



Original article

Imidazol-1-yl-acetic acid as a novel green bifunctional organocatalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions



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ABSTRACT

Imidazol-1-yl-acetic acid is introduced as a new, efficient and recyclable green bifunctional organocatalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions. This catalyst is water soluble and can be separated from the products by simple filtration. The filtrate can be evaporated to dryness and recrystallized from cool methanol to give the recovered catalyst. This organocatalyst was used for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions and recycled up to 8 consecutive runs without any losing of its efficiency.

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1. Introduction

Xanthenes and benzoxanthenes compounds have received great attention from many pharmaceutical and organic chemists because of their broad spectrum of biological and pharmaceutical properties, such as antibacterial [1], anti-inflammatory, and antiviral [2] properties. Moreover, these compounds are used as dyes [3], as fluorescent materials for visualization of biomolecules [4] and in laser technologies [5] because of their photochemical and photophysical properties. Various synthetic procedures have been developed for the preparation of xanthenediones. For example, copper iodide nanoparticles on poly(4-vinylpyridine) [6], trichloroisocyanuric acid and cyanuric chloride [7,8], carbon-based solid acid [9], Fe₃O₄ and ZnO nanoparticles [10,11], functionalized mesoporous materials [12], cellulose sulfuric acid and succinimide-*N*-sulfonic acid [13,14], I₂ [15], P₂O₅/Al₂O₃ [16] and DABCO-bromine [17] have been used as catalysts for the synthesis of xanthenediones. However, some of these methods involve the use of expensive reagents, toxic solvents, tedious workup, low yields, long reaction times and harsh reaction

conditions. Therefore, there is a focus on developing an alternative, facile and green method for the synthesis of xanthenes derivatives.

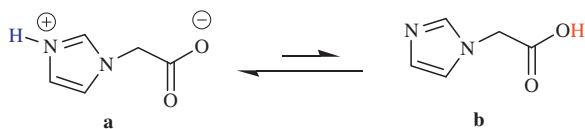
Organocatalytic reactions are becoming dominant tools for the production of complex molecular skeletons [18]. Organocatalysts are organic molecules that do not contain any metal which accelerate reactions in substoichiometric amounts. Bifunctional organocatalysts are organocatalysts with dual action. Imidazol-1-yl-acetic acid is an example of a bifunctional organocatalysts. This amino acid has two forms: a neutral and an ionized form. It is almost always in the ionized form (**a** in Scheme 1), except in the gaseous phase and in aprotic solvents (**b** in Scheme 1). Herein, we report imidazol-1-yl-acetic acid as a new, efficient and recyclable green bifunctional organocatalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions.

2. Experimental

All of the products were prepared by our own procedures; their spectroscopic and physical data were compared with those of authentic samples [6,10,21]. NMR spectra were recorded in CDCl₃ on Bruker AC 400 MHz instrument spectrometers using TMS as the internal standard. IR spectra were recorded on a BOMEMMB-Series 1998 FT-IR spectrometer. Elemental analyses were performed on a Thermo Finnigan CHNS-O analyzer, 1112 series. Chemicals were

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Scheme 1. The two forms of imidazol-1-yl-acetic acid.

purchased from Fluka, Merck and Aldrich Chemical companies. Yields refer to isolated pure products.

To a mixture of 5,5-dimethyl-1,3-cyclohexanedione or 1,3-cyclohexanedione (4 mmol) and aldehyde (2 mmol), imidazol-1-yl-acetic acid (1.2 mmol) was added and the reaction mixture was stirred at 60 °C for 7–15 min (Table 1). The progress of the reaction was monitored by TLC (eluent:EtOAc/*n*-hexane = 5/1, v/v). After completion of the reaction, the mixture was cooled to room temperature, water (20 mL) was added and the mixture was stirred for 10 min. The mixture was filtered and the solid residue was recrystallized from ethanol to afford the pure product. Evaporation of the filtrate gave the recovered catalyst which purified by recrystallization in cool methanol (30 mL), dried at 50 °C and used in the next consecutive runs.

9-(3-Methoxyphenyl)-3,3,6,6-tetramethyl-2,3,4,5,6,7,8,9-octahydro-1*H*-1,8-xanthenedion (Table 1, entry 15): White solid, mp 192–194 °C [6]; IR (KBr, cm⁻¹): ν_{max} 3070, 2950, 1650, 1605, 1580, 1450, 1360, 1265, 1220, 1200, 1180, 1130, 1050, 960; ¹H NMR (400 MHz, CDCl₃): δ 1.99–2.1 (m, 4H), 2.3–2.45 (m, 4H), 2.54–2.71 (m, 4H), 3.81 (s, 3 H), 4.83 (s, 1H), 6.69–6.71 (dd, 1H, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz), 6.89–6.95 (m, 2H), 7.17 (t, 1H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 20.3, 27.2, 31.5, 37.0, 55.2, 111.5, 114.5, 116.8, 121.0, 129.0, 146.0, 159.4, 164.0, 196.5. Elem. Anal. Calcd. for C₂₀H₂₀O₄: C, 74.06%; H, 6.21%; Found: C, 74.05%; H, 6.22%.

