

Synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives in water promoted by $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

Bi Bi Fatemeh Mirjalili^{1*},

Abdolhamid Bamoniri²,

Naimeh Salehi¹

¹*Department of Chemistry,
College of Science, Yazd University,
Yazd, I. R. Iran*

²*Department of Organic Chemistry,
Faculty of Chemistry,
University of Kashan,
Kashan, I. R. Iran*

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is a bench-top catalyst which is cheap, readily available, eco-friendly, versatile, and efficient for organic reactions. This catalyst was applied for synthesis of tetrahydrobenzo[*a*]xanthenes-11-ones in water and SDS. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of this protocol.

Key words: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, tetrahydrobenzo[*a*]xanthenes-11-one, heterogeneous condition, micelle core, surfactant

INTRODUCTION

Bismuth(III)nitrate with a favorable ecological behavior has low toxicity, low cost, stability in air, commercial availability, and ease of handling. According to the literature, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was applied for some organic transformations such as pechmann. condensation [1], acylal formation [2], carbonyl compound protection [3], and conversion of thiocarbonyls to their carbonyl compounds [4]. Benzoxanthene moiety in the structure of molecules causes important biological activities such as anti-inflammatory [5], anti-plasmodial [6], and photodynamic therapy [7]. Tetrahydrobenzo[*a*]xanthenes-11-ones as benzoxanthene derivatives could be synthesized via one-pot condensation of 2-naphthol, aldehyde, and 1,3-diketone in the presence of an acidic catalyst. According to the literature, this protocol was catalyzed by indium(III)chloride [8], proline triflate [9], *p*-toluenesulfonic acid [10], strontium triflate [11], dodecatungstophosphoric acid [12], tetrabutyl ammonium fluoride [13], and $\text{NaHSO}_4 \cdot \text{SiO}_2$ [14].

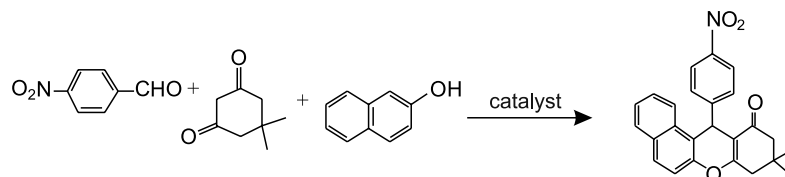
RESULTS AND DISCUSSION

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ can be applied for the efficient, atom-economic, and scalable synthesis of products with high purity. In this work, we investigated the synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives in the presence of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ under various conditions. The reaction of 4-nitrobenzaldehyde (1 mmol), dimedone (1.2 mmol) and 2-naphthol (1 mmol) was investigated for the optimization of the reaction conditions. Our endeavors revealed that the best condition is reaction in water as a solvent at 45 °C using 0.05 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.01 g of SDS (Table 1).

Water as a cheap, safe, ample and eco-friendly solvent is used for many organic processes. To increase the solubility of organic materials in water, the chemists use surfactants so as to form dispersed micelles. The hydrophobic materials were placed inside micelles and reacted similarly to a pressured system. In this protocol, we used sodium dodecyl sulfate (SDS) as a surfactant.

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ can be applied for the efficient, atom-economic, and scalable synthesis of products with high purity. The applicability of the present catalyst to a large scale process was

* Corresponding author. E-mail: fmirjalili@yazduni.ac.ir

Table 1. Synthesis of 12-(4-nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo-[*a*]xanthen-11-one under various conditions^a

