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Aluminium dodecyl sulfate trihydrate [Al(DS)$_3$].3H$_2$O: An efficient Lewis acid-surfactant-combined catalyst for synthesis of 1,8-dioxo-octahydroxanthens and 1,8-dioxo-decahydroacridines

A. Hasaninejad[1], T. Yousefy[2], and S. Firoozi[3]*

[1]*Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Iran*
[2]*Department of Chemistry, Islamic Azad University, Gachsaran, Iran*
[3]*Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Iran*
E-mail: firoozi.org.chem@gmail.com

Abstract

An efficient synthesis of 1, 8-dioxo-octahydroxanthens and 1, 8-dioxo-decahydroacridines from the reaction of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) with aromatic aldehydes bearing electron-donating or withdrawing substituents either in the presence or absence of primary amines has been described in a single pot using a catalytic amounts of aluminum tris (dodecyl sulfate) trihydrate [Al(DS)$_3$·3H$_2$O] as a Lewis acid-surfactant-combined catalyst. Both reactions occurred at 80 °C. 1, 8-dioxo-octahydroxanthens has been synthesized under solvent-free conditions and water is used as a green solvent for the synthesis of 1, 8-dioxo-decahydroacridines. This methodology offers several advantages such as very simple work-up procedure, short reaction times, and mild reaction conditions.

Keywords: Aluminium dodecyl sulfate trihydrate; Lewis acid; Lewis acid surfactant catalyst; Xanthenes; 1,8-Dioxo-octahydroxanthens; Acridinediones; 1,8-Dioxo-decahydroacridines; multi component reactions; green chemistry

1. Introduction

In recent years, there have been significant attention on synthesizing xanthenes and their related derivatives due to their useful spectroscopic properties and applications in the industry including dyes in laser technology (Menchen et al., 2003) and pH sensitive fluorescent materials for visualization of biomolecules (Bekaert et al., 1992; Buehler et al., 1943; Knight and Stephens, 1989; Sarma and Baruah, 2005). In addition, xanthene based on compounds which exhibit extensive activities in biological and pharmaceutical aspects such as antiinflamatory (Jonathan et al., 1988), antiviral (Lambert et al., 1997), antitumor (Rewcastle et al., 1991), antibacterial (Jonathan et al., 1988), and neuropharmacological (Kaiser et al., 1972) have been applied in photodynamic therapy (PDT) (Ion et al., 1998). Xanthene derivatives have been utilized as inflexible carbon skeletons for the assembly of chiral bidentate phosphine ligands with potential applications in catalytic processes (Malaise et al., 2001).

The preparation of xanthenes has gained considerable attentions in recent years and several procedures have been reported for the synthesis of these derivatives. A common approach for the synthesis of 1,8-dioxo-octahydroxanthens involves the condensation of aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (Bekaert et al., 1992; Horning and Horning, 1946; Kinjo et al., 1995) by utilizing different heterogeneous and homogeneous catalysts, e. g., piperidine (Horning and Horning, 1946), NaHSO$_4$-SiO$_2$ and silica chloride (Tu et al., 2002), PPA-SiO$_2$ (Jin et al., 2005), (NH$_4$)$_2$HPO$_4$ (Das et al., 2007), MCM-41-SO$_3$H under ultrasonic irradiation (Kantevari et al., 2007), 1-methylimidazolium triflouroacetate ([Hmim]TFA (Darvish et al., 2007), as well as Brønsted acidic imidazolium salts containing perfluoroalkyl tails (Rostamizadeh et al., 2010).

Acridinediones are a class of compounds that exhibit wide applicability as photosensitizers and as excellent initiators in photopolymerization (Dabiri et al., 2008). They have a high fluorescence quantum yield of about 0.9 (Shen et al., 2009) and fine lasing action (Timpe et al., 1993), which operates in the blue green region with efficiencies in comparison to coumarin-102 (Timpe et al.,

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*Corresponding author

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1998). The acridinedione dyes have a bichromophoric structure enabling them to act as both an electron donor and acceptor (Shanmugasundaram et al., 1996). The photochemical behavior of donor-acceptor of these compounds has received considerable interests due to their unique photophysical, photochemical, and nonlinear optical properties (Shanmugasundaram et al., 1991). Moreover, it has been previously reported that light-emitting materials based on acridinediones act as organic light-emitting diodes (OLED) (Mohan et al., 1997). Acridinediones are similar in structure to both 1,4-dihydropyridines (1,4-DHPs) and biologically important β-dihydronicotinamide adenine dinucleotide (NADH) and its analogues which are vital coenzymes in biological systems. It has also been shown that acridinedione dyes mimic NADH to a greater extent than 1,4-DHPs due to the tricyclic structure which has the capability for protecting the enamine moiety (Wang and Schanze, 1995). The presence of several reaction centers in acridinediones opens broad synthetic possibilities (Turker ei al., 2009). Furthermore, the chemical behaviors of acridinediones in catalytic hydrogenation reactions under various conditions have been studied (Singh et al., 1982).

Numerous acridinediones have been prepared by β-diketones reactions with different aldehydes and appropriate amines -in most cases primary amine- to produce a fluorescent heterocyclic system *via* various methods (Keefer and Lunn, 1989; Tu et al., 2002). In addition, these synthetic methods can be catalyzed by using diverse catalysts including *p*-dodecylbenzenesulfonic acid (DBSA) under microwave irradiation (Miao et al., 2004), Brønsted acidic imidazolium salts containing perfluoroalkyl tails (Rostamizadeh et al., 2010), and 1-Methylimidazolium triflouroacetate ([Hmim]TFA) (Darvish et al., 2007).

