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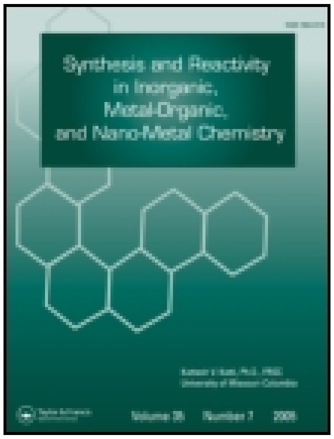

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Alumina Supported Acidic Ionic Liquid: Preparation, Characterization, and Its Application as Catalyst in the Synthesis of 1,8-dioxo-octahydroxanthenes

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Alumina Supported Acidic Ionic Liquid: Preparation, Characterization, and Its Application as Catalyst in the Synthesis of 1,8-dioxo-octahydroxanthenes

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Preparation of a novel heterogeneous acidic catalyst by impregnation of alumina support by N-(4-sulfonic acid)butyl triethylammonium hydrogen sulfate ([$Et_3NC_4SO_3H$][HSO_4]), an acidic ionic liquid, and its primary application as a solid acidic supported catalyst in the synthesis of 1,8-dioxo-octahydroxanthenes by reaction of dimedone with aromatic aldehydes are described. Characterization of the catalyst was performed by FT-IR, BET, TG/DTG, and XRD techniques. The results showed that the catalyst has high activity and the desired products were obtained in high yields. Moreover, the recovered catalyst was found to be reusable and a considerable catalytic activity still could be achieved after third run.

Keywords 1, 8-dioxo-octahydroxanthenes, alumina supported ionic liquid, heterogeneous catalysis, solvent-free condition

INTRODUCTION

Ionic liquids (ILs), which are generally defined as salts with a melting point below 100°C, are fascinating materials that have attracted rising interest in the last decade in organic chemistry as catalysts or solvents and have been shown to promote a variety of organic transformations effectively because they possess a number of unique physicochemical properties such as the negligible vapor pressure, unique solvation properties, good ion conductivity, and catalytic activity and selectivity.[1–4] The introduction of structural functionalities on the cationic or anionic part has made it possible to design new ILs with specific properties.[5] SO_3H-functionalized ILs can be used as highly efficient acid catalysts and have been receiving extensive interest as green substitute for H_2SO_4, HF, and $AlCl_3$ catalysts in chemical processes.[6–8] However, the danger of catalyst leaching and the difficulties of extracting products from ILs when polar products are produced[9] are still big challenges to overcome. The immobilization of ILs on solid supports can solve these problems and satisfy the requirements from chemical industry of the ease of separation and recovery of catalyst from reaction mixture.[10] By transferring the catalytic property of a homogeneous catalyst to a heterogeneous catalyst, the immobilization can combine the advantages of homogeneous ILs with those of heterogeneous catalysts. There are some reports for using of solid supports for immobilizing the ILs.[11–14] In supported catalysts, the catalytic behavior of the catalyst is strongly dependent on support properties. Among the various supported catalysts, particularly, alumina and silica supported reagents have advantages of low cost, ease of preparation, and catalyst recycling.[15–18]

Xanthenes have received great attention because of their wide range of therapeutic and biological properties, such as antibacterial,[19] antiviral,[20] and anti-inflammatory activities.[21] Apart from their use as valuable synthetic precursors for many organic compounds[22] and dyes[23] they also found uses in laser technologies,[24] and fluorescent materials for visualization of biomolecules.[20] In particular, xanthenediones constitute a structural unit in a number of natural products[25,26] and have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring.[27] One of the commonly used methods reported for the synthesis of xanthenediones involves the condensation of aromatic aldehydes with 1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione (dimedone). This reaction can be carried out in the presence of various catalysts such as cyanuric chloride,[28] $NaHSO_4$,[29] $InCl_3.4H_2O$,[30] Amberlyst-15,[31] $SbCl_3/SiO_2$,[32] Dowex-50W,[33] polyaniline-*p*-toluenesulfonate salt,[34] Fe^{3+}-montmorillonite,[35] trimethylsilylchloride,[36] *p*-dodecylbenzenesulfonic acid,[37] $H_3PW_{12}O_{40}$/MCM-41,[38] silica-supported preyssler nano particles (SPNP),[39] $SmCl_3$,[40] Hydrotrope,[41] L-proline,[42] triethylbenzylammonium chloride,[43] and PPA-SiO_2.[44] However, some of these methodologies suffer from disadvantages, such as low yields, prolonged reaction time, harsh reaction conditions, and the requirement of excess catalysts. Therefore, the development of simple, efficient, high-yielding, and environmentally friendly methods using

