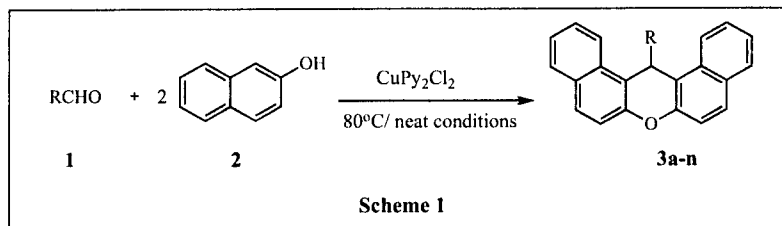


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Convenient and facile synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes is described through a one pot condensation of β -naphthol and aryl aldehydes in the presence of dipyridine copper chloride as the Lewis acid catalyst under solvent free conditions.

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INTRODUCTION

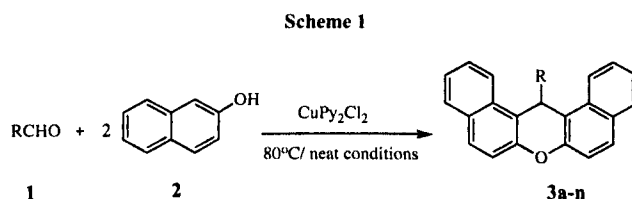
Xanthenes and benzoxanthenes are important classes of compounds, especially benzoxanthenes, has received significant importance in recent years because of their wide range of biological and therapeutic properties such as antibacterial [1], antiviral [2] and anti-inflammatory [3], moreover in photodynamic therapy [4] and antagonists for the paralyzing action of zoxazolamine [5]. These are also available from natural sources, as Santalin pigments [6]. Furthermore, these compounds can be employed as dyes [7], pH-sensitive fluorescent materials for visualization of biomolecules [8] and used in laser technologies [9]. For the synthesis of xanthenes and benzoxanthenes many procedures available including the cycloacylation of carbamates [10], trapping of benzynes by phenol [11], cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone [12], cyclodehydrations [13] and intramolecular phenyl carbonyl reaction of aldehydes with β -naphthol by dehydration [14]. In addition, synthesis of benzoxanthenes and their related products synthesized by the reaction of β -naphthol with formamide [15], carbon monoxide [16] and 2-naphthol-1-methanol [17]. Several reagents have been used for the synthesis of benzoxanthenes such as sulfamic acid [18], selectfluorTM [19], iodine [20] and Amberlyst-15 [21].

However, many of these methods have some drawbacks such as low yields, long reaction times, drastic reaction conditions, and use of toxic organic solvents and co-occurrence of several side reactions, requirement of harmful acids, excess of reagents/catalysts, tedious work-up procedures. In some cases more than one step is

involved in the synthesis of these compounds, moreover, some of the existing methods is that the catalysts are destroyed in the work-up procedure and cannot be recovered or re-used. In recent years, dipyridine copper chloride [22] has received great attention as a mild Lewis acid catalyst for some of the important organic transformations, like Pechmann [23], and Biginelli condensations [24]. The catalyst is a low cost and stable in water, reusable.