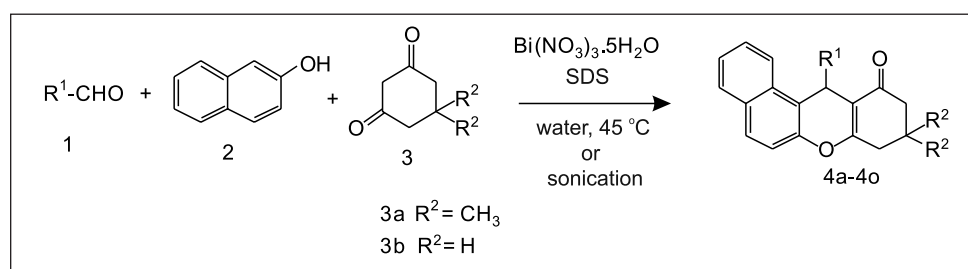
Entry	Catalyst	Catal., g : SDS, g	Solvent	Condition	Time, h	Yield, %	Ref
1	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	Ethanol	r. t.	4	10	–
2	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	n-Hexane	r. t.	4	40	–
3	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	CHCl ₃	r. t.	4	10	–
4	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	CH ₂ Cl ₂	r. t.	4	15	–
5	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	ClCH ₂ CH ₂ Cl	r. t.	4	15	–
6	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	Ethanol	Reflux	3	30	–
7	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	n-Hexane	Reflux	3	74	–
8	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	CHCl ₃	Reflux	3	79	–
9	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	CH ₂ Cl ₂	Reflux	3	76	–
10	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	ClCH ₂ CH ₂ Cl	Reflux	3	60	–
11	Bi(NO ₃) ₃ ·5H ₂ O	0.1 : 0	Solvent-free	90 °C	45 min	71	–
12	Bi(NO ₃) ₃ ·5H ₂ O	0.05 : 0.01	Water	r. t.	4.5	59	–
13	Bi(NO ₃) ₃ ·5H ₂ O	0.05 : 0.01	Water	45 °C	4.5	87	–
14	Bi(NO ₃) ₃ ·5H ₂ O, 2 nd run	0.05 : 0.01	Water	45 °C	4.5	80	–
15	Bi(NO ₃) ₃ ·5H ₂ O, 3 rd run	0.05 : 0.01	Water	45 °C	4.5	72	–
16	Bi(NO ₃) ₃ ·5H ₂ O	0.05 : 0.01	Water	Reflux	4.5	78	–
17	Bi(NO ₃) ₃ ·5H ₂ O	0.05 : 0.01	Water	Sonication	35 min	84	–
18	Sr(OTf) ₂	10 mol%	ClCH ₂ CH ₂ Cl	80 °C	5	85	11
19	InCl ₃	30 mol%	Solvent-free	120 °C	30 min	84	8
20	P ₂ O ₅	50 mol%	Solvent-free	120 °C	40 min	76	8
21	<i>p</i> -TSA	0.1 mmol	[bmim]BF ₄	80 °C	3	90	10
22	<i>p</i> -TSA	0.02 mmol	Solvent-free	120 °C	45 min	88	10
23	TBAF	10 mol%	Water	Reflux	9	99	13
24	NaHSO ₄ ·SiO ₂	100 mg	CH ₂ Cl ₂	Reflux	4	87	14
25	PWA	5 mol%	Solvent-free	60 °C	70 min	86	12
26	CAN	5 mol%	Solvent-free	120 °C	30 min	94	15
27	Proline triflate	10 mol%	Water	Reflux	3	85	9

^a Molar ratio of aldehyde: dimedone: β-naphthol is 1 : 1.2 : 1.

examined with 10 mmol of 2-naphthol, 11 mmol of dimedone, and 10 mmol of 4-nitrobenzaldehyde under a thermal and solvent free condition, which gave 9,9-dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo-[*a*]xanthen-11-one in a 85% yield. The reusability of the acidic water of the reaction medium containing the catalyst and SDS was also examined at 45 °C. After each run, the aqueous medium of the reaction was washed with chloroform to remove organic substances and re-use it for the next reaction (Table 1, entries 14 and 15).

2-Naphthol, dimedone or 1,3-cyclohexadione and various aldehydes were used as substrates for the synthesis of tetrahydrobenzo[*a*]xanthenes-11-one derivatives at 45 °C or sonication in water as a solvent (Scheme 1 and Table 2).

According to the literature, two types of mechanism are reported for the formation of tetrahydrobenzo[*a*]xanthenes-11-one from the condensation of β-naphthol, aldehyde and 1,3-diketone in the presence of an acidic catalyst. In the first one (a), initially, by the condensation of aldehyde and β-naphthol,



Scheme 1

Table 2. Synthesis of tetrahydrobenzo-[a]xanthen-11-ones in the presence of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Scheme)^a