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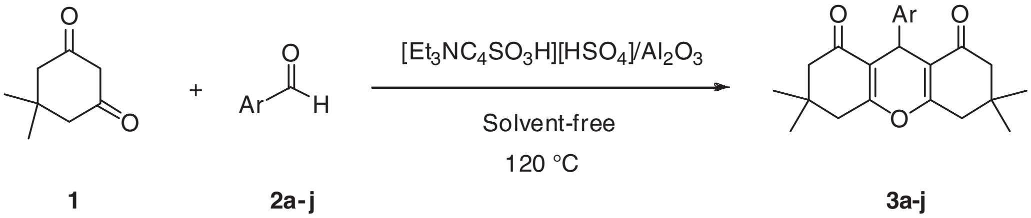


SCH. 1. $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ catalyzed synthesis of 1,8-dioxo-octahydroxanthenes.

novel catalysts for the synthesis of these compounds is still in great demand.

Based on these precedents and due to our interest in the application of reusable catalysts in organic reactions[40–48] herein firstly we report the preparation of a novel supported acidic IL by impregnation of alumina support by N-(4-sulfonic acid)butyl triethylammonium hydrogen sulfate (denoted as $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$), and then investigate its catalytic activity in the synthesis of 1,8-dioxo-octahydroxanthenes **3a–j** by cyclocondensation of dimedone **1** with aromatic aldehydes **2a–j** under solvent-free conditions (Scheme 1).

EXPERIMENTAL

Chemicals and Apparatus

All chemicals were available commercially and used without additional purification. The IL, $[Et_3NC_4SO_3H][HSO_4]$, was synthesized according to the literature.[49] Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. Thermal gravimetric and differential thermal gravimetry (TGA/DTG) analyses were performed using air as oxidant at the heating rate of 5°C min^{-1} in TGA-50, Shimadzu system. The BET surface area of the material was measured by nitrogen adsorption isotherm method with Quantachrome instrument model Autosorb1, USA. X-ray diffraction (XRD) was performed with a D8-Advance, Bruker X-ray diffractometer (Germany) using graphite monochromatized high-intensity CuKa radiation (k = 1.5406 Å). The ^1H NMR (400 & 500 MHz) spectra were recorded with Bruker 400 and 500 spectrometers (Germany).

Preparation of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$

The catalyst was prepared by impregnation method. Neutral alumina (Merck, Germany, 70–230 mesh, 1.0 g) was added to a solution of $[Et_3NC_4SO_3H][HSO_4]$ (0.6 g) in methanol (5 mL) and water (5 mL). The mixture was stirred at room temperature for 24 h to adsorb IL on surface of support. The methanol and water were removed with rotary evaporator and the resulting solid powder was washed with cold acetonitrile, and dried in vacuo at 100°C for 1 h.

General Procedure for the Synthesis of 1,8-dioxo-octahydroxanthenes 3a–j Catalyzed by $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$

To a mixture of dimedone **1** (0.8 mmol), and an aromatic aldehyde **2a–j** (0.4 mmol), in a round bottom flask, $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ (0.2 g) was added. The mixture was heated in the oil bath at 120°C for 30–40 min and the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and hot acetonitrile was added. The catalyst was insoluble in hot acetonitrile and could therefore be collected by a simple filtration. The filtrate was heated in vacuo to evaporate the solvent. The solid residue was collected and recrystallized from ethanol to give compounds **3a–j** in high yields.

