Dipyridine cobalt chloride: a novel and efficient catalyst for the synthesis of 14-aryl 14*H*-dibenzo[*a.j*]xanthenes under solvent-free conditions

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Abstract

A convenient procedure for the synthesis of 14-aryl 14*H*-dibenzo[*a.j*]xanthenes is reported using the condensation of β-naphthol with aryl and chromone aldehydes in the presence of dipyridine cobalt chloride as the catalyst under solvent-free conditions.

Keywords: Xanthene, aldehydes, β-naphthol, $CoPy_2Cl_2$, solvent-free conditions

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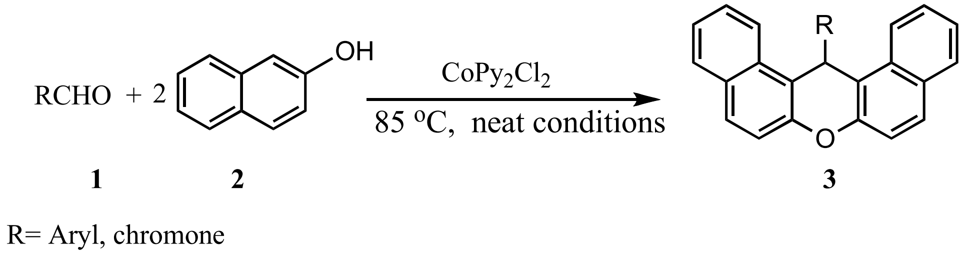
Introduction

The preparation of benzoxanthenes is important due to their broad spectrum of biological and therapeutic properties such as antiviral,[1] antibacterial,[2] and antiinflammatory[3] activities and efficiency in photodynamic therapy,[4] and in antagonism of the paralyzing action of zoxazolamine.[5] Further, these compounds can be employed as dyes,[6] pH- sensitive fluorescent materials for visualization of biomolecules[7] and in laser technologies.[8] For the construction of xanthenes and benzoxanthenes, various procedures are available including the cycloacylation of carbamates,[9] trapping of benzynes by phenol,[10] cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone,[11] cyclodehydrations [12] and intramolecular phenyl carbonyl reaction of aldehydes with β-naphthol by dehydration.[13] Other routes for the synthesis of benzoxanthenes and related products include the reaction of β-naphthol with formamide,[14] carbon monoxide[15] and 2-hydoxynaphth-1-ylmethanol.[16] Various reagents have been employed for the synthesis of benzoxanthenes such as $Al(HSO_4)_3$,[17] sulfamic acid,[18] Selectfluor^{TM},[19] molecular iodine,[20] Amberlyst-15,[21] hydrochloric acid or phosphoric acid,[22] H_2SO_4 in acetic acid as solvent,[23] and *p*-TSA,[24] silica sulfuric acid[25] and cation-exchange resins[26] as catalysts. However, many of these methods suffer from some limitations, such as low yields, prolonged reaction time, tedious work-up procedures and co-occurrence of side reactions. Some of the catalysts are destroyed in the work-up procedure and cannot be recovered or reused. Therefore, the search continues for a better catalyst for the synthesis of benzoxanthenes in terms of operational simplicity, reusability of catalyst, low cost and greater selectivity.

Results and Discussion

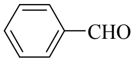
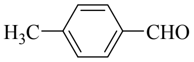
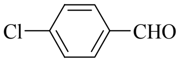
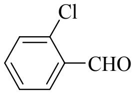
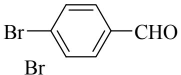
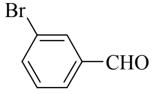
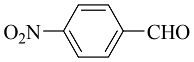
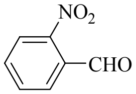
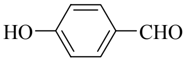
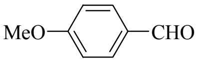
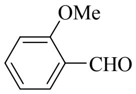
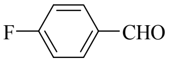
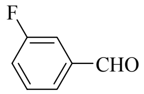
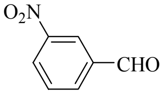
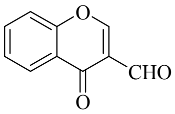
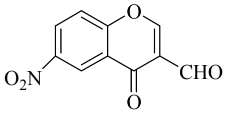
In continuation of our search for new catalysts,[27] we report in this paper the synthesis of benzoxanthenes *via* the condensation of aldehydes with β-naphthol promoted by dipyridine cobalt chloride under solvent-free conditions (Scheme 1). The catalyst is solid (violet color crystals), soluble in water, stable in air, and immiscible in common organic solvents; it is reusable and has high thermal stability. In addition, its toxicity is low.



Scheme 1

The reaction was carried out at 85 °C temperature for various times (Table 1) using a 2:1 mol ratio mixture of β-naphthol and the aldehyde in the presence of $CoPy_2Cl_2$ (0.1 mmol) to give the products in excellent yields.

Table 1. Dipyridine cobalt chloride catalysed synthesis of 14-aryl 14*H*dibenzo[a,j]xantenes **3**

Entry	Aldehyde	Time(h)	Yield(%)[a]	Mp(^{o}C)
1		2	97	183[12b]
2		2.5	93	228[12b]
3		2	95	287[12c]
4		3	92	215[12c]
5		2	96	296[12b]
6		2.5	93	190[12c]
7		2.5	96	312[12b]
8		3	92	293[18]
9		1.5	92	140[19]
10		2	94	205[12c]
11		3	93	258[12c]
12		2	94	238[12c]
13		2.5	95	258-259[18]
14		3	94	213[12c]
15		6	72	195
16		8	65	125

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[a] Yields refer to isolate pure products and which were characterized by NMR, IR and mass spectral data and by comparison with those of authentic samples.

