

ORIGINAL PAPER

Molybdate sulfonic acid: preparation, characterization, and application as an effective and reusable catalyst for octahydroxanthene-1,8-dione synthesis

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Molybdate sulfonic acid (MSA) as a highly efficient catalyst was synthesized and employed for the synthesis of octahydroxanthene-1,8-dione derivatives. MSA efficiently catalyzed condensation of a wide range of aryl aldehydes and cyclohexane-1,3-diones to obtain octahydroxanthene-1,8-diones. It was characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), and FT-IR spectroscopy. This catalyst can be recovered and reused several times in other reactions maintaining its high activity. This novel and green method is very cheap and has many advantages such as excellent yields, the use of recoverable and eco-friendly catalysts, and a simple work-up procedure. © 2012 Institute of Chemistry, Slovak Academy of Sciences

Keywords: molybdate sulfonic acid, catalyst, cyclic 1,3-diketone, condensation reaction, solvent-free

Introduction

Preparation and use of eco-friendly catalysts to improve the efficiency of reactions or provide a higher yield has been the subject of interests especially in the synthesis of organic compounds (Clark & Macquarrie, 1996; Prakash et al., 2004; Martins et al., 2004; Beletskava & Tvurin, 2010). Therefore, preparing and employing an effective and eco-friendly catalyst can be extremely valuable in chemical syntheses (Veverková & Toma, 2005). Solid acids play a significant role in green chemistry, especially in chemical manufacturing processes (Movassaghi & Jacobsen, 2002; Qi et al., 2010; Wedge & Hawthorne, 2003; Stone & Anderson, 2007). Solid acids as catalysts have generally high turnover numbers and they play a significant role in the synthesis of heterocyclic compounds (Chen et al., 2002; Kafuku et al., 2010; Kidwai & Bhatnagar, 2010; Karami et al., 2012a, 2012b, 2012c). Furthermore, they can be easily separated from organic components (Clark, 2002). Among organic compounds, xanthene, and its derivatives have received significant attention in recent years due to their wide range of bi-

ological and therapeutic properties (El-Brashy et al., 2004; Chibale et al., 2003). The importance of xanthene derivatives was clearly realized from their usage as dyes (Bhowmik & Ganguly, 2005), sensitizers in photodynamic therapy destroying tumor cells (Ion et al., 1998), pH-sensitive fluorescent materials for biomolecules visualization (Knight & Stephens, 1989), and in laser technologies (Ahmad et al., 2002). Moreover, some xanthene based compounds have found application as antagonists paralyzing the action of zoxalamine as well as in the photodynamic therapy (Saint-Ruf et al., 1975). Several polycyclic compounds containing the xanthene skeleton can be isolated from natural sources (Kinjo et al., 1995). Xanthene and its derivatives are prepared by different methods, including the reaction of aryloxymagnesium halides with triethylorthoformate (Casiraghi et al., 1973), cyclodehydration (Bekaert et al., 1992), trapping of benzynes by phenols (Knight & Little, 2001), intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones (Kuo & Fang, 2001), and the cyclocondensation of 2-hydroxy aromatic aldehydes and 2-tetralone (Jha & Beal, 2004). In view of the impor-

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Fig. 1. Preparation of MSA (I); *i* – hexane, 0 °C.

tance of xanthene derivatives, many methods for the synthesis of these compounds were reported including condensation of β -naphthol and aldehydes or acetals catalyzed by silica sulfuric acid, HCl/CH₃COOH, or H₃PO₄ (Seyyedhamzeh et al., 2008). However, some of these methods involve long reaction times, harsh reaction conditions, or unsatisfactory yields. Therefore, improvement of these syntheses has been continuously sought for. In the current study, a new route of xanthene derivatives preparation by molybdate sulfonic acid (MSA) as an eco-friendly, high efficient, and reusable catalyst is presented. This method not only affords the products in excellent yields but also avoids problems associated with catalyst costs, handling, safety, and pollution.