Recycling and Reusing of the Catalyst

Due to the fact that the catalyst was insoluble in hot acetonitrile, it could be recycled by simple filtration. The separated catalyst was washed with cold acetonitrile, dried at 100°C under vacuum for 1 h, and reused in another reaction. The catalyst could be used at least three times with only slight reduction in its catalytic activity.

TABLE 1
N_2 adsorption results of alumina, and $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ in BET measurements

	Specific surface area ($m^2.g^{-1}$)			Pore diameter (Å)		Pore volume ($mL.g^{-1}$)	
Sample	BET	BJH_{Ads}	DH_{Ads}	BJH_{Ads}	DH_{Ads}	BJH_{Ads}	DH_{Ads}
Alumina	113.8	121.3	122.6	61.92	61.92	0.233	0.231
$[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$	000.0	000.2	000.5	20.53	20.53	0.002	0.002

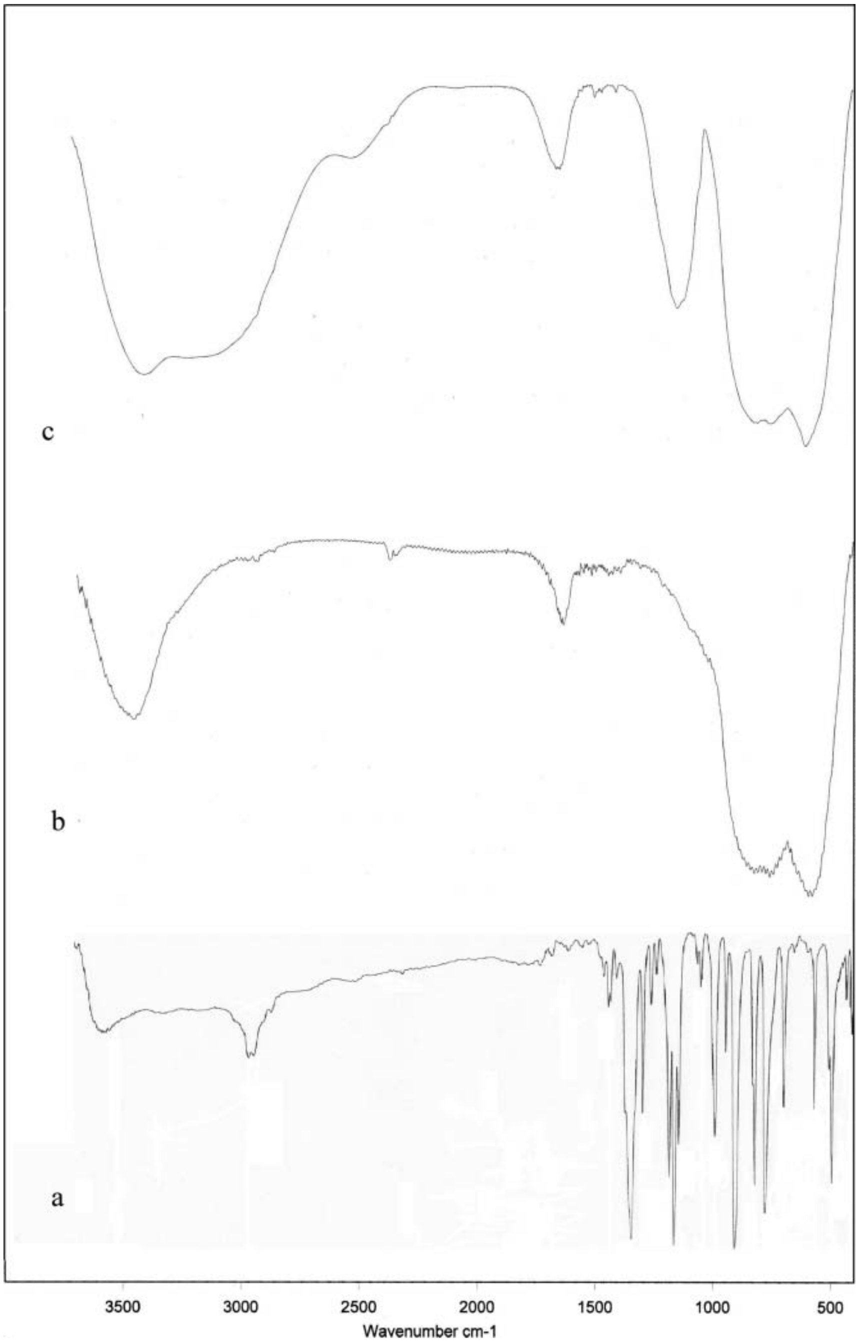


FIG. 1. FT-IR spectra of (a) $[Et_3NC_4SO_3H][HSO_4]$, (b) Al_2O_3, and (c) $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$.

RESULTS AND DISCUSSION

Characterization of the Catalyst

The catalyst $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ prepared by impregnation of alumina support by $[Et_3NC_4SO_3H][HSO_4]$ was characterized by FT-IR spectroscopy, the N_2 adsorption/desorption analysis (BET), thermal analysis (TG/DTG), and X-ray diffraction (XRD) techniques.

FT-IR spectra of $[Et_3NC_4SO_3H][HSO_4]$, Al_2O_3, and $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ are compared in Figure 1. Because of overlaping with the bands of Al_2O_3, most of the bands of $[Et_3NC_4SO_3H][HSO_4]$ are not observable in the IR spectrum of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ (Figure 1).