Lewis acids and Brønsted acids as surfactant-type acids can catalyze organic reactions without using harmful organic solvents. They have demonstrated a dual role in organic reactions as catalyst to activate substrate molecules and as a surfactant to increase the concentration of organic reactants to form micelle particles in water (Wang and Miao, 2006).

For the first time, Firouzabadi et al. applied aluminium tris (dodecyl sulfate) trihydrate $[Al(DS)_3].3H_2O$ (Fig. 1) as a combined Lewis acid-surfactant catalyst. This catalyst has been employed in the Michael addition of indoles and pyrrole to α,β-unsaturated electron-deficient compounds in aqueous medium at room temperature (Wang et al., 2003), efficient conversion of epoxides into corresponding thiiranes *via* thiourea, as well as regio- and chemoselective ring opening of different epoxides with diverse amines at room temperature in water media (Shiri and Zolfigol, 2009).

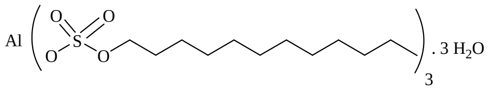
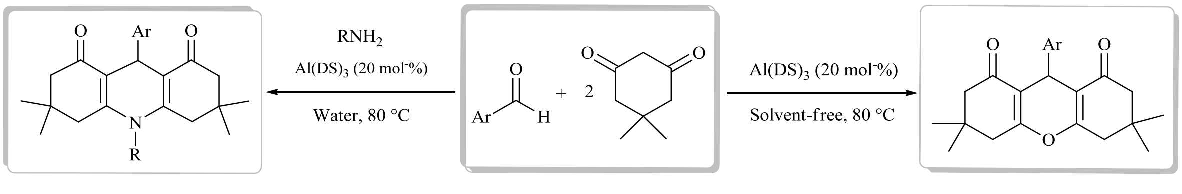


Fig. 1. Chemical structure of aluminum tris (dodecyl sulfate) trihydrate $[Al(DS)_3 \cdot 3H_2O]$ as a Lewis acid-surfactant combined catalyst

There are a few reports in the literature for using surfactant type catalysts in the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines compounds. In these reactions, Brønsted acid surfactant has been used as catalyst (Rostamizadeh et al., 2010; Wang and Miao, 2006). In addition, to the best of our knowledge, there is no report on using of Lewis acid-surfactant as catalyst in the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines. Most of these methods often suffer from one or more disadvantages for the synthesis of xanthene and acridine derivatives such as prolonged reaction time, poor yields, cumbersome work up procedure, expensive reagents, and generation of polluting effluents.

In continuation of our work to develop novel eco-friendly synthetic methodologies and synthesis of oxo or aza heterocycles (Firouzabadi et al., 2005; Firouzabadi et al., 2007; Hasaninejad et al., 2009; Hasaninejad et al., 2010; Hasaninejad et al., 2011; Hasaninejad et al., 2012; Hasaninejad et al., 2013; Hasaninejad and Firoozi, 2013), we would like to report the application of $[Al(DS)_3].3H_2O$ as a combined Lewis acid-surfactant catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines from the reaction of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) with an aromatic aldehyde and a primary amine, respectively (Scheme 1).



Scheme 1. Synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines in the presence of $Al(DS)_3$ as a Lewis acid-surfactant-combined catalyst

2. Experimental

All chemicals were purchased from Merck and Fluka Chemical Companies. All compounds are recognized and their structures were identified by comparing their melting points and ^{1}H and ^{13}C NMR data with those reported in the literature. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

2.1. Synthesis of Lewis acid $Al(DS)_3·3H_2O$

The synthesis of Lewis acid surfactant catalyst has been carried out using the reported procedure in the literature (Wang et al., 2003). Aluminum nitrate [$Al(NO_3)_3.9H_2O$] (0.3 g, 1 mmol) and sodium dodesyl sulfate [SDS] (1 g, 3 mmol) were firstly prepared in a flask with an amount of water at room temperature. Then, the reaction mixture was stirred for an additional period of 3 h. After the completion of reaction, the mixture was filtered and white solid was obtained.

2.2. General procedure for the synthesis of 1,8-dioxo-octahydroxanthene derivatives

In the solvent-free conditions, the mixture of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (2 mmol), an aromatic aldehyde (1 mmol), and $Al(DS)_3.3H_2O$ (20 mol-%) (Scheme 1) was heated and the mixture was magnetically stirred at 80 °C for the Table reaction time (Table 1). The progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of reaction that was indicated by TLC, water was added to the mixture and the organic phase as a solid residue was separated. The purification of the solid residue was performed by recrystallizing from ethanol to obtain pure 1,8-dioxo-octahydroxanthene derivative form. The spectroscopic properties of all products were characterized and were compared with authentic samples. In order to recover the catalyst, H_2O was evaporated under reduced pressure; the resulting solid was washed with t-butylmethyl ether (3 mL) and dried. The recovered $Al(DS)_3.3H_2O$ was reused for other processes with no loss in its activity.

2.3. General procedure for the synthesis of 1,8-dioxo-decahydroacridine derivatives

In water as solvent, Primary amine (1 mmol) was added to the mixture of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (2 mmol), an aromatic aldehyde (1 mmol) and $Al(DS)_3.3H_2O$ (20 mol-%) at 80 °C (Scheme 1). The reaction was conducted under the conditions as above. After the reaction was completed which was realized by TLC, water was added to the mixture and the organic phase as a solid residue was separated. The purification of solid residue was performed by recrystallizing from ethanol to obtain pure 1,8-dioxo-decahydroacridine derivative form. All of the products were characterized based on their spectroscopic properties by comparison with authentic samples. In order to recover the catalyst, H_2O was evaporated under reduced pressure, then, the resulting solid was washed with t-butylmethyl ether (3 mL) and dried. The recovered $Al(DS)_3.3H_2O$ was reused for other uses with no loss in its activity.