Experimental

Chemicals were purchased from Sigma-Aldrich (USA), and Merck (Germany) chemical companies. Hexane was dried prior use by distillation from calcium hydride (10 g L^{-1}). X-ray diffraction (XRD) pattern was obtained using a Philips X Pert Pro X diffractometer (PANalytical, The Netherlands) operated with an Ni-filtered CuK_{α} radiation source. Xray fluorescence (XRF) spectroscopy was recorded by an X-ray fluorescence analyzer, Bruker, S4 Pioneer (Bruker, Germany). Melting points were measured on an electrothermal KSB1N apparatus (Krüss, Germany). IR spectra were recorded in the KBr matrix on a Jasco FT-IR-680 plus spectrometer (Jasco, Japan) at the scanning range of 400–4000 cm⁻¹. ¹H $\rm NMR$ and $^{13}\rm C$ NMR spectra were determined on a FT-NMR Bruker Avance Ultra Shield Spectrometer (Bruker, USA) at 400.13 MHz (for ¹H NMR) and 100.62 MHz (for ${}^{13}C$ NMR) in CDCl₃ as the solvent in the presence of tetramethylsilane as the internal standard. TLC was performed on TLC-Grade silica gel-G/UV 254 nm plates (Merck, Germany) (eluent: hexane/ethyl acetate $\varphi_{\rm r} = 3:2$).

Preparation of MSA

Firstly, dry hexane (25 mL) was inserted into a 100 mL round bottom flask equipped with an ice bath and an overhead stirrer; anhydrous sodium molybdate (4.118 g, 20 mmol) was added followed by chloro-sulfonic acid (0.266 mL, 40 mmol) which was added dropwise to the flask for 30 min. This solution was

stirred for 1.5 h. The reaction mixture was gradually poured into 25 mL of chilled distilled water under agitation. The bluish solid which separated out was filtered. Then, the catalyst was washed with distilled water five times until the filtrate showed a negative test for the chloride ion, and it was dried at 120 °C for 5 h. The catalyst was obtained in a 90 % yield as a bluish solid which decomposed at 354 °C.

General procedure for the preparation of 9aryl-substituted octahydroxanthene-1,8-diones using MSA

A mixture of 1,3-diketone (2 mmol), aldehyde (1 mmol), and MSA (I) (16 mg, 0.05 mmol) was mechanically stirred under solvent-free conditions in a glass tube at 100 °C for 1 h. The progress of the reaction was monitored by TLC (hexane/ethyl acetate, $\varphi_{\rm r} = 3:2$). After the reaction completion, the reaction mixture was cooled to laboratory temperature, washed with CHCl₃ (10 mL), and filtered to remove the catalyst, the filtrate was concentrated in vacuum to afford the crude product which was recrystallized from ethanol to afford the crystalline pure product. The catalyst was washed with ethanol, dried at 120 °C for 1 h, and reused five times in other reactions.

Results and discussion

More recently, pressure from environmentalists has induced a search for more environmentally friendly forms of catalysis. Also, development of practical methods, reaction media, conditions, and/or the use of materials based on the idea of green chemistry is one of the important issues in the scientific community (Martins et al., 2009). Silica sulfuric acid and Nafion-H[®] have been applied in a wide variety of reactions (Olah et al., 1978; Zolfigol, 2001; Prakash et al., 2004). Accordingly, it was found that anhydrous sodium molybdate reacts with chlorosulfonic acid (1 : 2 mole ratio) to give (I). The reaction is easy and clean without any gas production (Fig. 1).

Fig. 2 shows the XRD patterns of *I*. It was reported that high-degree mixing of Mo–S in chlorosulfonic acid often leads to the absence of the XRD pattern for anhydrous sodium molybdate.

XRD patterns of sodium molybdate (Na₂MoO₄) (Ding et al., 2006) show broad peaks at around 2θ 17.0°, 27.0°, 32.0°, 48.0°, 53.0°, 57.5°, 78.5°, 82.0°,



Fig. 2. Powder X-ray diffraction pattern of I.