The data of specific surface area, pore size and pore volume of Al_2O_3, and $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ are presented in Table 1. The specific surface area of the supported catalyst measured by the BET method and other methods is near to zero (000.0–000.5 m^2/g). This may be due to the blockage of pores by active species and shows the impregnation of alumina by $[Et_3NC_4SO_3H][HSO_4]$.

Thermal gravimetric (TGA) and differential thermal gravimetry (DTG) analysis of the $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ were investigated by raising its temperature at the rate of 5°C/min in air up to 1000°C to analyze its thermal decomposition behavior. Figure 2 shows the TGA/DTG curves of the prepared $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$. Two main stages of mass loss were observed. The first small mass loss centered at 44.29°C was assigned to the loss of physically adsorbed water molecules and the second mass loss centered at 358.85°C was probably due to decomposition or removal of $[Et_3NC_4SO_3H][HSO_4]$.

The XRD pattern of the Al_2O_3 and $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ are also presented in Figure 3.

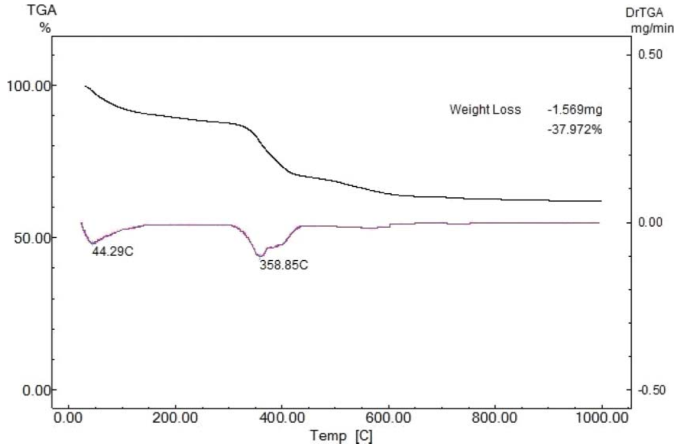


FIG. 2. TGA and DTG curves of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ (color figure available online).

