

ULTRASOUND ASSISTED EFFICIENT AND GREENER ONE POT SYNTHESIS OF ARYL-14-H-DIBENZO [a,j]XANTHENE DERIVATIVES

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Abstract

Aryl-14-H-dibenzo[a,j]xanthenes have been synthesized in high yields from the condensation of aryl aldehydes and 2-naphthol in presence of copper perchlorate hexahydrate as catalyst at room temperature gives aryl-14-H-dibenzo[a,j]xanthenes with excellent yields under ultrasound irradiation (35 kHz). This method has the advantages of high yield, simple methodology, greener and one pot procedure.

Keywords: Heterogeneous catalyst, dibenzoxanthene, copper perchlorate hexahydrate, ultrasound irradiation, dyes.

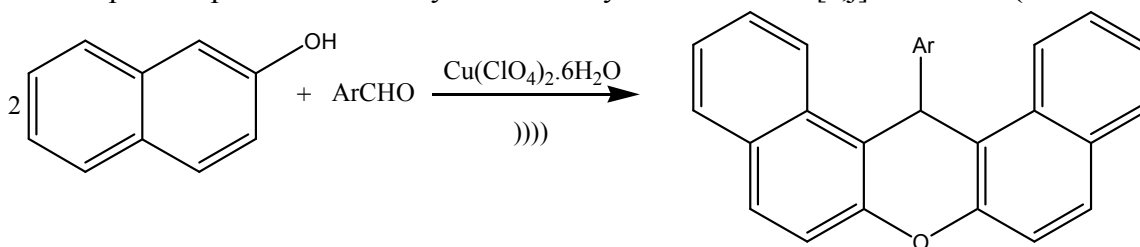
1. Introduction

Dyes have been most extensively used in dyeing, lasers, liquid crystalline displays, electro-optical devices and ink-jet printers.^{1,2} Xanthene derivatives occupy a significant position among different families of dyes due to photochemical and photophysical properties.³ Rose Bengal, Eosin, and other xanthene dyes are the most frequently employed dye-sensitizer.⁴ A number of analyte sensors have been designed using these scaffolds via synthesis of new xanthene based dyes.⁵ Xanthenes and benzoxanthenes are active oxygen heterocycles which are useful drug intermediates known to possess antibacterial,⁶ anti-inflammatory⁷ and antiviral properties.⁸ These compounds are also used as antagonist for paralyzing action of zoxazolamine and in photodynamic therapy (PDT).⁹ Furthermore, benzoxanthenes are also used as dyes, in laser technologies,¹⁰ and in fluorescent materials.¹¹ Xanthenes and Benzoxanthenes have been synthesized by different methods. Some of the important methods include reaction of aryloxymagnesium halides with triethylorthoformate,¹² cyclodehydration,¹³ trapping of benzynes by phenol,¹⁴ intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones,¹⁵ cyclization of polycyclic aryl triflate esters¹⁶ and cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone¹⁷. Also 14-H-dibenzo[a,j]xanthenes and its analogues are prepared by reaction of 2-naphthol with 2-naphthol-1-methanol, formamide, CO,¹⁸ and aldehydes.¹⁹ Recently, the synthesis of 14-H-dibenzo[a,j]xanthene has been reported by condensation of 2-naphthol and aldehydes in the presence of *p*-toluenesulfonic acid,^{20,21}

SelectfluorTM,²² molecular iodine,²³ sulfamic acid,²⁴ silica sulfuric acid,²⁵ Amberlyst-15,²⁶ and cation-exchange resins,²⁷ as catalyst. Many of these methods suffer from longer reaction times, unsatisfactory yields and harsh reaction conditions. It is therefore important to find more convenient methods for preparation of these compounds. Ultrasonic-assisted organic synthesis (UAOS) is a powerful and green approach which is being used more and more to accelerate synthesis of organic compounds.^{28,29} Increase in reaction rate and yields takes place on application of ultrasound waves.³⁰⁻³⁵ In order to enlarge the application of ultrasound irradiation in synthesis of heterocyclic compounds and in continuation of our work to develop new and eco-friendly synthetic methodologies,³⁶⁻³⁹ here in we report an efficient and eco-friendly procedure for synthesis of aryl-14-H-dibenzo[a,j]xanthene derivatives from the condensation of aryl aldehydes and 2-naphthol using in presence of copper perchlorate hexahydrate as catalyst under ultrasound irradiation.