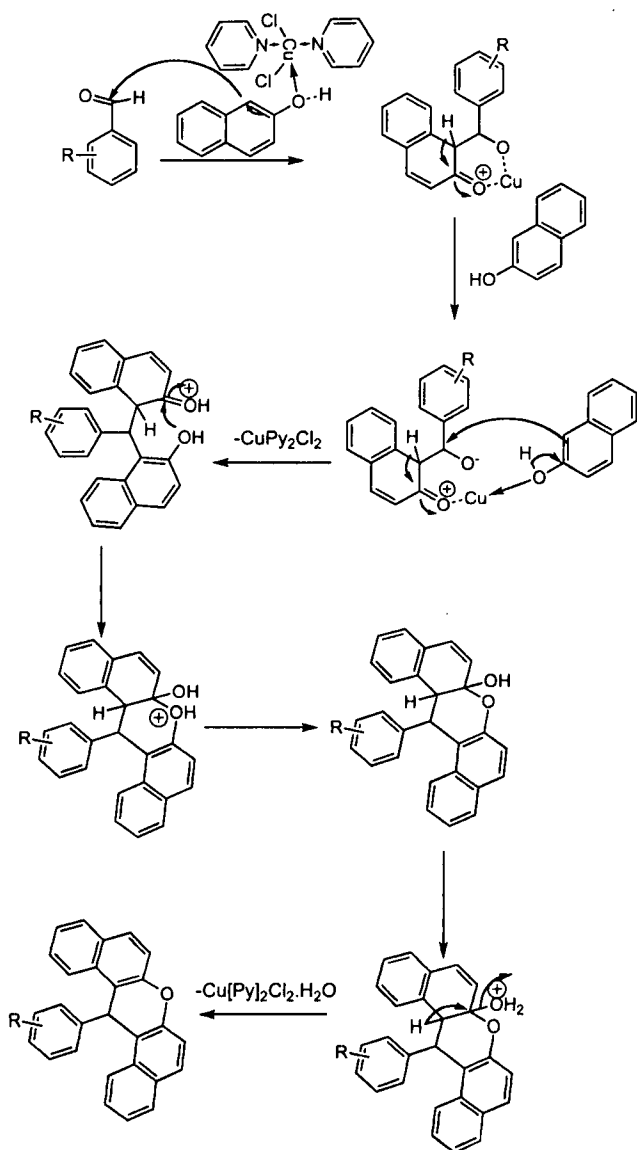
RESULTS AND DISCUSSION

The search continues for a better catalyst for the synthesis of xanthenes in terms of operational simplicity, economic viability and greater selectivity. Hence we wish to explore efficient, convenient and facile method for the condensation of aldehydes with β -naphthol to the corresponding benzoxanthenes in the presence of dipyridine copper chloride under solvent free conditions (Scheme-1)



All the reactions were carried out neat at 80°C, for appropriate time by taking a 1:2 mol ratio mixture of β -naphthol and the aldehydes in the presence of catalytic amount of CuPy_2Cl_2 to give desired products in excellent yield (Table 1). We also observed that without using the catalyst dehydration is very difficult.

Scheme 2



Proposed Mechanism

EXPERIMENTAL

All the melting points are uncorrected. The progress of the reaction was monitored by (TLC). IR spectra (KBr) were recorded on Shimadzu FTIR model 8010 spectrometer and the ^1H NMR spectra on Varian Gemini 200 MHz spectrometer using TMS as internal standard. The C, H, and N analysis of the compound was done on a Carlo Erba model EA1108. Mass spectra were recorded on a JEOL JMS D-300 Spectrometer.

General procedure for the reaction of aldehydes with β -naphthol. A mixture of the aldehydes (1 mmol) and β -naphthol (2 mmol), CuPy_2Cl_2 (catalytic amount) was stirred magnetically at 80°C for the appropriate time

Table 1. Dipyridine copper chloride catalysed synthesis of aryl-14H-dibenzo[a,j]xanthenes

Entry	R	Product	Time(h)	Yield(%) ^a	Mp($^\circ\text{C}$)
1	C_6H_5	3a	2	96	183 ^{13b}
2	$4\text{-CH}_3\text{-C}_6\text{H}_4$	3b	3	96	228 ^{13c}
3	$4\text{-Cl-C}_6\text{H}_4$	3c	2.5	95	287 ^{13c}
4	$2\text{-Cl-C}_6\text{H}_4$	3d	3	92	215 ^{13c}
5	$4\text{-Br-C}_6\text{H}_4$	3e	3	96	296 ^{13b}
6	$3\text{-Br-C}_6\text{H}_4$	3f	2	93	190 ^{13c}
7	$4\text{-NO}_2\text{-C}_6\text{H}_4$	3g	2.5	96	312 ^{13b}
8	$2\text{-NO}_2\text{-C}_6\text{H}_4$	3h	3	95	293 ¹⁸
9	$4\text{-OH-C}_6\text{H}_4$	3i	2	92	140 ¹⁹
10	$4\text{-CH}_3\text{O-C}_6\text{H}_4$	3j	2	94	205 ^{13c}
11	$2\text{-CH}_3\text{O-C}_6\text{H}_4$	3k	3	95	258 ^{13c}
12	$4\text{-F-C}_6\text{H}_4$	3l	2	94	238 ^{13c}
13	$3\text{-F-C}_6\text{H}_4$	3m	2.5	95	258-259 ¹⁸
14	$3\text{-NO}_2\text{-C}_6\text{H}_4$	3n	3	94	213 ^{13c}

^aYields refer to isolated pure products and were characterized by NMR, IR and mass spectral data with those of authentic samples

according to Table. Completion of the reaction was indicated by thin layer chromatography. The reaction mixture was cooled to room temperature, washed with water (10 ml) and *n*-hexane (2 ml), precipitate was separated; the crude product was purified by recrystallisation from ethyl alcohol. After washing with water, the water containing the catalyst could be evaporated under reduced pressure to give a blue solid. The recovered catalyst was dried at 85°C for 2 h under high-pressure prior to use in the other reaction.