Table 1. XRF data of I

Entry	Compound	Content/mass $\%$
1	SO_3	49.52
2	Na_2O	1.150
3	MoO_3	39.02
4	Cl	0.150
5	K_2O	0.064
6	Nb_2O_5	0.019
7	Fe_2O_3	0.012
8	CuO	0.010
9	LOI^a	10.03
10	Total	99.98

a) Loss on ignition.

some of which are absent in the XRD pattern of MSA due to high-degree mixing of Mo with sulfonic acid. Broad peaks around 2θ 23°, 29°, and 34° from the smaller inset can be attributed to the linking of Mo to sulfonic acid. Furthermore, FT-IR spectrum of anhydrous sodium molybdate and MSA shows characteristic bonds of anhydrous sodium molybdate and chlorosulfonic acid. Absorption at 3459 cm⁻¹, 2110 cm⁻¹, 1635 cm⁻¹, 1129 cm⁻¹, 909 cm⁻¹, 771 cm⁻¹, 637 cm⁻¹, 616 cm⁻¹, and 451 cm⁻¹ in the catalyst spectrum reveals both bonds in anhydrous sodium

molybdate and the -OSO₃H group.

In addition, titration of the catalyst with NaOH (0.1 M) was done for a more detailed characterization of the catalyst. First, 1 mmol of the catalyst was dissolved in 100 mL of water and titrated with NaOH (0.1 M) in the presence of phenolphthalein as an indicator. In the equivalent point, it can be seen that for 1 mmol of the catalyst, 2 mmol of NaOH had to be used. The catalyst titration showed that for the acid-base reaction two protons are available, which is in agreement with the proposed structure of the catalyst. XRF data of I indicate the presence of MoO₃ and SO₃ in the catalyst (Table 1).

MSA has a number of structural features, e.g. it contains an acidic proton and it is efficient under solvent-free conditions, which make it an attractive catalyst for organic transformations. This reagent has good thermal and mechanical stability and it can be filtered from the reaction mixture to be subsequently reused. In connection with our studies on new catalyzed organic reactions (Karami et al., 2012a, 2012b, 2012c; Karami & Kiani, 2011), MSA was found to be applicable as a powerful, safe and recyclable catalyst for the condensation reaction between cyclic 1,3-diketones (II) with aryl aldehydes (III) (Fig. 3). At first, the synthesis of 2,2'-(arylmethylene)bis(3hydroxycyclohex-2-enone) (IV) from the reaction of IIwith several aromatic aldehydes (III), was expected; however, as it can be seen from Fig. 3, under the given conditions, IV was not formed and II with III were effectively cyclized to give 9-aryl-substituted octahydroxanthene-1,8-diones (V). Structures of the products (V) were deduced from their IR, ¹H NMR, and ¹³C NMR spectroscopic data.

In another variation of the process, aromatic dialdehyde substrate was used instead of benzaldehyde derivatives which led to the condensation with II(1 : 4 mole ratio) to afford bisxanthene products. In this case, four 1,3-diketones (II) with a dialdehyde were effectively cyclized to obtain bis(9-arylsubstituted octahydroxanthene-1,8-diones) (Fig. 4).



Fig. 3. Synthesis of octahydroxanthene-1,8-diones catalyzed by MSA (I) as an effective catalyst; i – solvent free, 100 °C, MSA 5 mole %.



Fig. 4. Catalyzed synthesis of bis(octahydroxanthene-1,8-diones) using MSA (I); i – solvent free, 100 °C, MSA 5 mole %.



Product	Mole $\%$	Time/min	m Yield/%	
	1	180	55	
	5 10	60	96 88	
Me Me Me	20	90	70	

Table 3. Optimization of temperature for the model reaction

Product	Temperature/ $^{\circ}$ C	Time/min	m Yield/%	
	r.t.	180	60	
	50	180	75	
o V o	80	90	82	
	90	70	90	
$ \left(\right) \left(\left(\right) \left(\right) \left(\left(\right) \left(\right) \left(\right) \left(\left(\right) \left(\right) \left(\left(\right) \left(\right) \left($	100	60	96	
Me	110	60	92	
Me Me	120	60	85	

r.t. - room temperature.