2. Results and Discussion

The application of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in organic synthesis is gaining renewed interest. Herein, we report an expedient protocol for the synthesis of aryl-14-H-dibenzo[a,j]xanthenes. (**Scheme 1**).



Scheme 1

The reactions were carried out at room temperature for 2-3 hr by using 1 : 2 mol ratio of aldehyde and 2-naphthol respectively in presence of 20 mol% of copper perchlorate hexahydrate at 35 kHz under ultrasound irradiation. To determine the amount of catalyst in this reaction, 4-chlorobenzaldehyde was first reacted with 2-naphthol for 2 hrs under ultrasound irradiation in presence of 0, 5, 10, 15, 20, 40 mol% of copper perchlorate separately. The best results were obtained using 20 mol% of catalyst. Using lesser amount of catalyst resulted in lower yields, while higher amount of catalyst did not affected reaction times and yields. In absence of catalyst yield was found to be very low (**Table 1**).

Table 1: Effect of amounts of catalyst copper perchlorate hexahydrate with or without sonication for synthesis of 14-(4-Chloro-phenyl)-14H-dibenzo[a,j]xanthene.

Entry	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ mol%	With Sonication		Without Sonication	
		Yield (%)	Time(min.)	Yield (%)	Time(min.)
1.	0	Nil	360	Nil	360
2.	5	38	160	10	360
3.	10	55	145	25	360
4.	15	70	130	35	300
5.	20	90	120	40	300
6.	40	90	120	40	300

To verify the effect of ultrasound irradiation on this procedure the synthesis of aryl-14-H-dibenzo[a,j]xanthenes was done in presence of 0, 5, 10, 15, 20, 40 mol% of copper perchlorate hexahydrate with and without ultrasound irradiation (**Table 1**). In all reactions it was found that use of ultrasound radiations lead to faster reaction and higher yields. So it shows use of ultrasound radiations improves the rate of reaction and also yields of products formed. A wide range of Substituted aldehydes were used to give excellent yield of products (1a-h). The formation of products was confirmed by comparing the melting points, elemental analysis IR and NMR data with authentic samples and literature data.

3. Experimental

Liquid carbonyl compounds were purified by distillation before use. All melting points recorded are uncorrected, open capillary measurements, using sulphuric acid bath. IR spectra were recorded using KBr pellets on a Perkin-Elmer spectrophotometer, NMR spectra on AL-300F (Bruker) FT NMR spectrophotometer using tetramethylsilane (TMS) as internal standard. All solvents were reagent grade and used as received. The reactions were performed in open vessels.

General procedure for the preparation of aryl-14-H-dibenzo[a,j]xanthenes (1a-1h).

To a mixture of aryl aldehyde (1mmol) and 2-naphthol (2 mmol) was added $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (20 mol%) and the reaction mixture was exposed to ultrasound irradiation 2-3 hr (completion of the reactions was monitored by TLC). After the completion of reaction, the reaction mixture was diluted with ethyl alcohol and stirred for 10 minutes at 80°C . The residue was filtered hot and kept at room temperature and the resulting crystalline product (**Table 2**) was collected by filtration. The product formed was recrystallized from ethanol. The formation of products was confirmed by comparing the melting points, elemental analysis IR and NMR data with authentic samples and literature data.

Table 2: Copper perchlorate hexahydrate catalyzed synthesis of 14-H-dibenzo[a,j]xanthenes under ultrasound irradiation.

Entry	Products	Ar	Time(min.)	Yield (%)	M.Pt. $^\circ\text{C}$
1.	1a	Ph	120	90	183-184
2.	1b	4-OMePh	135	91	204-205
3.	1c	4-ClPh	120	88	289-290
4.	1d	4-NO ₂ Ph	125	91	312-313
5.	1e	3-NO ₂ Ph	180	84	209-210
6.	1f	4-FPh	135	87	238-240
7.	1g	4-OHPh	155	81	137-138
8.	1h	2-NO ₂ Ph	140	92	292-293

Spectral Data of Products

14-Phenyl-14H-dibenzo[a,j]xanthene (1a)