Entry	R ¹	Diketone	Time, h / Yield ^b , %	Time, min / Yield ^c , % ^c	M. p. found, °C	M. p. reported ^{lit} , °C
4a	C ₆ H ₅	3a	5/86	40/85	151–153	151–153 ⁸
4b	4-ClC ₆ H ₄	3a	4.5/89	30/91	178–180	180–182 ⁸
4c	4-BrC ₆ H ₄	3a	4.5/87	35/87	181–183	186–187 ¹²
4d	3-BrC ₆ H ₄	3a	5/84	40/80	175–176	–
4e	4-NO ₂ C ₆ H ₄	3a	4.5/87	35/84	178–180	178–180 ⁸
4f	3-NO ₂ C ₆ H ₄	3a	5/85	40/79	167–168	168–170 ⁸
4g	4-CH(CH ₃) ₂ C ₆ H ₄	3a	6/84	45/83	160–162	–
4h	4-OHC ₆ H ₄	3a	6/86	50/87	150–151	150–151 ¹²
4i	4-OMeC ₆ H ₄	3a	6.5/84	50/85	206–207	204–205 ⁸
4j	2,3-OHC ₆ H ₃	3a	6.5/84	50/85	243–245	–
4k	C ₆ H ₅	3b	5/84	45/86	186–187	188–189 ¹²
4l	4-ClC ₆ H ₄	3b	4.7/85	40/88	202–204	205–206 ¹²
4m	4-NO ₂ C ₆ H ₄	3b	4.5/88	35/86	236–238	234–235 ¹²
4n	4-MeC ₆ H ₄	3b	6/77	60/75	207–208	205–206 ¹²

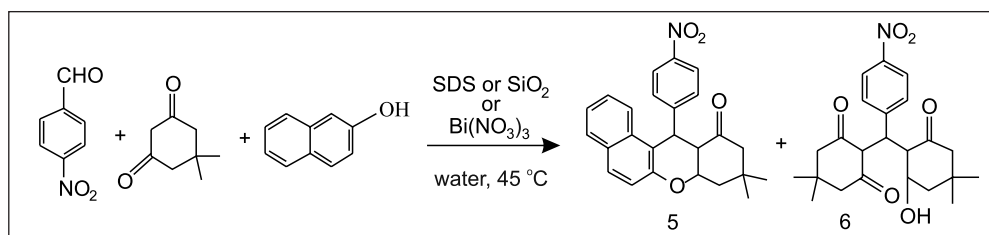
^a Molar ratio of aldehyde: dimedone: β -naphthol is 1 : 1.2 : 1.

^b Ratio of catalyst: SDS (g) is 0.05 : 0.01 in water at 45 °C.

^c Ratio of catalyst: SDS (g) is 0.05 : 0.01 under sonication in water as solvent.

ortho-quinone methide (*o*-QM) was formed as an intermediate [8, 10, 11]. In the second one (b), the intermediate was formed by the condensation of aldehyde and 1,3-diketone [9]. Our investigation has shown that in a one-pot reaction between β -naphthol, 4-nitrobenzaldehyde and dimedone in the presence of SDS, SiO₂ or low-amount Bi(NO₃)₃·5H₂O, the side product (6) could be formed (Scheme 2). Also, the same

product was formed in a reaction of 4-nitrobenzaldehyde and dimedone in the absence of β -naphthol. According to the obtained data, we confirm that the reaction mechanism is the same as the second one (b). Meanwhile, SDS in water forms micelles and the reaction occurs in a micelle core. The Bi(NO₃)₃ as a catalyst activates aldehyde for the condensation reaction (Figure).