2.4. Selected spectral data of the products

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene- 1,8-(5H,9H)-dione (3a): mp 202–204 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.02 (s, 6H, CH_3), 1.13 (s, 6H, CH_3), 2.19 (d, 2H, J =16.2 Hz, CH_2), 2.26 (d, 2H, J = 16.2 Hz, CH_2), 2.50 (s, 4H, CH_2), 4.78 (s, 1H, CH), 7.12 (t, 1H, J = 7.2 Hz, ArH), 7.24 (t, 2H, J = 7.5 Hz, ArH), 7.32 (d, 2H, J = 7.6 Hz, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.75, 29.69, 32.26, 32.61, 41.29, 51.18, 116.07, 126.76, 128.45, 128.80, 144.54, 162.70, 196.76.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(4-bromophenyl)-2Hxanthene- 1,8-(5H,9H)-dione (3b): mp 238–240 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.03 (s, 6H, CH_3), 1.14 (s, 6H, CH_3), 2.20 (d, 2H, J = 16.3 Hz, CH_2), 2.27 (d, 2H, J = 16.3 Hz, CH_2), 2.50 (s, 4H, CH_2), 4.74 (s, 1H, CH), 7.21 (d, 2H, J = 8.4 Hz, ArH), 7.37 (d, 2H, J = 8.4 HzArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.73, 29.69, 31.98, 32.62, 41.28, 51.12, 115.63, 120.66, 130.60, 131.57, 143.64, 162.82, 196.69.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(4-chlorophenyl)-2Hxanthene- 1,8-(5H,9H)-dione (3c): mp 228–230 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.03 (s, 6H, CH_3), 1.14 (s, 6H, CH_3), 2.20 (d, 2H, J = 16.3 Hz, CH_2), 2.27 (d, 2H, J = 16.3 Hz, CH_2), 2.50 (s, 4H, CH_2), 4.75 (s, 1H, CH), 7.22 (d, 2H, J = 8.5 Hz, ArH), 7.27 (d, 2H, J = 8.5 Hz, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.72, 29.68, 31.89, 32.61, 41.28, 51.13, 115.69, 128.63, 130.19, 132.45, 143.13, 162.83, 196.71.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-p-tolyl-2H-xanthene- 1,8-(5H,9H)-dione (3d): mp 215–217 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.98 (s, 6H, CH_3), 1.09 (s, 6H, CH_3), 2.15 (d, 2H, J = 16.3 Hz, CH_2), 2.20–2.23 (m, 5H, CH_3 and CH_2), 2.45 (s, 4H, CH_2), 4.70 (s, 1H, CH), 7.00 (d, 2H, J = 8.0 Hz, ArH), 7.17 (d, 2H, J = 8.0 Hz, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 21.47, 27.80, 29.69, 31.86, 32.62, 41.30, 51.20, 116.19, 128.66, 129.20, 136.17, 141.63, 162.51, 196.80.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(4-nitrophenyl)-2Hxanthene-1,8-(5H,9H)-dione (3e): mp 220–222 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.02 (s, 6H, CH_3), 1.15 (s, 6H, CH_3), 2.20 (d, 2H, J = 16.3 Hz, CH_2), 2.29 (d, 2H, J = 16.3 Hz, CH_2), 2.53 (s, 4H, CH_2), 4.86 (s, 1H, CH), 7.51 (dd, 2H, J = 7.0 Hz, J = 1.7 Hz, ArH), 8.12 (dd, 2H, J = 7.0 Hz, J = 1.7 Hz, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.70, 29.64, 32.64, 32.79, 41.27, 51.03, 114.96, 123.83, 129.78, 146.92, 151.94, 163.36, 196.63.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(4-methoxyphenyl)-2H-xanthene-1,8-(5H,9H)-dione (3f): mp 238-239 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.98 (s, 6H, CH_3), 1.08 (s, 6H, CH_3), 2.15 (d, 2H, J = 16.3 Hz, CH_2), 2.21 (d, 2H, J = 16.3 Hz, CH_2), 2.44 (s, 4H, CH_2), 3.71 (s, 3H, OCH_3), 4.68 (s, 1H, CH), 6.74 (dd, 2H, J = 6.8 Hz, J = 1.9 Hz, ArH), 7.19 (dd, 2H, J = 6.8 Hz, J = 1.9 Hz, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.76, 29.69, 31.38, 32.61, 41.29, 51.20, 55.52, 113.89, 116.21, 129.73, 136.98, 158.38, 162.48, 196.86.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(3-nitrophenyl)-2Hxanthene-1,8-(5H,9H)-dione (3i): mp 164-166 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.98 (s, 6H, CH_3), 1.10 (s, 6H, CH_3), 2.15 (d, 2H, J = 16.3 Hz, CH_2), 2.24 (d, 2H, J = 16.3 Hz, CH_2), 2.49 (s, 4H, CH_2), 4.82 (s, 1H, CH), 7.38 (t, 1H, J = 7.9 Hz, ArH), 7.79 (d, 1H, J = 7.7 Hz, ArH), 7.94-8.05 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.72, 29.61, 32.52, 32.66, 41.23, 51.06, 114.96, 122.06, 123.02, 129.21, 136.07, 146.74, 148.73, 163.46, 196.76.

