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Ultrasound Promoted One Pot Synthesis of 14-Aryl-14*H*-dibenzo[a,j]xanthene Derivatives

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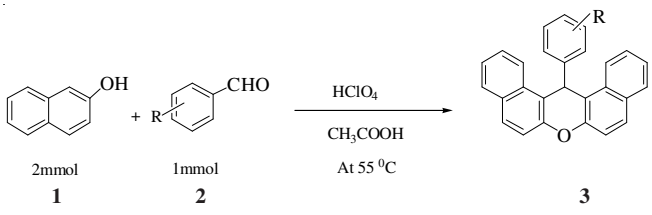
A simple and facile ultrasound promoted one pot synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthene derivatives, *via* perchloric acid catalyzed condensation reaction of β-naphthol and aryl aldehydes is described, having the advantages of excellent yields, short reaction time and mild reaction conditions.

Key Words: Xanthene derivatives, Perchloric acid, Sonochemistry.

INTRODUCTION

Xanthene derivatives are well known heterocyclic units in the realms of natural and synthetic organic chemistry, especially aryl-14*H*-dibenzo[a,j]xanthene has attracted the attention of organic chemists due to their wide range of a key structural element of many biologically active compounds such as antibacterials[1], antivirals[2] and antiinflammatory agents[3]. Furthermore, due to their useful spectroscopic properties, they are used as dyes[4], in laser technologies[5], as antagonists of the paralyzing action of oxazolamine[6] and in fluorescent materials for visualization of biomolecules[7]. It is also noteworthy that dibenzoxanthenes derivatives are candidates as sensitizers in photodynamic therapy (PDT)[8]. Natural xanthene dyes are extracted from soil and plants such as *Indigofera longeracemosa*[9]. In past years, many synthetic methods have been reported for preparation of xanthenes which include reaction of β-naphthol with aldehydes or acetals under acidic conditions, cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone, cyclodehydrations, alkylations γ to the heteroatom and intermolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones[10-13]. However, most of these synthetic procedures involve conventional methods and suffer from drawbacks such as longer reaction times, low yields, harsh reaction conditions and utilization of excess of reagents and catalysts. Thus, the synthesis of benzoxanthene derivatives currently is of great interest. Recently, various methods have been reported for the synthesis of benzoxanthenes, including the reaction of 2-naphthol with aldehydes in the presence of a catalyst, such as amberlyst[14], sulfamic acid[15], I_2[16], AcOH-H_2SO_4[17], heteropoly acids (HPAs)[18,19], Dowex50W[20], $NH_4H_2PO_4$[21], PW acid[22], cyanuric chloride[23], $Yb(OTf)_3$[24] and alum[25]. In continuation of our interest to develop environment friendly protocols, we report the synthesis of aryl-14*H*-dibenzo[a,j]xanthene analogs in moderate to excellent yields by the reaction of aromatic aldehydes and β-naphthol using perchloric acid as catalyst under ultrasound irradiation (**Scheme-I**).



Scheme-I

EXPERIMENTAL

All melting points were measured in open capillaries and are uncorrected. Silica gel used for TLC was 200-300 mesh with Binder. IR spectra were recorded on a Shimadzu instruments. Proton magnetic resonance spectra were recorded on a Varion T-60, FT 80 A MSL-300 instrument. All spectra were recorded in $CDCl_3$ and chemical shifts are reported in parts per million (ppm) down field from tetramethyl silane (TMS) as the internal standard.

General procedure for synthesis of xanthene derivatives: A mixture of the aldehyde (1 mmol) and β-naphthol (2 mmol) with $HClO_4$ (0.1 mmol) was refluxed in ultrasonic cleaning bath at 55 ºC in glacial acetic acid (2 mL) for the appropriate time. After completion of the reaction as indicated by TLC, the reaction contents were cooled to room temperature,

followed by addition of water (3 mL) and the mixture stirred for 2 min. The solid product obtained was separated by filtration and recrystallized from ethanol to give pure compound as white solid. All compounds obtained according to this protocol were characterized and identified by their melting points and spectral data in comparison to those reported in the literature.

Physical and spectral data for all the compounds

14-Phenyl-14*H*-dibenzo[a,j]xanthene (1): White solid: m.p. 183-185 ºC. IR (KBr, cm^{-1}): 3076, 3022, 2887, 1627, 1593, 1512, 1489, 1456, 1402, 1251, 1080, 1030, 962, 825, 744, 702; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.36 (2H, d, *J* = 8.5 Hz), 7.78 (2H, d, *J* = 8.3 Hz), 7.75 (2H, d, *J* = 9.0 Hz), 7.54 (2H, t, *J* = 7.7 Hz), 7.48 (2H, d, *J* = 6.3 Hz), 7.42 (2H, d, *J* = 13.2 Hz), 7.36 (2H, d, *J* = 7.2 Hz), 7.11 (2H, t, *J* = 7.7 Hz), 6.96 (1H, d, *J* = 7.4 Hz), 6.45 (1H, s).