Scheme 2

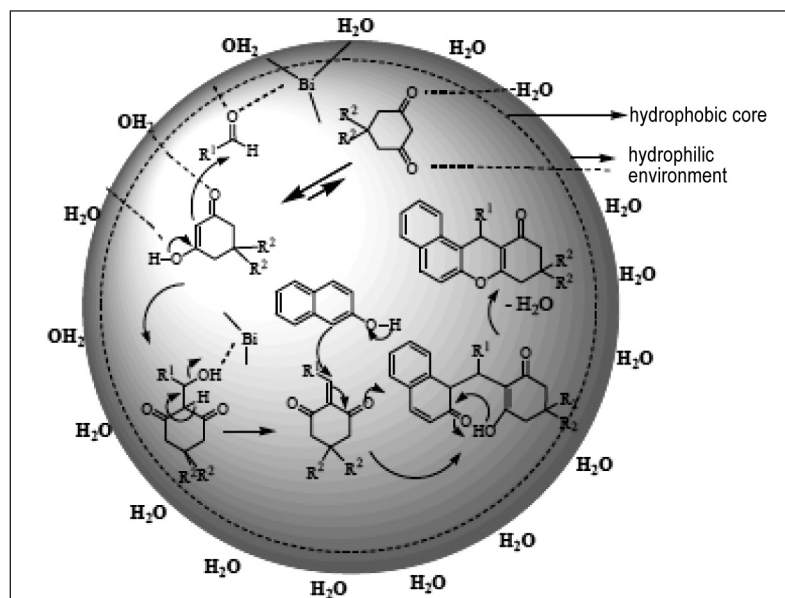


Figure. A proposed mechanism for the preparation of tetrahydrobenzo[a]xanthenes-11-one in a micelle core

EXPERIMENTAL

The chemicals were purchased from Fluka and Merck companies. Products were characterized by IR, ^1H NMR and by comparison of their physical properties with those reported in the literature. IR spectra were run on a Bruker, Equinox 55 spectrometer. ^1H NMR spectra were obtained using a Bruker Avans 400 MHz spectrometer (DRX). Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus. BANDELIN Sonopuls HD 3200 ultrasonic apparatus (20 kHz, 150 W) was used for sonication.

General procedure for the synthesis of tetrahydrobenzo[a]xanthenes-11-one derivatives in water

A mixture of 2-naphthol (1 mmol), aldehyde (1 mmol), 1,3-diketone (1.2 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.05 g), 0.01 g of SDS, and 2 ml of water was heated at 45 °C in a water bath or by an ultrasonic apparatus. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was charged in to an isolating funnel and extracted with chloroform to isolate the product. The chloroform layer was evaporated carefully and the obtained solid was crystallized in ethanol: water (80 : 20) to afford the pure tetrahydrobenzo[a]xanthenes-11-one derivatives in good to excellent yields. The aqueous layer containing SDS and the catalyst was reused for another reaction.

SPECTROSCOPIC DATA

12-Phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4a)

FT-IR (KBr): ν_{max} : 3 053, 2 957, 2 891, 1 649, 1 620, 1 596, 1 469, 1 452, 1 372, 1 241, 1 226, 1 184, 1 032, 837, 747, 723, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, J = 16 Hz, 1H, COCH_2), 2.32 (d, J = 16.4 Hz, 1H, COCH_2), 2.58 (s, 2H), 5.71 (s, 1H), 7.06 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 8 Hz, 2H), 7.32–7.46 (m, 5H), 7.77 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 6.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 27.59, 29.72, 32.69, 35.14, 41.85, 51.34, 114.71, 117.46, 118.14, 124.11, 125.31, 126.65, 127.42, 128.65, 128.80, 128.85, 129.25, 131.85, 131.93, 145.18, 148.19, 164.30, 197.29 ppm.

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4b)

FT-IR (KBr): ν_{max} : 2 957, 2 884, 1 644, 1 622, 1 596, 1 487, 1 469, 1 372, 1 234, 1 221, 1 141, 1 088, 1 013, 845, 838, 750 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, J = 16.4 Hz, 1H, COCH_2), 2.32 (d, J = 16 Hz, 1H, COCH_2), 2.58 (s, 2H), 5.69 (s, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 1H), 7.40 (td, J = 6.8, 1.2 Hz, 1H), 7.45 (td, J = 6.8, 1.2 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.8 (d, J = 5.6 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H) ppm.

12-(4-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4c)

FT-IR (KBr): ν_{max} : 2 966, 2 876, 1 640, 1 622, 1 593, 1 484, 1 372, 1 274, 1 220, 1 174, 1 071, 1 010, 837, 811, 756 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.97 (s, 3H), 1.13 (s, 3H), 2.25 (d, J = 16.4 Hz, 1H, COCH_2), 2.32 (d, J = 16 Hz, 1H, COCH_2), 2.58 (s, 2H), 5.67 (s, 1H), 7.22 (d, J = 7.2 Hz, 2H), 7.29 (d, J = 7.2 Hz, 2H), 7.33 (d, J = 9.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 6.8 Hz, 1H), 7.91 (d, J = 8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 27.59, 29.72, 32.68, 34.70, 41.83, 51.29, 114.18, 117.41, 117.46, 120.54, 123.88, 125.46, 127.56, 128.92, 129.54, 130.62, 131.64, 131.77, 131.95, 144.19, 148.17, 164.49, 197.27 ppm.