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(3-chlorophenyl)-2Hxanthene-1,8-(5H,9H)-dione (3j): mp 184–186 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.99 (s, 6H, CH_3), 1.09 (s, 6H, CH_3), 2.17 (d, 2H, J = 16.2 Hz, CH_2), 2.22 (d, 2H, J = 16.2 Hz, CH_2), 2.46 (s, 4H, CH_2), 4.71 (s, 1H, CH), 7.06 (dt, 1H, J = 9.1 Hz, J = 1.5 Hz, ArH), 7.13 (t, 1H, J = 7.9 Hz, ArH), 7.21 (d, 1H, J = 1.2 Hz, ArH), 7.23 (t, 1H, J = 1.3 Hz, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.79, 29.62, 32.16, 32.63, 41.27, 51.13, 115.51, 127.05, 127.40, 128.75, 129.65, 134.28, 146.54, 162.99, 196.67.

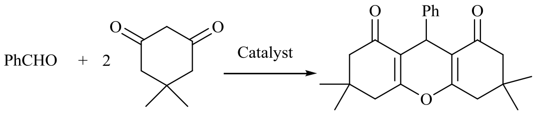
3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(2-chlorophenyl)-2Hxanthene-1,8-(5H,9H)-dione (3n): mp 222–224 °C, ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.05 (s, 6H, CH_3), 1.13 (s, 6H, CH_3), 2.19 (d, 2H, J = 16.2 Hz, CH_2), 2.26 (d, 2H, J = 16.2 Hz, Ch_2), 2.48 (s, 4H, CH_2), 5.03 (s, 1H, CH), 7.09 (dt, 1H, J = 7.6 Hz, J = 1.6 Hz, ArH), 7.19 (dt, 1H, J = 7.6 Hz, J = 1.1 Hz, ArH), 7.26 (dd, 1H, J = 7.9 Hz, J = 1.0 Hz, ArH), 7.46 (d, 1H, J = 7.3 Hz, ArH). 13C NMR ($CDCl_3$, 125 MHz), δ: 27.79, 29.69, 32.28, 32.43, 41.25, 51.14, 114.13, 126.74, 128.20, 130.56, 133.34, 133.88, 140.32, 163.37, 196.84.

3-(1,2,3,4,5,6,7,8,9,10-decahydro-3,3,6,6-tetramethyl-1,8-dioxo-10-p-tolylacridin-9-yl)benzonitrile (4f): mp 255-257 °C ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 0.85 (s, 6H, CH_3), 0.99 (s, 6H, CH_3), 1.98 (d, 2H, J = 17.5 Hz, CH_2), 2.11, (d, 2H, J=17.5 Hz, CH_2), 2.17 (d, 2H, J = 16.5 Hz, CH_2), 2.24 (d, 2H, J=16.5 Hz, CH_2), 2.52 (s, 3H, CH_3), 5.29 (s, 1H, CH), 7.10-7.13 (m, 3H, ArH), 7.19-7.22 (m, 1H, ArH), 7.39-7.41 (m, 4H, ArH); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 21.6, 27.1, 30.0, 32.7, 33.0, 42.1, 50.6, 114.3, 126.4, 126.6, 128.4, 128.9, 129.6, 130.0, 134.1, 136.5, 140.0, 148.6, 150.8, 196.0.

3,3,6,6-tetramethyl-9-(3-nitrophenyl)-10-p-tolyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4g): Mp 289-291 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 0.82 (s, 6H, CH_3), 0.99 (s, 6H, CH_3), 1.92 (dd, 2H J = 17.5, J = 1.0 Hz, CH_2), 2.13-2.26 (m, 6H, CH_2), 2.53 (s, 3H, CH_3), 5.39 (s, 1H, CH), 7.14 (m, 1H, ArH), 7.25 (m, 1H, ArH), 7.39 (m, 1H, ArH), 7.43-7.47 (m, 2H, ArH), 7.99-8.02 (m, 2H, ArH), 8.25 (t, 1H, J = 2.0 Hz, ArH); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 21.7, 27.0, 30.1, 32.8, 33.3, 42.1, 50.5, 114.2, 121.5, 122.3, 129.2, 129.9, 130.9, 131.7, 135.7, 136.3, 140.22, 148.8, 151.2, 196.1

3. Results and Discussion

In order to establish the optimum conditions for the synthesis of 1,8-dioxo-octahydroxanthenes, the condensation reaction of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) with benzaldehyde (1 mmol) was selected as a model reaction to provide 1,8-dioxo-octahydroxanthene **3a** (Scheme 2 and Table 1).



3a

Scheme 2. The condensation reaction of benzaldehyde (1 mmol) with dimedone (2 mmol)

Table 1. The solvent-free condensation reaction of benzaldehyde (1 mmol) with dimedone (2 mmol) in the presence of some salts of Al^{+3}

Entry	Catalyst (mol %)	Temperature (°C)	Time (min)	Yield[a] (%)
1	$Al(NO_3)_3$ (20)	80	25	78
2	$Al(OAc)_3$ (20)	80	90	54
3	$Al_2(SO_4)_3$ (20)	80	20	80
4	$Al(SD)_3$ (20)	80	15	88
5	$Al(SD)_3$ (15)	80	20	81
6	$Al(SD)_3$ (25)	80	15	88
7	$Al(SD)_3$ (20)	30	240	-
8	$Al(SD)_3$ (20)	70	30	75
9	$Al(SD)_3$ (20)	90	15	88