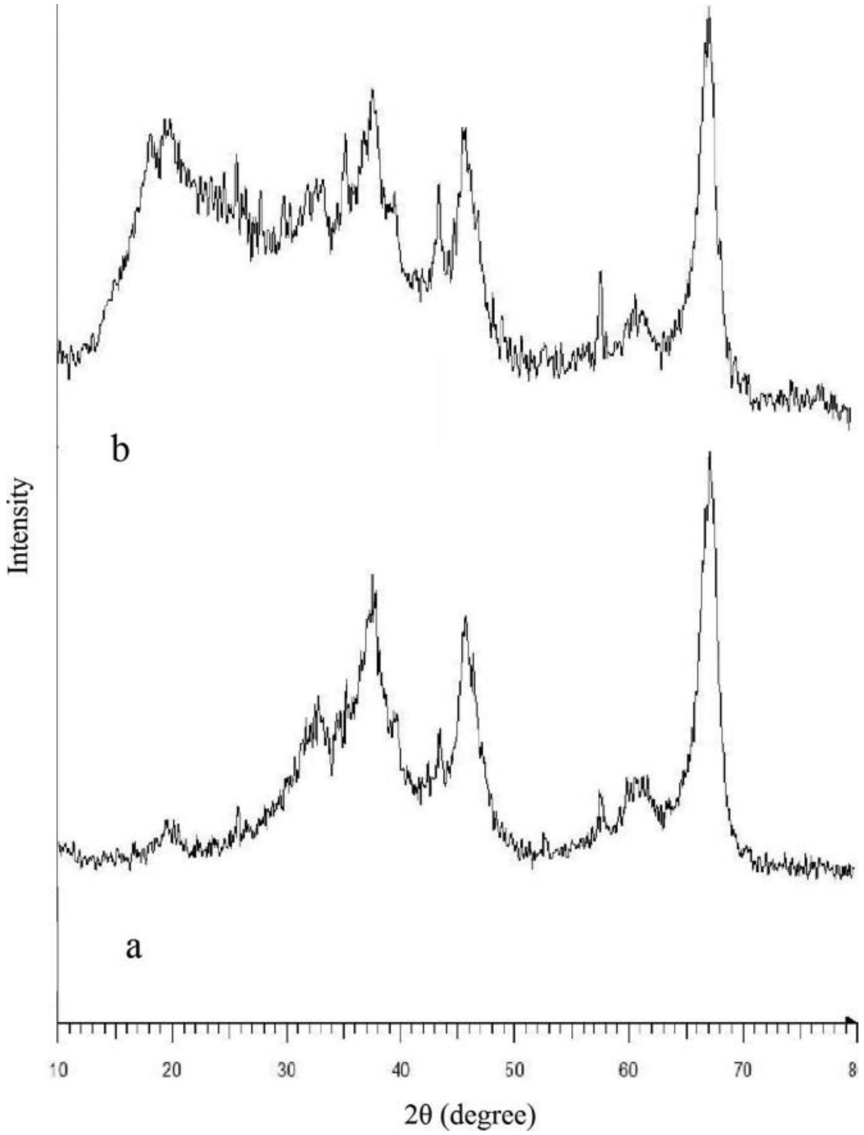


FIG. 3. XRD patterns of (a) Al_2O_3 and (b) $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$.

Catalytic Performance of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ in the Synthesis of 1,8-dioxo-octahydroxanthenes

The performance of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ as a solid acidic supported catalyst was evaluated in the synthesis of 1,8-dioxo-octahydroxanthenes. The possibility of performing organic reactions under solvent-free conditions with solid catalysts could enhance their efficiency from an economic as well as an ecological point of view, so solvent-free chemical reactions have received much attention. These reactions offer several advantages in preparative procedures such as environmental compatibility, simplification of work-ups, formation of cleaner products, enhanced selectivity, reduction of by-products, a reduction in waste produced, and much improved reaction rates. Therefore, we decided to investigate the efficiency of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ in the synthesis of 1,8-dioxo-octahydroxanthenes under solvent-free conditions. To find the optimal conditions, the synthesis of compound **3d** was used as a model reaction. The reaction was carried out by heating a mixture of dimedone (0.8 mmol), and 4-chlorobenzaldehyde (0.4 mmol) in the presence of various amounts of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ and at different temperatures under solvent-free conditions (Table 2). As can be seen, the efficiency of the reaction is affected mainly by the amount of the catalyst and the reaction temperature. No product was obtained in the absence of the catalyst (entry 1) indicating that the catalyst is necessary for the reaction. The best result was conducted at 120°C in the presence of 0.2 g of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ (entry 13). An increase in the reaction temperature and amount of the catalyst did not change the yields significantly (entries 14 and 15).