Solvent-free conditions or the use of a solid reaction catalyst reduce the pollution and costs due to the simplification of the experimental and workup procedures and savings in labor. Recently, interest in the environmental control of chemical processes has increased remarkably as a response to public concern about the pollution of environment by hazardous chemical materials. Also, it is important to know which reaction process is the most economic and eco-friendly one, with the shortest reaction time and highest yield of the product. Therefore, finding optimal conditions of the reaction is inevitable. For this purpose, the amount of catalyst and the temperature of the process were optimized. First, condensation of dimedone (II, R_1 , $R_2 = Me$; Fig. 3) and benzaldehyde (III, Ar = Ph; Fig. 3) was chosen as a model reaction (preparation of compound Va). It was found that in the absence of a catalyst, there is no appreciable progress in the condensation reaction even at high temperatures, and thus, the catalyst plays a crucial role in the reaction. Required amount of the catalyst in the synthesis of octahydroxanthene-1,8-dione derivatives for the model reaction is shown in Table 2. As can be seen from this table, when 5 mole % of MSA as an effective catalyst was added to the reaction mixture, maximum yield of the product (96 %) was obtained.

Aldebude III	ebyde III Product Time/min Vield ^a /		Violda /07	M.p./°C	
Aldenyde III	rioduci	1 me/ mm	Tierd"/70	Found	Reported
СНО	Me Me Va	60	96	202–204	$201-202^{b}$
CHO	Me O Me Vb	45	90	230–232	$230-232^{b}$
CHO Me	Me Me Me Me VC	90	88	215–217	$216 – 217^c$
CHO NO ₂	Me of Me Me Vd	30	95	219–221	221–223°
CHO Br	Br Me Me Me Me Me Me Ve	60	89	226–227	$226 – 228^d$
MeO OMe	MeO Me Me Me Me Me	60	93	209–211	$210 – 212^{e}$
CHO F	Me O Me Vg	35	92	223–225	$224 – 226^d$
Br OH	$\overset{\text{Br}}{\underset{\text{Me}}{\overset{\text{OH}}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}{\overset{\text{OH}}}{\overset{\text{OH}}{\overset{OH}}{\overset{\text{OH}}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}}{\overset{OH}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}{\overset{OH}}}{\overset{OH}}}{\overset{OH}}}{\overset{OH}}}{\overset{OH}}}}}}}}}}$	50	90	250-252	249–252 ^c
CHO CH ₃ CH ₃	Me Vi	110	86	189–191	190–191 ^{<i>f</i>}

Table 4. MSA catalyzed synthesis of 9-aryl substituted octahydroxanthene-1,8-diones

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Table 4. (continued)

	Product Time/min Viold ^a /07		V: 110 /07	Viold ^a /%	
Aldenyde III	Froduct	1 me/ mm	r leid 7 70	Found	Reported
H ₃ C CHO	Me We Vj	90	88	238–239	236–239 ^g
СНО	$Me \rightarrow 0 \rightarrow Me \rightarrow Me$ $Me \rightarrow 0 \rightarrow Me \rightarrow Me$ $Me \rightarrow 0 \rightarrow Me \rightarrow Me$ $Me \rightarrow Me \rightarrow Me$	60	90	245–247	_
СНО	Me M	75	86	238–240	_
CHO	V_{I}	45	95	271–273	272–273 ^h
CHO	V_{n}^{Me}	65	89	260-262	$262-263^{b}$
CHO NO ₂		30	92	224–227	224–226 ⁱ
Br		55	88	250-252	249–252 ^j
H ₃ C CHO	$\bigcup_{0}^{H_3C} \bigcup_{0}^{CH_3} Vq$	60	86	170–172	$169 - 171^k$

Aldehyde III Produc	Product	Time /min	Viold ^a $\sqrt{2}$	M.p	o./°C	
Aldenyde III	Floquet	1 mie/ mm	Tield / 70	Found	Reported	
СНО		50	92	252–255	_	

Table 4. (continued)

a) Refers to isolated yield; b) Kantevari et al. (2007); c) Venkatesan et al. (2008); d) Fan et al. (2005); e) Zhang and Lui (2008); f) Horning and Horning (1946); g) Bekaert et al. (1992); h) Das et al. (2006); i) John et al. (2006); j) Casiraghi et al. (1973); k) Tavakoli et al. (2009).