14-(4-Chlorophenyl)-14*H*-dibenzo[a,j]xanthene (2): Yellow solid: m.p. 186-188 ºC. IR (KBr, cm^{-1}): 3070, 2914, 1626, 1593, 1485, 1431, 1400, 1246, 1085,962, 829, 744, 711; ^{1}H NMR ($CDCl_3$): δ = 8.31 (2H, d, *J* = 8.5 Hz,), 7.88 (2H, d, *J* = 8.5 Hz),7.82 (2H, d, *J* = 9.6 Hz), 7.78 (2H, d, *J* = 5.5 Hz), 7.73 (2H, d, *J* = 8.8 Hz), 7.57 (2H, t, *J* = 7.2 Hz), 7.47 (2H, d, *J* = 9.0 Hz), 7.42 (2H, t, *J* = 7.7 Hz), 7.36 (2H, t, *J* = 7.7 Hz), 7.31 (1H, s).

14-(2-Chlorophenyl)-14*H*-dibenzo[a,j]xanthene (3): Yellow solid: m.p. 213-215 ºC. IR (KBr, cm^{-1}): 3061, 2953, 1626, 1593, 1460, 1435, 1400, 1244, 1068,960, 829, 744, 688; ^{1}H NMR ($CDCl_3$): δ 8.53 (2H, d, *J* = 8.8 Hz), 7.80 (2H, d, *J* = 7.7 Hz),7.69 (2H, d, *J* = 4.0 Hz), 7.59 (2H, d, *J* = 7.4 Hz), 7.47 (2H, d, *J* = 8.8 Hz), 7.41 (2H, t, *J* = 7.9 Hz), 7.37 (2H, d, *J* = 4.4Hz), 7.32 (2H, t, *J* = 7.9 Hz), 7.24 (1H, s).

14-(4-Methoxyphenyl)-14*H*-dibenzo[a,j]xanthene (4): Yellow solid: m.p. 204-205 ºC. IR (KBr, cm^{-1}): 3070,2912, 1617, 1593, 1510, 1460, 1435, 1398, 1247, 1109,1078, 960, 831, 810, 744; ^{1}H NMR: δ = 8.35 (2H, d, *J* = 8.5 Hz), 7.95 (2H, d, *J* = 8.8 Hz), 7.83 (2H, d, *J* = 9.3 Hz), 7.77 (2H, t, *J* = 8.8Hz), 7.65 (2H, d, *J* = 7.5 Hz), 7.55-7.23 (4H, m), 6.65 (2H, d, *J* = 8.5 Hz), 6.42 (1H, s), 3.67(3H, s).

14-(2-Methoxyphenyl)-14*H*-dibenzo[a,j]xanthene (5): Yellow solid: m.p. 259-261 ºC. IR (KBr, cm^{-1}): 3057, 2962, 1617, 1591, 1514, 1456, 1431, 1402, 1249, 1139,1047, 962, 813, 800, 738; ^{1}H NMR: δ = 8.37 (2H, d, *J* = 8.5 Hz), 7.80 (2H, d, *J* = 8.3 Hz), 7.76 (2H, d, *J* = 8.8 Hz), 7.55 (2H, t, *J* = 8.3 Hz), 7.45 (2H, d, *J* = 8.8 Hz), 7.40-7.02 (4H, m), 6.51 (2H, d, *J* = 8.3 Hz), 6.43 (1H, s), 3.60 (3H, s).

14-(4-Nitrophenyl)-14*H*-dibenzo[a,j]xanthene (6): Yellow solid: m.p. 310-312 ºC. IR (KBr, cm^{-1}): 3070, 2928, 1626, 1593, 1514, 1458, 1400, 1340, 1244, 1161, 1109, 1012, 960, 852, 827, 810, 744, 702; ^{1}H NMR (CDCl, 300 MHz): δ = 8.28 (2H, d, *J* = 8.3 Hz), 7.99 (2H, d, *J* = 8.8 Hz), 7.85 (2H, d, *J* = 4.9 Hz), 7.83 (2H, d, *J* = 5.8 Hz), 7.67 (2H, d, *J* = 8.8 Hz), 7.61 (2H, t, *J* = 5.8 Hz), 7.58 (2H, d, *J* =7.2 Hz), 7.52 (2H, t, *J* =9.0 Hz), 6.60 (1H, s).