For showing the effect of solvent, the same model reaction was also carried out in different solvents including H_2O, CH_3CN, AcOEt, EtOH, and CH_2Cl_2 in the presence of 0.2 g of the catalyst (Table 2, entries 16–20). As shown, the compound **3d** was obtained in moderate yields in H_2O, CH_3CN, AcOEt, and EtOH (entries 16–19), but in high-yield in CH_2Cl_2 (entry 20) and also in solvent-free conditions (entry 13). Although, there is no significant difference between solvent-free conditions and CH_2Cl_2 as solvent in the model reaction, based on our investigations, in CH_2Cl_2 as solvent, the catalyst has poor reusability, but in solvent-free condition, the reusability of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ was found to be favorable and it could be recovered and subsequently reused several times. Consequently, all subsequent reactions were carried out in the presence of 0.2 g of the catalyst at 120°C under solvent-free conditions.

To evaluate the scope of this catalytic transformation, a range of 1,8-dioxo-octahydroxanthenes were prepared by the reaction of dimedone and aromatic aldehydes under optimized reaction conditions. The results are summarized in Table 3. In all cases, aromatic aldehydes with electron-donating or -withdrawing substituents reacted efficiently and quickly with dimedone, to give cyclocondensation products **3a–j** in high yields over short reaction times. On the other hand, easy separation of obtained products from the catalyst makes this method useful for the synthesis of 1,8-dioxo-octahydroxanthenes.

TABLE 2

Effect of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ amount, solvent, and temparature on the model reaction[a]

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Yield (%)[b]
1	None	Solvent-free	120	90	None
2	0.06	Solvent-free	80	50	54
3	0.06	Solvent-free	100	40	57
4	0.06	Solvent-free	120	30	75
5	0.10	Solvent-free	80	50	67
6	0.10	Solvent-free	100	40	69
7	0.10	Solvent-free	120	30	63
8	0.14	Solvent-free	80	50	70
9	0.14	Solvent-free	100	40	75
10	0.14	Solvent-free	120	30	72
11	0.20	Solvent-free	80	40	78
12	0.20	Solvent-free	100	30	81
13	0.20	Solvent-free	120	30	85
14	0.20	Solvent-free	140	30	84
15	0.26	Solvent-free	120	30	86
16	0.20	H_2O	Reflux	30	68
17	0.20	CH_3CN	Reflux	30	69
18	0.20	AcOEt	Reflux	30	69
19	0.20	EtOH	Reflux	30	67
20	0.20	CH_2Cl_2	Reflux	30	86

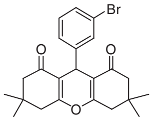
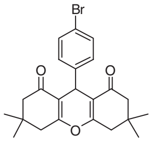
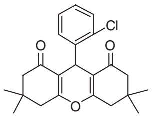
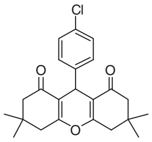
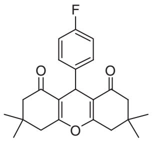
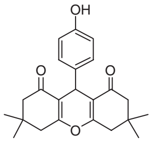
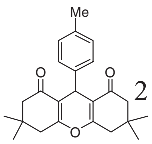
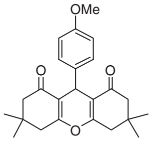
[a] 0.8 mmol dimedone and 0.4 mmol 4-chlorobenzaldehyde.

[b] The yields were calculated based on 4-chlorobenzaldehyde and refer to the pure isolated product.

To show the merit of the present methodology, we compared our results with those of the other methods reported for the synthesis of 1,8-dioxo-octahydroxanthenes. This comparison is shown in Table 4. As can be seen, our method reduces reaction times and produces high yields of the products.