Table 5. Synthesis of Va (model reaction) using different catalysts

Catalyst	Mole $\%$	Solvent	${\rm Temperature}/{}^{\circ}\!{\rm C}$	Time/min	Yield/%	Reference
MSA	5	Solvent free	100	60	96	This paper
$p\text{-}\mathrm{TsOH}$	5	$MeOH/H_2O$	80	20	80	Venkatesan et al. (2008)
DBSA	10	H_2O , ultrasonic	25 - 30	60	89	Jin et al. (2006)
TMSCl	100	CH_3CN	Reflux	420	84	Kantevari et al. (2006)
TBAHS	10	$Dioxane, H_2O$	Reflux	210	88	Karade et al. (2007)
DBSA	20	H_2O	Reflux	180	91	Bin et al. (2006)
$Select fluor^{TM}$	10	Solvent free	120	60	95	Poor Heravi (2009)
$PPA-SiO_2$	10	Solvent free	140	30	92	Kantevari et al. (2007)
$HClO_4-SiO_2$	10	Solvent free	140	180	32	Kantevari et al. (2007)
$\rm SbCl_3-SiO_2$	10	Solvent free	120	50	93	Zhang and Lui (2008)

p-TSOH – p-Toluenesulfonic acid, DBSA – p-dodecylbenzenesulfonic acid; TMSCl – trimethylsilyl chloride, TBAHS – tetrabutylammonium hydrogen sulfate, SelectfluorTM – 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate), PPA–SiO₂ – polyphosphoric acid supported on silica.

As can be seen from Table 2, the best mole ratio of the catalyst for this reaction was found to be 5 mole %, whereas adding higher amounts of the catalyst did not improve the catalysis results.

In the following study on the model reactions, the reactions were examined at various temperatures in the presence of 5 mole % of MSA to determine the effect of temperature on the progress of the reaction (Table 3). This observation revealed that the maximum yield of the product in the shortest reaction time was obtained at 100 °C.

According to the archived optimal conditions, the synthesis of xanthene derivatives under solvent-free condition in the presence of 5 mole % of MSA and at 100 °C was attempted.

Under these conditions, several aromatic aldehydes (III) containing electron donating as well as electron withdrawing groups with different substitution patterns were effectively condensed to give 9-aryl substituted octahydroxanthene-1,8-dione derivatives (V). In all cases, the corresponding xanthene derivatives were obtained in good to excellent yields (Table 4).

Comparison of the presented method with others for the synthesis of 3,3,6,6-tetramethyl-9-phenyl3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Va) is shown in Table 5. These results show that the used catalysts created good to excellent conditions for the synthesis of xanthene derivatives compared to other catalysts and methods reported previously.

All the prepared products (V) were characterized by their IR, ¹H NMR, and ¹³C NMR spectroscopic data. Spectral data of the newly prepared products are summarized in Tables 6 and 7.

At the end of the reactions, the catalysts were filtered, washed with ethanol, dried at 120 °C for 1 h, and reused in another reaction. MSA showed high catalytic activity with very short reaction times. Moreover, it can be recovered and reused five times without a significant loss of activity. Results of these observations for the model reaction are shown in Table 8.

Fig. 5 shows the proposed mechanism for the preparation of 9-aryl-substituted octahydroxanthene-1,8-diones in the presence of I.

MSA is a strong solid acid able to activate the carbonyl group of aldehydes (*III*) and decrease the energy of their transition state. Nucleophilic attack of β -diketone (*II*) on the activated carbonyl group of aldehydes results in the formation of intermediate

Compound	Formula	М	$w_{ m i}({ m cal}) \ w_{ m i}({ m four})$		
Compound	Formula	m _r	С	Н	
Vk	$\mathrm{C}_{40}\mathrm{H}_{46}\mathrm{O}_{6}$	622.79	77.14 77.26	7.44 7.28	
Vl	$\mathrm{C}_{40}\mathrm{H}_{46}\mathrm{O}_{6}$	622.79	77.14 77.21	7.44 7.32	
Vr	$C_{32}H_{30}O_{6}$	510.58	75.28 75.32	$5.92 \\ 5.86$	