[a] Isolated Yield

First, the reaction was examined in the presence of some simple salts of Al^{+3} (20 mol-%) under solvent-free conditions at 80 °C. The results are exhibited in Table 1. Table 1 indicates that $Al(OAc)_3$ gave low yield of compound **3a**, but $Al_2(SO_4)_3$ and $Al(NO_3)_3$ gave good yields of product, and excellent results for yield and reaction time were observed when $Al(DS)_3$ was used as catalyst (Table 1, entry 4). In the next step, the influence of reaction temperature and the amounts of $Al(DS)_3$ were tested for synthesis of 1,8-dioxo-octahydroxanthene **3a**. For this purpose, the reaction model was examined in the presence of different amounts of $Al(DS)_3$ at 80 °C (Table 1, entries 4-6). It should be noted that the optimal catalyst loading in the synthesis of 1,8-dioxo-octahydroxanthene **3a** peaked at a concentration of 20-mol-%. When the amount of catalyst was low, the yield of the product decreased. Whereas raising the catalyst concentration did not lead to a pronounced increase in the product yield. In another investigation to evaluate the effect of reaction temperature, the reaction of benzaldehyde and 5,5-dimethyl-1,3-cyclohexanedione in the presence of 20-mol% of $Al(DS)_3$ under solvent-free conditions was studied at various temperatures. At room temperature, the reaction rate was found to be very slow and it was increased at higher temperatures. Although the maximum rate was found at 80 °C, further increases in temperature did not show more enhancements. During our optimization studies, various solvents were examined and it was observed that solvent-free conditions are the most optimum conditions in terms of reaction rate and isolated yield. Scheme 1 shows the optimized conditions.

Several aromatic aldehydes (1 mmol) were reacted with 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) in the presence of $Al(DS)_3$ as catalyst (20 mol-%) under solvent-free conditions at 80 °C in order to investigate the generality and the functional group tolerance of this procedure in the direct synthesis of 1,8-dioxo-octahydroxanthenes. The respective results are displayed in Table 2. As shown in Table 2, aromatic aldehydes containing either electron-donating or electron, withdrawing substituents gave the desired 1,8-dioxo-octahydroxanthene in high yields. The method uses key functional groups including halides, alkyl, nitro, methoxy and nitrile (Table 2, 3b-o) besides the *para* and *meta* positions on the aromatic ring of aldehyde. Different functional groups were also introduced to *ortho* position indicating the method is not sensitive to steric or electronic *ortho* variation of substituents.

Table 2. Preparation of 1,8-dioxo-octahydroxanthenes using $Al(DS)_3$ (20 mol-%) as catalyst

Entry	Ar	Product	Time (min)	Yield[a] (%)	M.P. Found (Reported) (ref)
1	C_6H_5	3a	15	88[b]	202-204 (201-203) (John et al., 2006)
2	$4\text{-}Br\text{-}C_6H_4$	3b	15	85	238-240 (228-231) (John et al., 2006)
3	$4\text{-}Cl\text{-}C_6H_4$	3c	10	93	228-230 (231-233) (John et al., 2006)
4	$4\text{-}Me\text{-}C_6H_4$	3d	20	89	215-217 (216-218) (John et al., 2006)
5	$4\text{-}NO_2\text{-}C_6H_4$	3e	10	80	220-222 (224-246) (John et al., 2006)
6	$4\text{-}OMe\text{-}C_6H_4$	3f	45	83	238-239 (241-243) (John et al., 2006)
7	$4\text{-}CN\text{-}C_6H_4$	3g	25	84	215-217 (215-217) (Dabiri et al., 2008)
8	$4\text{-}F\text{-}C_6H_4$	3h	35	90	220-222 (223-225) (Fang et al., 2009)
9	$3\text{-}NO_2\text{-}C_6H_4$	3i	18	85	164-166 (168-170) (Jin et al., 2004)
10	$3\text{-}Cl\text{-}C_6H_4$	3j	40	83	184-186 (184-186) (Jin et al., 2005)
11	$3\text{-}Me\text{-}C_6H_4$	3k	55	90	205-207
12	$3\text{-}Br\text{-}C_6H_4$	3l	45	83	186-188 (190-192) (Chebanov et al., 2004)
13	$2\text{-}Me\text{-}C_6H_4$	3m	22	86	190-192
14	$2\text{-}Cl\text{-}C_6H_4$	3n	15	78	222-224 (226-228) (Jin et al., 2004)
15	$2\text{-}OH\text{-}C_6H_4$	3o	10	75	210-212 (203-205) (Bose and Kumar, 2006)

[a] Isolated Yield

[b] The reaction was performed on a 20-mmol scale

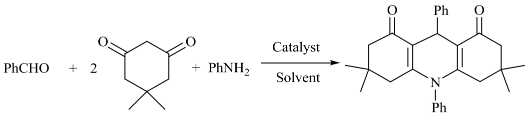
To check the recyclability of Al(DS)$_3$, the aluminum dodecyl sulfate trihydrate was used in the condensation reaction of benzaldehyde with dimedone, to **3a.** After the completion of reaction, water was added to the mixture and the solid residue of product was separated. The purification of solid residue was performed by recrystallization from ethanol to obtain pure form of 1,8-dioxo-octahydroxanthene derivative. In order to recover the catalyst, H_2O was evaporated under reduced pressure. The resulting solid was washed with t-butylmethyl ether (3 mL) and then dried. The recovered Al(DS)$_3$.3H_2O was reused five times for model reaction with no loss in its activity (Table 3).