White solid, mp $183-184^\circ\text{C}$. IR (KBr) ν_{max} [cm^{-1}]: 3021, 1623, 1592, 1402, 1250, 805. ^1H NMR (400 MHz, CDCl_3) δ : 6.55 (s, 1H), 7.03 (t, 1H, $J = 7.6$ Hz), 7.17 (t, 2H, $J = 7.6$ Hz), 7.42 (t, 2H, $J = 6.9$ Hz), 7.52 (d, 2H, $J = 9.2$ Hz), 7.58 (m, 4H), 7.79 (d, 2H, $J = 9.15$ Hz), 7.83 (d, 2H, $J = 7.65$ Hz), 8.42 (d, 2H, $J = 9.15$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ : 38.2, 117.4, 118.2, 122.8, 124.4,

126.53, 126.9, 128.4, 128.6, 128.9, 129.0, 131.2, 131.6, 145.2, 148.8. MS m/z: 358 [M⁺]. Anal. Calcd for C₂₇H₁₈O C, 90.47; H, 5.06; O, 4.46; Found C, 90.45; H, 5.07; O, 4.47

14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthene (1b)

Yellow solid, mp 204-205^oC. IR (KBr) ν_{\max} [cm⁻¹]: 2922, 1592, 1510, 1030, 810. ¹H NMR (400 MHz, CDCl₃) δ : 3.60 (s, 3H), 6.44 (s, 1H), 6.66 (d, 2H, J = 8.4 Hz), 7.39 (m, 4H), 7.47 (d, 2H, J = 8.4 Hz), 7.56 (t, 2H, J = 8.4 Hz), 7.77(d, 2H, J = 9.15 Hz), 7.81 (d, 2H, J = 8.4 Hz), 8.37 (d, 2H, J = 8.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 37.18, 55.1, 113.9, 117.6, 118.1, 122.8, 124.3, 126.9, 128.8, 128.9, 129.2, 131.1, 131.5, 137.5, 148.7, 157.9. MS m/z: 389.8 (M + 1). Anal. Calcd for C₂₈H₂₀O₂ C, 86.57; H, 5.19; O, 8.24; Found C, 86.59; H, 5.18; O, 8.23

14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene (1c)

White solid, mp 289-290^oC. IR (KBr) ν_{\max} [cm⁻¹]: 2925, 1590, 1484, 1242, 1083, 807. ¹H NMR (400 MHz, CDCl₃) δ : 6.71 (s, 1H), 7.16 (d, 2H, J = 7.6 Hz), 7.4 (t, 4H, J = 7.6 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.60 (m, 4H), 7.89 (d, 4H, J = 7.6 Hz), 8.62 (d, 2H, J = 7.6 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 39.9, 117.5, 118.2, 123.8, 125.1, 127.6, 128.9, 129.2, 129.8, 130.2, 131.2, 131.3, 131.4, 145.0, 148.5. MS m/z: 393 (M + 1). Anal. Calcd for C₂₇H₁₇ClO C, 82.54; H, 4.36; Cl, 9.02; O, 4.07 Found C, 82.51; H, 4.37; Cl, 9.03; O, 4.08.

14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthene (1d)

Pink-brown solid, mp 312-313^oC. IR (KBr) ν_{\max} [cm⁻¹]: 2930, 1594, 1517, 1343, 1241, 828. ¹H NMR (400 MHz, CDCl₃) δ : 6.93 (s, 1H), 7.50 (m, 2H), 7.67 (m, 4H), 8.03 (m, 8H), 8.71 (d, 2H, J = 8.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 36.4, 116.2, 117.7, 123.1, 123.6, 124.7, 127.2, 128.7, 129.6, 130.7, 130.8, 145.9, 148.1, 152.6. MS m/z: 403 [M⁺]. Anal. Calcd for C₂₇H₁₇NO₃ C, 80.38; H, 4.25; N, 3.47; O, 11.90; Found C, 80.35; H, 4.26; N, 3.48; O, 11.91

14-(3-Nitrophenyl)-14H-dibenzo[a,j]xanthene (1e)