 Table 6. Characterization data of newly prepared compounds

Table	7.	Representative	spectral	data	of	newly	synthesized	products
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Product	Spectral data
Vk	IR, $\tilde{\nu}/\text{cm}^{-1}$: 808, 1003, 1162, 1200, 1365, 1425, 1462, 1620, 1666, 2957, 3040 ¹ H NMR (CDCl ₃), δ : 0.97 (s, 12H, 4 × CH ₃), 1.07 (s, 12H, 4 × CH ₃), 2.18 (s, 8H, 4 × CH ₂), 2.44 (dd, 8H, ¹ J = 36.4 Hz, ⁴ J = 17.6 Hz, 4 × CH ₂), 4.71 (s, 2H, 2 × CH), 7.08 (s, 2H, Ar-H), 7.27 (s, 2H, Ar-H) ¹³ C NMR (CDCl ₃), δ : 25.0, 27.7, 29.0, 30.7, 32.2, 40.9, 50.6, 115.7, 127.9, 141.7, 162.4, 196.4
Vl	IR, $\tilde{\nu}/\text{cm}^{-1}$: 769, 1158, 1203, 1462, 1629, 1659, 2957, 3095 ¹ H NMR (CDCl ₃), δ : 1.03 (s, 12H, 4 × CH ₃), 1.08 (s, 12H, 4 × CH ₃), 2.15 (dd, 8H, ² J = 24.0 Hz, ⁴ J = 16.0 Hz, 4 × CH ₂), 2.48 (dd, 8H, ² J = 45.2 Hz, ⁴ J = 17.6 Hz, 4 × CH ₂), 4.72 (s, 2H, 2 × CH), 7.07–7.09 (m, 3H, Ar-H), 7.15 (1H, s, Ar-H) ¹³ C NMR (CDCl ₃), δ : 28.0, 29.6, 31.8, 32.6, 41.3, 51.3, 116.0, 126.8, 128.2, 144.0, 162.7, 196.7
Vr	IR, $\tilde{\nu}/\text{cm}^{-1}$: 802, 1001, 1165, 1210, 1425, 1460, 1623, 1665, 2950, 3038 ¹ H NMR (CDCl ₃), δ : 2.29 (m, 8H, 4 × CH ₂), 2.39 (m, 8H, 4 × CH ₂), 2.57 (4H, m, 2 × CH ₂), 2.67 (m, 4H, 2 × CH ₂), 4.74 (s, 2H, 2 × CH), 7.18 (d, 4H, $J = 7.6$ Hz, Ar) ¹³ C NMR (CDCl ₃), δ : 20.1, 27.1, 30.8, 36.9, 116.9, 128.0, 141.9, 164.0, 196.7



Fig. 5. Suggested mechanism for the synthesis of octahydroxanthene-1,8-diones derivatives; catalyst H_2A -MSA.

Table 8. Reusability of MSA in the reaction process for the model reaction

Product	Total reusability	Time/min	Yield/%
	1	60	96
	2	60	92
	3	60	88
Me Me	4	90	85
$Me^{\prime} \sim 10^{\prime} \sim Me^{\prime}$	5	90	80

VI followed by a nucleophilic attack of the second β diketone on intermediate VI which is activated by the acidic proton of MSA giving intermediate VII. From the cyclization of intermediate VII and its subsequent dehydration, the corresponding octahydroxanthene-1,8-diones V are produced.

Conclusions

A new application of MSA as a catalyst for the preparation of 9-aryl substituted octahydroxanthene-1,8-diones derivatives is presented. All products were obtained in excellent yields in the presence of the catalytic amount of MSA. The presence of MSA in the condensation of cyclic 1,3-diketones with aromatic aldehydes is a key factor of the reaction progress. This catalyst not only provides cheap and facile process, it is also considered to be a green catalyst. Other advantages of this method are its simple experimental procedure, utilization of a clean and recyclable catalyst, the use of ready available starting materials, and the short period of the reaction.

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