Table 3. The catalytic activity of Al(DS)$_3$ in five cycles for the synthesis of 1,8-dioxo-octahydroxanthene **3a**

Run	Time (min)	Yield[a] (%)
1	15	88
2	15	89
3	18	88
4	20	85
5	20	84

[a] Isolated Yields

In the same way, the catalytic effects of these Al^{+3} salts for the synthesis of 1,8-dioxo-decahydroacridines were studied. For this propose, benzaldehyde (1 mmol), dimedone (2 mmol), and aniline (1 mmol) were selected as a model reaction to achieve 1,8-dioxo-decahydroacridine **4a** in different conditions (Scheme 3 and Table 4).



4a

Scheme 3. Synthesis of 1,8-dioxo-decahydroacridine **4a** using aniline, dimedone and benzaldehyde in different conditions

Table 4. Condensation reaction of benzaldehyde (1 mmol), dimedone (2 mmol) and aniline (1 mmo) in the presence of some salts of Al^{+3} in different conditions

Entry	Catalyst (mol %)	Solvent	Temperature (^{o}C)	Time (min)	Yield[a] (%)
1	Al$(NO_3)_3$ (20)	H_2O	80	25	78
2	Al(OAc)$_3$ (20)	H_2O	80	90	54
3	$Al_2(SO_4)_3$ (20)	H_2O	80	20	80
4	Al(SD)$_3$ (20)	H_2O	80	15	88
5	Al(SD)$_3$ (15)	H_2O	80	20	81
6	Al(SD)$_3$ (25)	H_2O	80	15	88
7	Al(SD)$_3$ (20)	-	80	240	-
8	Al(SD)$_3$ (20)	EtOH	reflux	30	75
9	Al(SD)$_3$ (20)	CH_3CN	reflux	30	75
10	Al(SD)$_3$ (20)	THF	reflux	30	75
11	Al(SD)$_3$ (20)	$CHCl_3$	reflux	15	88

[a] Isolated Yield

Optimum conditions were studied such as using primary amine (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (2 mmol), aromatic aldehydes (1 mmol), and catalytic amount of Al(DS)$_3$ (20 mol-%) in water as solvent at 80 °C (Table 5).

It can be observed from Table 5 (4a-i) that steric and electronic variation in the aromatic aldehyde were tolerated and did not change the efficiency of the reaction in the presence of aliphatic (4i) or aromatic amine (4a-h). In both cases, besides the introduction of key functional group including halides, alkyl, nitro, methoxy, and nitrile, several aromatic aldehydes bearing two functional groups were also tested and resulted in the corresponding products. In the syntheses of both 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines, based on the proposed mechanism, a positive effect in the higher isolated yields of products as well as shorter reaction times in those entries containing electron withdrawing groups on the aromatic aldehyde ring was detected which could be a result of facile Schiff base formation in Knoevenagel condensation step followed by Michael addition.

Table 5. Preparation 1,8-dioxo-decahydroacridines using Al(DS)$_3$ (20 mol-%) as catalyst

Entry	Ar	R	Product	Time (h)	Yield[a] (%)	M.P. Found (Reported) (ref)
1	C_6H_5	C_6H_5	4a	7	82	266-268 (254-256) (Das et al., 2006)
2	C_6H_5	4-Me-C_6H_4	4b	7	89	262-264 (265-267) (Bose and Kumar, 2006)
3	4-OMe-C_6H_4	C_6H_5	4c	3	86	220-222 (220–222) (Das et al., 2006)
4	3-NO_2-C_6H_4	C_6H_5	4d	2.7	90	280-282 (276–278) (Das et al., 2006)
5	4-OMe-C_6H_4	4-Me-C_6H_4	4e	5.5	80	285-287 (220-222) (Das et al., 2006)
6	3-CN-C_6H_4	4-Me-C_6H_4	4f	4.5	83	255-257 (255-257) (Rashedian et al., 2010)
7	3-NO_2-C_6H_4	4-Me-C_6H_4	4g	2.5	82	289-291 (289-291) (Das et al., 2006)
8	3-Cl-C_6H_4	4-Me-C_6H_4	4h	3	87	318-320 (315-317) (Das et al., 2006)
9	4-Me-C_6H_4	C_6H_5-CH_2	4i	5	85[b]	viscose (viscose) (Das et al., 2006)