12-(3-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4d)

FT-IR (ATR, neat): ν_{max} : 2 958, 2 891, 1 646, 1 622, 1 594, 1 470, 1 432, 1 370, 1 282, 1 218, 1 175, 1 076, 1 024, 805, 879, 775, 692, 744 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.99 (s, 3H), 1.13 (s, 3H), 2.26 (d, J = 16.4 Hz, 1H), 2.32 (d, J = 16 Hz, 1H), 2.59 (s, 2H), 5.68 (s, 1H), 7.06 (t, J = 8 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.39–7.42 (m, 2H), 7.47 (t, J = 8 Hz, 1H), 7.79 (d, J = 5.2 Hz, 1H), 7.81 (d, J = 6.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H) ppm.

12-(4-Nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4e)

FT-IR (KBr): ν_{max} : 2 956, 1 643, 1 622, 1 594, 1 477, 1 513, 1 477, 1 376, 1 342, 1 244, 1 221, 1 183, 1 031, 850, 830, 751 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.95 (s, 3H), 1.14 (s, 3H), 2.25 (d, J = 16.4 Hz, 1H, COCH_2), 2.34 (d, J = 16 Hz, 1H, COCH_2), 2.61 (s, 2H), 5.82 (s, 1H), 7.36 (d, J = 9.2, 1H), 7.39–7.47 (m, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.81–7.85 (m, 3H), 8.05 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 27.50, 29.72, 32.69, 35.30, 41.85, 51.21, 113.42, 116.47, 117.52, 123.54, 124.05, 125.67, 127.81, 129.09, 129.79, 130.06, 131.46, 132.01, 146.78, 148.22, 152.29, 165.05, 197.14 ppm.

12-(3-Nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4f)

FT-IR (KBr): ν_{max} : 2 969, 2 891, 1 645, 1 622, 1 594, 1 465, 1 536, 1 477, 1 371, 1 355, 1 249, 1 218, 1 174, 1 024, 830, 806, 779, 689, 741 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.96 (s, 3H), 1.14 (s, 3H), 2.25 (d, J = 16.4 Hz, 1H, COCH_2), 2.34 (d, J = 16 Hz, 1H, COCH_2), 2.62 (s, 2H), 5.82 (s, 1H), 7.36–7.48 (m, 4H), 7.81–7.84 (m, 3H), 7.78 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8 Hz, 1H), 8.12 (s, 1H) ppm.

12-(4-Isopropylphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4g)

FT-IR (ATR, neat): ν_{max} : 2 960, 2 873, 1 649, 1 622, 1 596, 1 469, 1 370, 1 241, 1 227, 1 145, 1 016, 833, 818, 745 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.99 (s, 3H), 1.12 (s, 3H), 1.13 (d, J = 6.8, 6H), 2.26 (d, J = 16 Hz, 1H), 2.31 (d, J = 16.4 Hz,

1H), 2.58 (s, 2H), 2.76 (m, 1H), 5.68 (s, 1H), 7.01 (d, $J = 8$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.8$ Hz, 1H), 7.38 (t, $J = 8.4$ Hz, 1H), 7.43 (t, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H) ppm.

12-(4-Hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4h)

FT-IR (KBr): ν_{\max} : 3610, 3141–3440, 3029, 2952, 2891, 1649, 1615, 1595, 1510, 1466, 1371, 1234, 1227, 1174, 1014, 837, 818, 747 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): $\delta = 0.99$ (s, 3H), 1.14 (s, 3H), 2.31 (d, $J = 16.4$ Hz, 1H, COCH_2), 2.35 (d, $J = 16$ Hz, 1H, COCH_2), 2.48 (s, 1H), 2.59 (s, 2H), 5.65 (s, 1H), 6.62 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 2H), 7.39 (d, $J = 6.8$ Hz, 1H), 7.45 (t, $J = 8.4$ Hz, 1H), 7.47 (t, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.80 (d, $J = 6.9$ Hz, 1H), 8.0 (d, $J = 8.4$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 27.56$, 27.76, 29.64, 32.77, 34.31, 41.84, 51.28, 114.90, 115.67, 117.42, 118.28, 124.17, 125.34, 127.39, 128.80, 129.18, 129.95, 131.79, 131.96, 137.18, 148.01, 154.67, 164.82 ppm.

