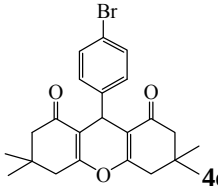
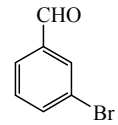
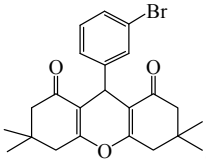
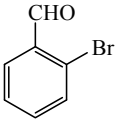
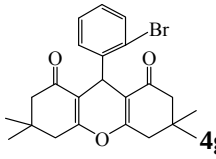
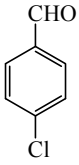
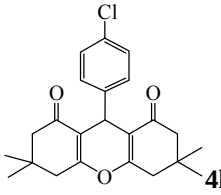
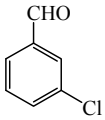
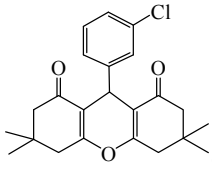
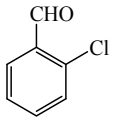
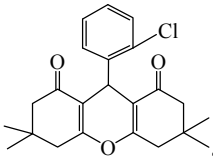
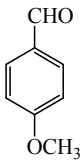
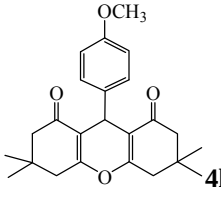
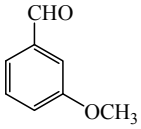
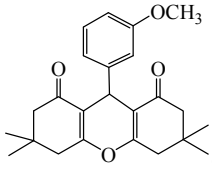
5		 **4e**	5	91	240-243	240-242[24]
		 **4f**	9	89	190-191	190-192[24]
7		 **4g**	8	93	226-227	226-229[24]
8		 **4h**	6	92	230-233	230-232[24]
9		 **4i**	8	94	184-185	183-185[24]
10		 **4j**	9	95	225-227	226-227[24]
11		 **4k**	10	93	241-242	242-243[24]
12		 **4l**	11	91	161-162	161-162[24]

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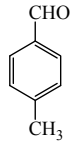
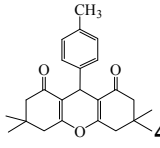
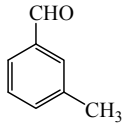
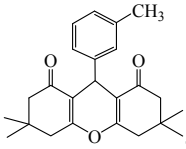
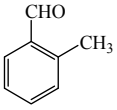
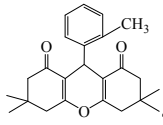
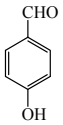
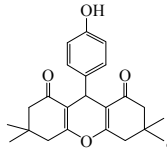
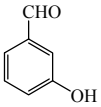
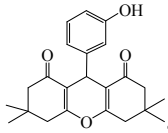
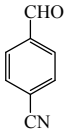
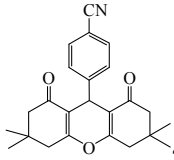
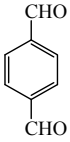
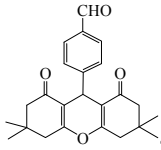
13		 **4m**	14	98	214-216	215-216[24]
14		 **4n**	15	88	207-208	208-210[24]
15		 **4o**	11	93	209-211	210-212[24]
16		 **4p**	12	94	249-250	246[24]
17		 **4q**	14	92	225-226	225-227[26]
18		 **4r**	8	90	218-220	217-218[26]
19		 **4s**	13	91	>300	>300[26]

[a]Purity determined by TLC &[1]H and [13]C NMR. [b]Isolated yield

The products were obtained as colorless crystalline solids. All compounds were characterized by IR, ^{1}H, ^{13}C {^{1}H} NMR and Mass Spectra. The reaction between aldehyde and dimedone under ultrasonic irradiation in acetonitrile without catalyst gave only chain compound **3b** as the major product which was confirmed by the presence of singlet at δ 11.77, and 5.52 corresponding to -OH and methyne protons, respectively in the ^{1}H NMR spectrum. Similarly a singlet at δ 4.86, characteristic of the methyne proton was observed for the cyclized compound **4b**. The spectra of synthesized compounds were compared with the literature Values[17-25].

All the spectroscopic data obtained were found to be in good agreement with the reported valves. The recyclability of catalyst TiO_2 was also studied. The catalyst can be easily filtered out from the aqueous layer and dried for reuse. It is apparent from Figure 1 that the catalyst can be used up to five times without the significantly of catalytic activity.

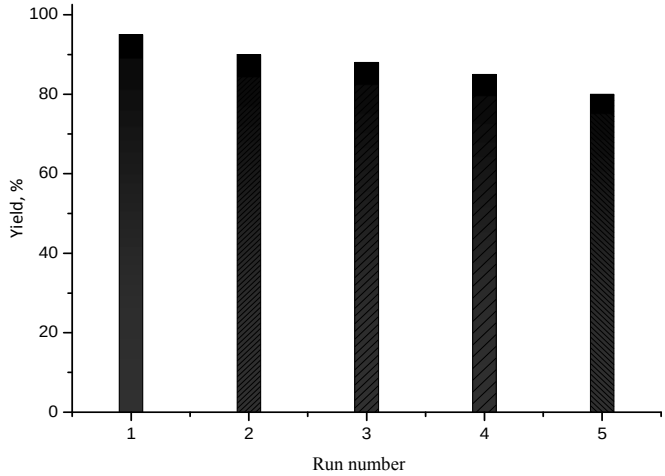


Figure 1. Reusability of catalyst

Conclusion

Our studies clearly demonstrates that TiO_2 is a versatile, cheap, and reusable catalyst for the synthesis of 9-Aryl-1,8-dioxo-octahydroxanthene from aldehyde and dimedone under ultrasonic radiations.

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