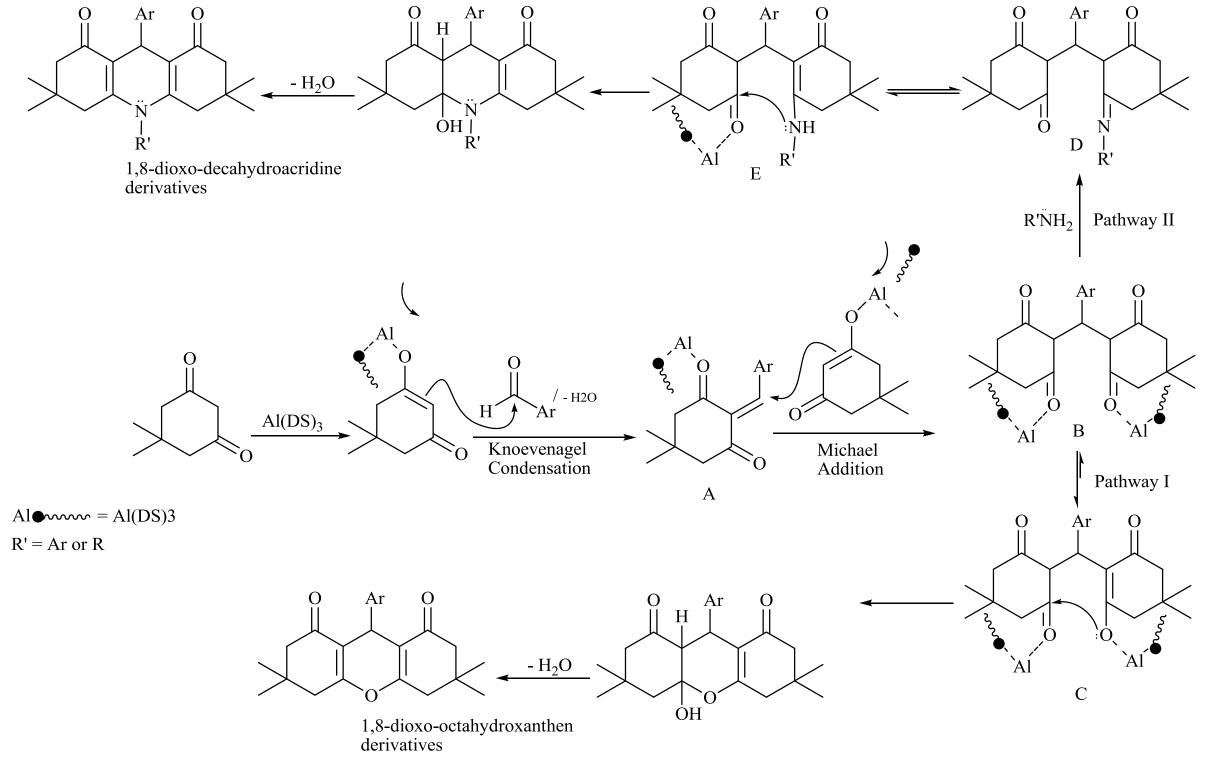
[a] Isolated Yield

[b] The reaction was performed on a 20-mmol scale

To assess the feasibility application of this method on a preparative scale, both of the model reactions for the synthesis of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine were performed on a 20-mmol scale. As expected, the reactions procedure was similar to the smaller scale (3a, 4i) and produced the desired products in high yield.

To explore the reaction mechanism, consumed aldehyde separation was monitored by GC analysis in both of model compounds for the synthesis of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine, and it was found that the Schiff base is formed very rapidly (within the first 5 minutes of the beginning of reaction) and the rate-determining step (RDS) was observed to be for dehydrative cyclization step. Furthermore, it was realized that there is no need to prepare the Schiff base in advance. Equimolar amounts of dimedone and aromatic aldehydes (and primary amine) can be used as starting materials in the presence of Al(DS)$_3$, which should be practical and synthetically useful. A plausible pathway for the formation of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine involves the formation of intermediate Schiff bases **A** which is produced through the Michael adduct **B**. In the next step, Michael adduct **B** is converted to adduct **C** *via* an Al(DS)$_3$ catalyzed enolization through enolate intramolecular participation followed by dehydration which results in the corresponding 1,8-dioxo-octahydroxanthene. For pathway II, it is proposed that the primary amine condenses with Michael adduct **B** to form the corresponding imine **D,** which is in equilibrium with its enamine counterpart **E**. Then, imine E collapses into the corresponding 1,8-dioxo-decahydroacridine through intramolecular participation of the enamine followed by dehydration (Scheme 4) (Shen et al., 2009).

Regarding to the comparison between Al(DS)$_3$ and other Lewis acid or Brønsted acid catalysts, as well as the comparison between this method with the reported methods in the literature, this method has some advantages including lower reaction temperature, shorter reaction times, higher yields, and it uses green solvent in the reaction for the synthesis of both target compounds (Table 6).



Scheme 4. Proposed mechanism for the aluminum tris (dodecyl sulfate) trihydrate [$Al(DS)_3 \cdot 3H_2O$]-catalyzed synthesis of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine

Table 6. Comparison use of [$Al(DS)_3 \cdot 3H_2O$]-catalyzed for the synthesis of 1,8-dioxo-octahydroxanthene and 1,8-dioxo-decahydroacridine with the literature

Entry	Condition	Product	Time (h)	Yield (%)	(ref)
1	$Al(DS)_3.3H_2O$, solvent-free, 80 °C	3a	0.25	88	(in this work)
2	Catalyst-free, Ethylene glycol, 80 °C	3a	1.50	94	(Tu et al., 2002)
3	silica chloride	3a	6.00	93	(Das et al., 2007)
4	$NaHSO_4.SiO_2$	3a	6.50	90	(Das et al., 2007)
5	PPA–SiO_2, CH_3CN, reflux	3a	10.00	52	(Kantevari et al., 2007)
6	[Hmim]TFA, 80 °C	3a	3.00	85	(Dabiri et al., 2008)
7	PANI-PTSA salt, reflux, H_2O	3a	6.00	79	(John et al., 2006)
8	TSILs, reflux, H_2O	3a	1.00	94	(Fang et al., 2009)
9	Amberlyst-15, CH_3CN, reflux	3a	5.00	92	(Das et al., 2006)
10	$SmCl_3$(20 mol%),Neat, 120 °C	3a	9.00	98	(Ilangovan et al., 2011)
11	TMSCl, reflux, CH_3CN	3a	8.00	84	(Kantevari et al., 2006)
12	[Hbim]BF_4, , ultrasound irradiation, rt, MeOH	3a	0.75	85	(Venkatesan et al., 2008)
13	PPA–SiO_2, CH_3CN, reflux	3a	10.00	52	(Kantevari et al., 2007)
14	PANI-PTSA, H_2O, reflux	3a	6.00	75	(John et al., 2006)
15	ZnO–acetyl chloride, CH_3CN, reflux	3a	5.00	86	(Maghsoodlou et al., 2010)
16	$HClO_4$–SiO_2, Solvent-free, 140 °C	3a	3.00	32	(Kantevari et al., 2007)
17	SBSSA, EtOH, reflux	3a	10.00	98	(Niknam et al., 2010)
18	L-proline, DCE, 60 °C	3a	6.00	83	(Das et al., 2012)
19	$Al(DS)_3.3H_2O$, Water, 80 °C	4a	۷.00	8۲	(in this work)
20	*p*-Dodecylbenzensulfunic acid, H_2O, reflux	4a	6.00	72	(Jin et al., 2004)
21	Amberlyst-15, reflux, CH_3CN	4a	5.00	81	(Das et al., 2006)
22	FSG-Hf(NPf_2)$_4$, water/ethanol, reflux	4a	6.00	49	(Hong and Xiao, 2012)
23	$Al(DS)_3.3H_2O$, Water, 80 °C	4b	7.00	89	(in this work)
24	FSG-Hf(NPf_2)$_4$, water/ethanol, reflux	4b	7.00	66	(Hong and Xiao, 2012)
25	DBSA, H_2O, reflux	4b	6.00	79	(Jin et al., 2004)
26	TsOH, H_2O, reflux	4b	6.00	13	(Jin et al., 2004)
27	SDS, TsOH, H_2O, reflux	4b	6.00	68	(Jin et al., 2004)
28	$Sc(DS)_3$, H_2O, reflux	4b	6.00	83	(Jin et al., 2004)