12-(4-Methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4i)

FT-IR (KBr): ν_{\max} : 2957, 2898, 1644, 1611, 1594, 1509, 1460, 1371, 1245, 1249, 1223, 1164, 1027, 1025, 833, 812, 747 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.98$ (s, 3H), 1.12 (s, 3H), 2.25 (d, $J = 16$ Hz, 1H, COCH_2), 2.32 (d, $J = 16.4$ Hz, 1H, COCH_2), 2.57 (s, 2H), 3.69 (s, 3H), 5.66 (s, 1H), 6.71 (d, $J = 8.4$ Hz, 2H), 7.20–7.27 (m, 2H), 7.32 (d, $J = 8.8$ Hz, 1H), 7.38 (t, $J = 8$ Hz, 1H), 7.44 (t, $J = 8$ Hz, 1H), 7.76 (d, $J = 9.2$ Hz, 1H), 7.78 (d, $J = 9.2$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H) ppm.

12-(2,3-Dihydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4j)

FT-IR (KBr): ν_{\max} : 3511, 3130–3400, 2960, 2880, 1626, 1611, 1592, 1474, 1469, 1377, 1228, 1179, 1030, 838, 758 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , DMSO): $\delta = 1.02$ (s, 3H), 1.18 (s, 3H), 2.39 (d, $J = 16.6$ Hz, 1H, COCH_2), 2.46 (d, $J = 16.6$ Hz, 1H, COCH_2), 2.63 (s, 2H), 5.78 (s, 1H), 6.10 (s, 1H), 6.13 (dd, $J = 8, 1.4$ Hz, 1H), 6.56 (t, $J = 7.9$ Hz, 1H), 6.71 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.36 (d, $J = 8.9$ Hz, 1H), 7.41 (td, $J = 6.8, 1.3$ Hz, 1H), 7.46 (td, $J = 6.8, 1.3$ Hz, 1H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 2H), 9.51 (s, 1H) ppm.

12-Phenyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4k)

FT-IR (KBr): ν_{\max} : 3059, 2930, 1644, 1616, 1593, 1511, 1453, 1249, 1227, 1189, 1032, 830, 757, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.94$ –2.06 (m, 2H), 2.35–2.49 (m, 2H), 2.63–2.73 (m, 2H), 5.75 (s, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 7.18 (t, $J = 7.6$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.39–7.45 (m, 3H), 7.77 (d, $J = 7.2$ Hz, 1H), 7.79 (d, $J = 6.8$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 20.71$, 28.17, 35.10, 37.50, 116.01, 117.43, 118.16, 123.12, 124.14, 125.34, 126.71, 127.44, 128.73, 128.83, 128.95, 129.29, 131.85, 145.52, 148.24, 166.03, 197.46 ppm.

12-(4-Chlorophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4l)

FT-IR (KBr): ν_{\max} : 3063, 1645, 1622, 1593, 1488, 1458, 1226, 1189, 1089, 1014, 838, 818, 751 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.94$ –2.10 (m, 2H), 2.35–2.50 (m, 2H), 2.63–2.78 (m, 2H), 5.72 (s, 1H), 7.15 (d, $J = 8$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.8$ Hz, 1H), 7.39 (t, $J = 8$ Hz, 1H), 7.44 (t, $J = 8$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 20.72$, 28.16, 34.61, 37.46, 115.56, 117.44, 122.86, 123.93, 124.81, 125.47, 127.56, 128.94, 129.06, 129.56, 130.35, 131.97, 132.42, 144.02, 148.21, 166.17, 197.43 ppm.

12-(4-Nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4m)

FT-IR (KBr): ν_{\max} : 2891, 1651, 1630, 1592, 1492, 1514, 1458, 1340, 1253, 1237, 1187, 1036, 851, 827, 742 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): $\delta = 1.92$ –1.99 (m, 1H), 2.05–2.10 (m, 1H), 2.39–2.46 (m, 2H), 2.67–2.77 (m, 2H), 5.82 (s, 1H), 7.35 (d, $J = 9$ Hz, 1H), 7.37–7.44 (m, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.78–7.81 (m, 3H), 8.01 (d, $J = 8.8$ Hz, 2H) ppm.