14-(2-Nitrophenyl)-14*H*-dibenzo[a,j]xanthene (7): Yellow solid: m.p. 212-215 ºC. IR (KBr, cm^{-1}): 3103, 3057, 2922, 1626,1593, 1518, 1352, 1244, 1141, 810, 750; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (2H, d, *J* = 8.5 Hz), 7.80 (2H, d, *J* = 2.8 Hz), 7.77 (2H, d, *J* = 3.6 Hz), 7.60-7.39 (8H, m), 7.21 (2H, d, *J* = 7.7 Hz), 7.17 (1H, s).

14-(4-Hydroxyphenyl)-14*H*-dibenzo[a,j]xanthene (8): Pink solid: m.p. 137-139 ºC. IR (KBr, cm^{-1}): 3414, 1591, 1512, 1396, 1344, 1246, 815, 746, 695; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35-6.56 (16H, m, Ar-H), 6.40 (1H, s, CH), 4.88 (1H, br s, OH).

RESULTS AND DISCUSSION

To evaluate the effect of the catalyst under different conditions, the reaction of benzaldehyde and β-naphthol was selected as a model reaction and the results are presented in Table-1. Initially the effect of the solvent on the reaction was studied (Table-1, compounds **1-7**) and glacial acetic acid was found to be the best. The catalyst of $HClO_4$ and solvent were examined and the results are summarized in Table-1, compounds **1-7**. It could be seen that $HClO_4$ with glacial acetic acid give the excellent result (Table-1, compound **8**), whereas in the absence of $HClO_4$ or solvent or both and under the same reaction conditions, there was no reaction (Table-1, compounds **1-3** and **7**). The influence of the reaction time on the yield was also investigated, as shown in Table-1, compounds **4-6** and **8**. It was found that higher yield occurred when the reaction time was 1 h. Hence the perchloric acid with glacial acetic acid as the catalyst deserves special mention. The catalyst has shown strong surface acidic sites and with low toxicity. Also, this catalyst is safe, easy to handle, environmentally benign and with fewer disposal problems.

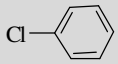
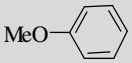
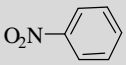
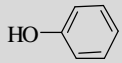
TABLE-1
EFFECT OF CATALYST $HClO_4$ UNDER DIFFERENT REACTION CONDITIONS FOR CONDENSATION OF BENZALDEHYDE AND β-NAPHTHOL*

Compd.	Solvent	Catalyst	Time (h)	Yield (%)**
1	Nil	Nil	7	–
2	H_2O	Nil	7	–
3	Nil	1 mmol	7	–
4	H_2O	1 mmol	7	Trace
5	EtOH	1 mmol	7	33
6	CH_3CN	1 mmol	7	20
7	AcOH	Nil	7	–
8	AcOH	1 mmol	1	98

*Reaction conditions: benzaldehyde (1 mmol), β-naphthol (2 mmol) and catalyst in solvent (3 mL), 55 ºC; **Isolated yield.

The process was promoted by directly immersing of standard glass reaction vessels with the reaction mixture into the ultrasonic cleaning bath which provides a fairly even distribution of energy into the reaction medium. We observed dissolutions of the source compounds and precipitation of target product in the course of the reaction. The reaction was completed within 30-90 min (monitored by TLC). In all the cases the corresponding benzoxanthenes were obtained in excellent yields (**1-8**) (Table-2). In this work, a highly efficient and environmentally benign methodology for the synthesis of 14- aryl-14*H*-dibenzo[a,j]xanthenes from the reaction of aldehydes and β-naphthol in the presence of catalytic amounts of ($HClO_4$) under ultrasound irradiation is developed. The protocol offers several advantages such as mild reaction conditions, short reaction time, easy isolation, fast and low cost procedure for the synthesis of benzoxanthenes.

TABLE-2
$HClO_4$ CATALYZED ONE POT SYNTHESIS OF
14-aryl-14*H*-DIBENZO[a,j]XANTHENES

Compd.	R	Time (min)	Yield (%)	m.p. (ºC)	
				Found	Reported
1		60	98	183-185	185[26]
2		60	90	186-188	189[26]
3		45	97	213-215	215[26]
4		45	90	204-205	204[26]
5		45	92	259-260	260[26]
6		30	95	310-312	214[26]
7		90	98	212-215	214[27]
8		30	96	137-139	140[28]

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