Yellow solid, mp 209-210^oC. IR (KBr) ν_{\max} [cm⁻¹]: 3077, 1592, 1527, 1347, 1250, 810. ¹H NMR (400 MHz, CDCl₃) δ : 6.55 (s, 1H), 7.23 (t, 1H, J = 7.65 Hz), 7.41 (t, 2H, J = 6.9 Hz), 7.49 (d, 2H, J = 8.4 Hz), 7.59 (t, 2H, J = 7.6 Hz), 7.79 (m, 6H), 8.27 (d, 2H, J = 8.4 Hz), 8.41 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 37.8, 115.9, 118.2, 121.8, 122.1, 122.8, 124.7, 127.3, 129.2, 129.6, 129.7, 131.1, 134.4, 147.0, 148.3, 148.8. MS m/z: 403 [M⁺]. Anal. Calcd for C₂₇H₁₇NO₃ C, 80.38; H, 4.25; N, 3.47; O, 11.90; Found C, 80.35; H, 4.26; N, 3.48; O, 11.91

14-(4-Fluorophenyl)-14H-dibenzo[a,j]xanthene (1f)

Brown solid, mp 238-240^oC. IR (KBr) ν_{\max} [cm⁻¹]: 3068, 1623, 1592, 1242, 959, 744. ¹H NMR (400 MHz, CDCl₃) δ : 6.47 (s, 1H), 6.80 (t, 2H, J = 9.15 Hz), 7.40 (t, 2H, J = 7.65 Hz), 7.45 (m, 4H), 7.57 (t, 2H, J = 7.65 Hz), 7.78 (d, 2H, J = 9.15 Hz), 7.82 (d, 2H, J = 7.6 Hz), 8.32 (d, 2H, J = 8.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 37.3, 115.3, 115.5, 117.2, 118.1, 122.6, 124.4, 126.9, 128.9, 129.1, 129.7, 129.7, 131.1, 131.4, 140.9, 148.0 160.2, 162.08. MS m/z: 377.1 (M + 1). Anal. Calcd for C₂₇H₁₇FO C, 86.15; H, 4.55; F, 5.05; O, 4.25 Found C, 86.19; H, 4.53; F, 5.04; O, 4.24.

14-(4-Hydroxyphenyl)-14H-dibenzo[a,j]xanthene (1g)

Pink solid, mp.137-138^oC. IR (KBr) ν_{\max} [cm⁻¹]: 3404,1592, 1511, 1401, 1250, 1242, 816; ¹H NMR (400 MHz, CDCl₃) δ : 4.97 (br s, 1H, OH), 6.42(s, 1H, CH), 6.56-8.36 (m, 16H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3) δ : 37.5, 115.7, 117.9, 118.4, 123.1, 124.6, 127.2, 129.1, 129.2, 129.8, 131.5, 131.8, 137.9, 149.1, 154.2, MS m/z : 374 [M^+]. Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{O}_2$: C, 86.61; H, 4.85; O, 8.55; Found: C, 86.63; H, 4.84; O, 8.54.

14-(2-Nitrophenyl)-14H-dibenzo[a,j]xanthene (1h)

Yellow solid, mp 292-293 $^{\circ}\text{C}$. IR (KBr) ν_{max} [cm^{-1}]: 2921, 1581, 1350, 1241, 809. ^1H NMR (400 MHz, CDCl_3) δ : 7.02 (t, 1H, $J = 7.6$ Hz), 7.18 (t, 1H, $J = 7.65$ Hz), 7.41 (t, 2H, $J = 6.85$ Hz), 7.47 (t, 3H, $J = 8.4$ Hz), 7.54 (s, 1H), 7.58 (t, 2H, $J = 7.6$ Hz), 7.78 (t, 5H, $J = 7.65$ Hz), 8.51 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ : 32.6, 117.6, 118.1, 122.7, 124.8, 125.0, 127.4, 127.7, 128.8, 129.5, 131.0, 131.8, 132.3, 134.2, 140.9, 147.1, 149.5. MS m/z : 404.69 ($\text{M} + 1$). Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{NO}_3$ C, 80.38; H, 4.25; N, 3.47; O, 11.90; Found C, 80.35; H, 4.26; N, 3.48; O, 11.91

Conclusion

An efficient one pot, green protocol for synthesis of aryl-14-H-dibenzo[a,j]xanthenes have been developed by reaction of substituted aldehydes and 2-naphthol under ultrasound irradiation in excellent yields using copper perchlorate hexahydrate as catalyst. The present methodology gives several advantages such as simple procedure, easy work up and milder conditions.

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