12-(4-Methylphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4n)

FT-IR (KBr): ν_{\max} : 2947, 1647, 1622, 1596, 1509, 1406, 1372, 1253, 1224, 1188, 1032, 838, 808, 742 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.99$ –2.06 (m, 2H), 2.22 (s, 3H), 2.38–2.46 (m, 2H), 2.67–2.74 (m, 2H), 5.72 (s, 1H), 6.99 (d, $J = 8$ Hz, 2H), 7.23 (d, $J = 8$ Hz, 2H), 7.34 (d, $J = 8.8$ Hz, 1H), 7.35–7.50 (m, 2H), 7.76 (d, $J = 7.2$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 20.74$, 21.47, 28.17, 34.70, 37.53, 116.17, 117.44, 118.35, 123.17, 124.17, 125.32, 127.43, 128.83, 129.20, 129.47, 131.89, 131.96, 136.19, 142.69, 148.21, 165.94, 197.50 ppm.

CONCLUSIONS

We have demonstrated simple methods for the synthesis of tetrahydrobenzo-[a]xanthen-11-one using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as an eco-friendly and efficient catalyst. Short reaction times, high yields, clean process, simple methodology, easy work-up and green conditions are advantages of these protocols.

ACKNOWLEDGEMENTS

The Research Council of Yazd University is gratefully acknowledged for the financial support of this work.

Received 16 January 2012

Accepted 6 February 2012

References

1. V. M. Alexander, R. P. Bhat, S. D. Samant, *Tetrahedron Lett.*, **46**, 6957 (2005).
2. D. H. Aggen, J. N. Arnold, P. D. Hayes, N. J. Smoter, R. S. Mohan, *Tetrahedron*, **60**, 3675 (2004).
3. N. Srivastava, S. K. Dasgupta, B. K. Banik, *Tetrahedron Lett.*, **44**, 1191 (2003).
4. I. Mohammadpoor-Baltork, M. M. Khodaei, K. Nikoofar, *Tetrahedron Lett.*, **44**, 591 (2003).
5. J. P. Poupelin, G. Saint-Ruf, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, R. Lacroix, *Eur. J. Med. Chem.*, **13**, 67 (1978).
6. F. Zelefack, D. Guilet, N. Fabre, C. Bayet, S. Chevalley, S. Ngouela, B. N. Lenta, A. Valentin, E. Tsamo, M. G. Dijoux-Franca, *J. Nat. Prod.*, **72**, 954 (2009).
7. R. M. Ion, A. Planner, K. Wiktorowicz, D. Frackowiak, *Acta Biochim. Pol.*, **45**, 833 (1998).
8. G. C. Nandi, S. Samai, R. Kumar, M. S. Singh, *Tetrahedron*, **65**, 7129 (2009).
9. J. Li, L. Lu, W. Su, *Tetrahedron Lett.*, **51**, 2434 (2010).
10. J. M. Khurana, D. Magoo, *Tetrahedron Lett.*, **50**, 4777 (2009).
11. J. Li, W. Tang, L. Lu, W. Su, *Tetrahedron Lett.*, **49**, 7117 (2008).
12. H.-J. Wang, X.-Q. Ren, Y.-Y. Zhang, Z.-H. Zhang, *J. Braz. Chem. Soc.*, **20**, 1939 (2009).
13. S. Gao, C. H. Tsai, C.-F. Yao, *Synlett*, 949 (2009).
14. B. Das, K. Laxminarayana, M. Krishnaiah, Y. Srinivas, *Synlett*, 3107 (2007).
15. A. Kumar, S. Sharma, R. A. Maurya, J. Jayant Sarkar, *J. Comb. Chem.*, **12**, 20 (2010).

Bi Bi Fatemeh Mirjalili, Abdolhamid Bamoniri, Naimeh Salehi

**TETRAHIDROBENZO[A]KSANTEN-11-ONO
DARINIŲ SINTEZĖ VANDENYJE, KATALIZUOJAMA
BI(NO₃)₃·5H₂O**

S a n t r a u k a

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ yra pigus, lengvai prieinamas, ekologiškas, universalus organinių reakcijų katalizatorius. Šis katalizatorius panaudotas tetrahydrobenzo[a]ksanten-11-ono darinių sintezei vandens terpėje.