Reusability of a catalyst, especially for supported catalysts, is a very important parameter before recommending any catalyst for industrial-scale use. Therefore, in this work, the reusability of $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ was also investigated. For this purpose, the same model reaction was again studied under optimized conditions. After the completion of the reaction, the catalyst was recovered according to the procedure mentioned in experimental section and reused for a similar reaction. The catalyst could be used at least three times with only slight reduction in the catalytic activity (85% for first use; 84% for second use; 82% for third use).

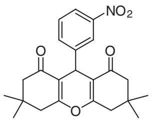
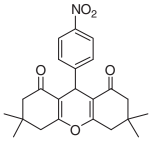
TABLE 3
Synthesis of 1,8-dioxo-octahydroxanthenes **3a–j** using $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ as catalyst[a]

Entry	Ar	Products[b]	Time (min)	Yield (%)[c]
1	3-BrC_6H_4	 **3a**	30	97
2	4-BrC_6H_4	 **3b**	30	98
3	2-ClC_6H_4	 **3c**	40	84
4	4-ClC_6H_4	 **3d**	30	85
5	4-FC_6H_4	 **3e**	35	80
6	4-HOC_6H_4	 **3f**	40	88
7	4-MeC_6H_4	 **3g**	40	89
8	4-$MeOC_6H_4$	 **3h**	40	78

(Continued on next page)

TABLE 3

Synthesis of 1,8-dioxo-octahydroxanthenes **3a–j** using $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ as catalyst[a] *(Continued)*

Entry	Ar	Products[b]	Time (min)	Yield (%)[c]
9	$3\text{-}O_2NC_6H_4$	 **3i**	30	94
10	$4\text{-}O_2NC_6H_4$	 **3j**	30	96

[a] 0.8 mmol dimedone, 0.4 mmol aromatic aldehyde, and 0.20 g $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$ at 120°C under solvent-free conditions.

[b] All the products were characterized by IR spectral data and comparision of their melting points with those of authentic samples. Also, the structures of some products were confirmed by ^1H NMR spectral data.

[c] The yields were calculated based on aromatic aldehyde and refer to the pure isolated product.

TABLE 4

Comparison of efficiency of various catalysts in the synthesis of 1,8-dioxo-octahydroxanthenes

	Conditions				
Catalyst	Solvent	T (°C)	Time (min)	Yield (%)	Ref.
Dowex-50W	—	100	150–300	78–91	33
Polyaniline-*p*-toluenesulfonate salt	H_2O	reflux	360	73–84	34
Fe^{3+}-montmorillonite	EtOH	reflux	360	84–96	35
Trimethylsilyl chloride	CH_3CN	reflux	480–600	72–84	36
p-Dodecylbenzenesulfonic acid	H_2O or EtOH	25–30	60–180 (ultrasound irradiation)	63–94	37
$H_3PW_{12}O_{40}$/MCM-41	EtOH	reflux	300	74–94	38
SPNP	H_2O	reflux	180	82–96	39
$SmCl_3$	—	120	480–1440	20–98	40
Hydrotrope	H_2O	80	60–90	80–92	41
L-proline	$ClCH_2CH_2Cl$ (DCE)	60	360	59–90	42
$[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$	—	120	30–40	78–98	This work

CONCLUSION

In summary, a new solid acidic supported catalyst, $[Et_3NC_4SO_3H][HSO_4]/Al_2O_3$, was prepared by impregnation of alumina support by $[Et_3NC_4SO_3H][HSO_4]$ and characterized by FT-IR, BET, TG/DTG, and XRD techniques. The catalyst showed high catalytic activity in the synthesis of 1,8-dioxo-octahydroxanthenes by the reaction of dimedone and aromatic aldehydes under solvent-free conditions. Some attractive features of this protocol are good to high yields, relatively short reaction times, simple procedure, absence of any volatile and hazardous organic solvents, and recyclability and reusability of the catalyst. Further applications of this new catalyst for other reaction systems are currently under investigation.

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