Experimental Section

General Procedures. All the melting points were uncorrected. The progress of the reaction was monitored by (TLC). IR spectra (KBr) were recorded on Shimadzu FTIR model 8010 spectrometer and the ^{1}H NMR spectra on Varian Gemini 200 MHz spectrometer using TMS as the 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.

Typical procedure

A mixture of the aldehyde (1 mmol) and β-naphthol (2 mmol) was well stirred with CoPy$_2$Cl$_2$ (0.1 mmol) at 85 ^{o}C for the appropriate time according to Table. After completion of the reaction, the reaction contents were cooled to room temperature, water (3 ml) was added and the mixture stirred for 2 min. The solid obtained was separated by filtration and recrystallized from ethanol. After filtration, the filtrate (water) containing the catalyst could be evaporated under reduced pressure to give a violet solid. The recovered catalyst was washed with ether, dried at 85 ^{o}C for 2 h under high-pressure prior to use in the other reaction.

Selected product data

14-(4-Chlorophenyl)-14*H*-dibenzo[*a,j*]xanthene (Table 1, entry 3). Brown solid: mp 287 ^{o}C. IR (KBr, cm^{-1}): 3133, 1618, 1590, 1450, 1225, 1105, 820, 776; ^{1}H NMR (CDCl$_3$): δ 6.50 (s, 1H), 7.07-8.31 (m, 16H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 36.7, 117.8, 118.5, 124.2, 125.5, 127.9, 129.2, 129.5, 130.1, 130.5, 131.5, 131.6, 131.8, 145.3, 148.8; EIMS, 70 Ev, *m/z*: 392 (M^{+}), 281, 268; Anal. Calcd for C$_{27}$H$_{17}$ClO: C, 82.54; H, 4.36%; Found: C, 82.52; H, 4.33%.

14-(2-Nitrophenyl)-14*H*-dibenzo[*a,j*]xanthene (Table 1, entry 8). Yellow solid: mp 293 ^{o}C. IR (KBr, cm^{-1}): 3400, 3056, 1593, 1522, 1351, 1240, 1142, 807, 746; ^{1}H NMR (CDCl$_3$): δ 7.52 (s, 1H), 7.10-8.54 (m, 16H); ^{13}C NMR (75 MHz, 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 C$_{27}$H$_{17}$NO$_3$: C, 80.38; H, 4.25; N, 3.47%; Found: C, 80.25; H, 4.23; N, 3.57%.

14-(4-Hydroxyphenyl)-14*H*-dibenzo[*a,j*]xanthene (Table 1, entry 9). Pink solid: mp 140 ^{o}C. IR (KBr, cm^{-1}): 3400, 1581, 1511, 1405, 1250, 1241, 814; ^{1}H NMR (CDCl$_3$): δ 4.95 (br s, 1H, OH), 6.42 (s, 1H CH), 6.58-8.39 (m, 16H); ^{13}C NMR (75 MHz, 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, 70 Ev, *m/z*: 374 (M^{+}), 281, 268; Anal. Calcd for C$_{27}$H$_{18}$O$_2$: C, 86.61; H, 4.85% Found: C, 86.62; H, 4.81%.

14-(3-Fluorophenyl)-14*H*-dibenzo[*a,j*]xanthene (Table 1, entry 13). Brown solid: mp 258-259 ^{o}C. IR (KBr, cm^{-1}): 3153, 1594, 1403, 1240, 1206, 1067, 817, 745; ^{1}H NMR (CDCl$_3$): δ 6.51(s, 1H), 6.72-8.35 (m, 16H); ^{13}C NMR (75 MHz, 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, 130.1and130.2 ($J_{\text{C-F}}$ 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, 70 Ev, *m/z*: 376 (M^+), 281, 268; Anal. Calcd for $C_{27}H_{17}FO$: C, 86.15; H, 4.55; F, 5.05%; Found: C, 86.12; H, 4.53; F, 5.06%.

3-(14*H*-Dibenzo[a,j]xanthen-14-yl)chromen-4-one: (Table 1, entry 15). Light yellow solid: mp 195 °C. IR (KBr, cm^{-1}): 3075, 1617, 1594, 1407, 1235, 1208, 1060, 819, 740; ^1H NMR ($CDCl_3$): δ 6.10(s, 1H chromone 2-H), 6.42 (s, 1H), 7.24-7.96 (m, 16 H); EIMS, 70 Ev, *m/z*: 426 (M^+); Anal. Calcd for $C_{30}H_{18}O_3$: C, 84.49; H, 4.25%; Found: C, 84.42; H, 4.29%.

3-(14*H*-Dibenzo[a,j]xanthen-14-yl)-6-nitrochromen-4-one: (Table 1, entry 16). Brown solid: mp 125 °C. IR (KBr, cm^{-1}): 3151, 1635, 1590, 1403, 1240, 1206, 1067, 817, 745; ^1H NMR ($CDCl_3$): δ 6.15(s, 1H chromone 2-H), 6.51 (s, 1H), 7.31-8.10 (m, 15 H); EIMS, 70 Ev, *m/z*: 471 (M^+); Anal. Calcd for $C_{30}H_{17}NO_5$: C, 76.43; H, 3.63; N, 2.97%; Found: C, 76.47; H, 3.61; N, 2.94%.

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