Lewis acid-surfactant type catalysts have a dual role in organic reactions, which is substrate molecules activation as a catalyst and increase the concentration of organic reactants as a surfactant to form micelle particles in water (Shiri and Zolfigol, 2009). In the presented reactions, we propose that not only are the substrate molecules activated by the catalyst, but also $Al(DS)_3$ surfactant increases the concentration of organic reactants to form micelle particles and they are also accompanied by inherent Lewis acidity of Al^{3+} groups, which have ability to bond with carbonyl oxygen of the substrates assisting in generation of ionic intermediates through activation of reactants. In other words, these intermediates are generated inside the micelle moiety by sufficient energy released during the collapse and strong polarity of the Al^{3+} groups. The reaction rates and yields under the reaction condition are enhanced using $Al(DS)_3$. Whereas no product is obtained in the absence of mentioned Lewis acid. Regarding solvent effect in the synthesis of 1,8-dioxo-octahydroxanthene, it should be noted that the nucleophilic oxygen is already incorporated to the skeleton of this intermediate by enolizating of intermediate **B** to enolate **C**. An intramolecular cyclization occurs without the help of solvent because of the proper spatial orientation caused by simple rotation of the carbon-carbon and carbon-oxigen bonds "symphoria" between this hydroxy group and the carbonyl group. However, for synthesis of 1,8-dioxo-decahydroacridine, primary amine should attack the carbonyl group of intermediate **B** as a separate reagent, therefore the presence of solvent is necessary to provide the moiety facilitating the collision of substrate with sufficient energy. In this way, micelle particles could be easily formed in water, which was tested and selected as the solvent in terms of reaction rate and isolated yield. We believe that the presented method is an example of substantial rate acceleration when insoluble reactants are stirred in aqueous suspension. This method denotes "on water" conditions (Narayan et al., 2005; Wang and Sharpless, 1994). Vigorous stirring promotes the reaction most likely by increasing the area of surface contact between the organic and aqueous phases. The observed rate acceleration does not depend on the amount of used water as long as sufficient water is present to clear phase separation occurranc (Demko and Sharpless, 2001). The use of water as an environmentally benign solvent offers practical convenience, such as: it alleviates the need to handle flammables, and reduce or eliminate environmental damage caused by organic solvents, and frequently, better selectivity is obtained in water. It also simplifies the tedious protection–deprotection sequence for molecules containing acidic sites, increases the overall synthetic efficiency (Chan and Li, 1992; Firouzabadi et al., 2005; Loh et al., 1998; Loh et al., 2000), and it is the cheapest and safest solvent available, thanks to its high heat capacity (Loh and Lye, 2001), unique redox stability and other extraordinary physical properties. Then, there is a general agreement about the future usage of water as a solvent (Cornils and Herrmann, 1996; Grieco, 1998; Li and Chan, 1997).

4. Conclusion

In summary, we have presented an example about the application of combined Lewis acid-surfactant catalyst [aluminum tris (dodecyl sulfate) trihydrate [$Al(DS)_3 \cdot 3H_2O$] for the synthesis of 1,8-dioxo-octahydroxanthens and 1,8-dioxo-decahydroacridines. This method is a novel, efficient, and one-pot catalytic approach that provides good functional group tolerance. The reaction is experimentally simple, proceeding well with no requirement for protection from atmospheric air, generates virtually no by-products, and requires only stoichiometric amounts of starting materials. The high selectivity and high isolated yields of this transformation are important. No additives and/or toxic reagent(s) were used, no by-product(s) were observed, and no laborious purifications were necessary. In addition, we have shown that the reaction can be scaled up to prepare larger and multi-gram quantities of the product without remarkable problems. The method avoids isolation and handling of in-situ generated intermediates, which reduces the reaction time and improves the overall yield. In addition, this safe and clean procedure is ideally suited to automated applications because the entire synthetic sequence can be carried out in the presence of a reusable catalyst. These conditions are also cost effective, environmentally friendly, and possess high generality, which make our methodology suitable as a valid contribution to the existing processes in the field of 1,8-dioxo-octahydroxanthens and 1,8-dioxo-decahydroacridines synthesis.

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