9-(4-Cyanophenyl)-3,3,6,6-tetramethyl-2,3,4,5,6,7,8,9-octahydro-1*H*-1,8-xanthenedion (Table 1, entry 16): White solid, mp 270–272 °C [6]; IR (KBr, cm⁻¹): ν_{max} 3070, 2950, 2900, 2220, 1652, 1619, 1356, 1200, 1173, 1125, 958, 830, 610, 550; ¹H NMR (400 MHz, CDCl₃): δ 1.95–2.11 (m, 4H), 2.30–2.42 (m, 4H), 2.57–2.73 (m, 4H),

4.84 (s, 1H), 7.44 (d, 2H, *J* = 8.0 Hz), 7.53 (d, 2H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 20.2, 27.1, 32.3, 36.8, 110.2, 115.8, 119.10, 129.4, 132.0, 149.7, 164.5, 196.5. Elem. Anal. Calcd. for C₂₀H₂₀O₄: C, 74.06%; H, 6.21%; Found: C, 74.05%; H, 6.22%.

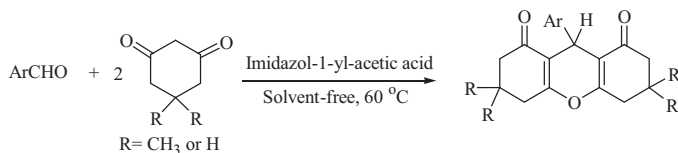
9-(3-Bromophenyl)-3,3,6,6-tetramethyl-2,3,4,5,6,7,8,9-octahydro-1*H*-1,8-xanthenedion (Table 1, entry 17): White solid, mp 281–282 °C [6]; IR (KBr, cm⁻¹): ν_{max} 3070, 2910, 2890, 1660, 1620, 1560, 1470, 1420, 1358, 1200, 1170, 1122, 957, 800, 680; ¹H NMR (100 MHz, CDCl₃): δ 1.95–2.1 (m, 4H), 2.30–2.44 (m, 4H), 2.55–2.63 (m, 2H), 2.66–2.73 (m, 2H), 4.79 (s, 1H), 7.11 (t, 1H, *J* = 7.6 Hz), 7.26–7.36 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 20.3, 27.2, 31.6, 36.9, 116.3, 122.3, 127.7, 129.6, 131.0, 146.6, 164.3, 196.4. Elem. Anal. Calcd. for C₂₀H₁₇NO₃: C, 75.22%; H, 5.37%; N, 4.39%; Found: C, 75.22%; H, 5.39%; N, 4.39%.

3. Results and discussion

Imidazol-1-yl-acetic acid contains both acidic and basic functionalities. The existence of such functionalities makes this molecule an ideal bifunctional organocatalyst for condensation reactions [19]. In fact the bifunctional catalytic activities of imidazol-1-yl-acetic acid arise from its ionized form (a in Scheme 1). To the best of our knowledge there is only one report that has investigated the catalytic activity of this simple and interesting bifunctional organocatalyst [20]. Consequently, we decided to study the potential catalytic activity of this simple bifunctional catalyst for the preparation of 1,8-dioxooctahydroxanthenes under solvent-free conditions.

In an initial attempt, a mixture of 1,3-cyclohexanedione (4 mmol) and benzaldehyde (2 mmol) in the presence of imidazol-1-yl-acetic acid (0.6 mmol, 75 mg) was stirred at room temperature. After 30 min, 48% of the expected product **3** (Scheme 2) was obtained. Another run was performed using 1.2 mmol (150 mg) of imidazol-1-yl-acetic acid which led to 88% of the title compound after 30 min. To improve the yield and rate of the reaction, the same reaction was carried out under solvent-free conditions using

Table 1
Imidazol-1-yl-acetic acid catalyzed synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions.



Entry	Aldehyde	R	Time (min)	Yield (%)	Mp (°C)	
					Found	Reported
1	PhCHO	H	8	95 ^a , 90 ^b	266–268	267–269 [21]
2	PhCHO	CH ₃	10	88 ^a , 86 ^b	203–204	202–204 [10]
3	4-MeC ₆ H ₄ CHO	CH ₃	12	87 ^a	217–218	215–216 [10]
4	2-MeOC ₆ H ₄ CHO	CH ₃	15	87 ^a	189–191	188–190 [10]
5	4-MeOC ₆ H ₄ CHO	CH ₃	15	89 ^a	241–243	242–243 [10]
6	3,4-(MeO) ₂ C ₆ H ₃ CHO	CH ₃	15	86 ^a	176–178	175–176 [10]
7	4-MeOC ₆ H ₄ CHO	H	15	88 ^a	202–203	200–201 [10]
8	4-NO ₂ C ₆ H ₄ CHO	CH ₃	7	90 ^a	222–224	223–225 [10]
9	2-ClC ₆ H ₄ CHO	CH ₃	8	89 ^a , 86 ^b	225–227	226–227 [10]
10	4-FC ₆ H ₄ CHO	CH ₃	8	87 ^a	227–228	226–227 [10]
11	4-CNC ₆ H ₄ CHO	CH ₃	10	85 ^a	215–217	217–218 [10]
12	4-OHC ₆ H ₄ CHO	CH ₃	15	89 ^a , 85 ^b	248–250	247–248 [10]
13	4-ClC ₆ H ₄ CHO	H	8	92 ^a , 89 ^b	284–286	286–288 [10]
14	4-BrC ₆ H ₄ CHO	H	9	89 ^a	283–285	284–286 [21]
15	3-MeOC ₆ H ₄ CHO	H	15	90 ^a	192–194	192–194 [6]
16	4-CNC ₆ H ₄ CHO	H	10	93 ^a , 90 ^b	273–275	270–272 [6]
17	3-BrC ₆ H ₄ CHO	H	8	90 ^a	281–283	281–282 [6]

^a Refer to pure and isolated yield in the first run.

^b Refer to pure and isolated yield in the eighth run.

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