Product Characterization Data.

14-(4-Chloro-phenyl)-14H-dibenzo[a,j]xanthene. (Table 1, entry 3): Brown solid: mp 287°C . IR (KBr, cm^{-1}): 3133, 1618, 1590, 1450, 1225, 1105, 820, 776; ^1H NMR (CDCl_3): δ = 6.50 (s, 1H), 7.07-8.31 (m, 16H); ^{13}C NMR (75MHz, CDCl_3): δ = 32.5, 115.0, 118.2, 118.6, 124.2, 124.6, 127.7, 130.5, 131.8, 132.6, 132.8, 133.9, 134.1, 136.5, 137.9, 139.8, 141.9, 145.4, 147.8; EIMS, 70Ev, m/z : 392 (M^+), 281, 268; Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{ClO}$: C, 82.54; H, 4.36; Found: C, 82.52; H, 4.33.

14-(2-Nitrophenyl)-14H-dibenzo[a,j]xanthene. (Table 1, entry 8). Yellow solid: mp 293°C . IR (KBr, cm^{-1}): 3400, 3056, 1593, 1522, 1351, 1240, 1142, 807, 746; ^1H NMR (CDCl_3): δ =7.52 (s, 1H), 7.10-8.54 (m, 16H); ^{13}C NMR (75MHz, CDCl_3): δ =32.7, 118.0, 118.3, 123.2, 124.5, 125.1, 125.3, 127.7, 128.0, 129.3, 129.6, 129.9, 130.6, 132.2, 132.6, 134.4, 141.2, 147.5, 149.8; EIMS, 70Ev, m/z : 403 (M^+), 281, 268; Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{NO}_3$: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.25; H, 4.23; N, 3.57.

14-(4-Hydroxyphenyl)-14H-dibenzo[a,j]xanthene. (Table 1, entry 9): Pink solid: mp 140°C . IR (KBr, cm^{-1}): 3400, 1581, 1511, 1405, 1250, 1241, 814; ^1H NMR (CDCl_3): δ = 4.95 (br s, 1H, OH), 6.42 (s, 1H CH), (m, 16H, Ar-H). ^{13}C NMR (75MHz, CDCl_3): δ = 37.5, 115.8, 117.6, 118.4, 123.3, 124.6, 127.6, 129.2, 129.3, 129.9, 131.4, 131.9, 137.9, 149.2, 154.2; EIMS, 70Ev, m/z : 374 (M^+), 281, 268; Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{O}_2$: C, 86.61; H, 4.85. Found: C, 86.62; H, 4.81.

14-(3-Fluorophenyl)-14H-dibenzo[a,j]xanthene. (Table 1, entry 13): Brown solid: mp $258\text{-}259^\circ\text{C}$. IR (KBr, cm^{-1}): 3153, 1594, 1403, 1240, 1206, 1067, 817, 745; ^1H NMR (CDCl_3): δ =

6.51(s, 1H), 6.72-8.35 (m, 16H). ^{13}C NMR (75MHz, CDCl_3): δ = 38.2, 113.8 and 90, 114.0 ($J_{\text{C-F}}$ 21.5 Hz), 115.4 and 115.8 ($J_{\text{C-F}}$ 21.5 Hz), 117.2, 118.2, 122.7, 124.31, and 124.32 ($J_{\text{C-F}}$ 2.8 Hz) 124.7, 127.3, 129.3, 129.5, 130.1 and 130.2 ($J_{\text{C-F}}$ 8.3Hz), 131.4, 131.7 ($J_{\text{C-F}}$ 19.4 Hz), 147.8, 147.9 ($J_{\text{C-F}}$ 6.2 Hz), 149.2, 161.7, 165.1; EIMS, 70Ev, m/z : 376 (M^+), 281, 268; Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{FO}$: C, 86.15; H, 4.55; F, 5.05. Found: C, 86.12; H, 4.53; F, 5.06.

CONCLUSION

In conclusion, we have described a simple and efficient method for the synthesis of benzoxanthenes. The easy work-up procedure, non-toxic cost efficiency providing recyclability of the catalyst, excellent yields make this method a valid contribution to the existing methodologies.

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