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One-pot synthesis of aryl 14*H*-dibenzo[*a*,*j*]xanthene leuco-dye derivatives

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Abstract

A novel, efficient, one-pot, and solvent-free method for the preparation of aryl 14*H*-dibenzo[*a*,*j*]xanthene leuco-dye derivatives by condensation of 2-naphthol and substituted benzaldehydes is reported under thermal conditions. This method has the advantages of high yields, a cleaner reaction, simple methodology, convenient reaction times, easy workup and greener conditions.

Keywords: Solvent-free; β-Naphthol; Aldehyde; Dibenzoxanthene; Leuco-dye; Thermal condition

1. Introduction

14*H*-Dibenzo[*a*,*j*]xanthene derivatives are important intermediates as they display biological and therapeutic properties such as antibacterial [1] and antiviral activities [2] as well as offering potential use in photodynamic therapy (PDT) [3,4]. In PDT, photosensitizers are injected directly into malignant tissue and then light, of a specific wavelength, is used to excite the photosensitizer drug, which destroys the tumor cells [3,4]. Furthermore, benzoxanthenes are used as leuco-dyes [5], in laser technology [6] and in fluorescent materials [7].

The synthesis of 14*H*-dibenzo[*a*,*j*]xanthene is generally achieved by either:

- the dehydration of bis(2-hydroxy-1-naphthyl) methane using $POCl_3$ [8] or by boiling the acetic acid diester of bis(2-hydroxy-1-naphthyl) methane [9];
- the condensation of β-naphthol with aliphatic and aromatic aldehydes in the presence of hydrochloric acid or phosphoric acid [10] and also sulfuric acid [11] in acetic acid as solvent.

Each of these methods involves the use of harsh reaction conditions, long reaction times and tedious experimental procedures which afford the product in unsatisfactory yields. Recently, the synthesis of 14*H*-dibenzo[*a*,*j*]xanthene has been reported by the condensation of β-naphthol and aldehydes in the presence of *p*-toluenesulfonic acid [12,13], sulfamic acid [14], Amberlyst-15 [15], potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) [16] and molecular iodine [17] as catalyst. This paper concerns a one-pot synthesis of aryl 14*H*-dibenzo[*a*,*j*]xanthene derivatives by the reaction of various aromatic aldehydes with β-naphthol in solvent-free condition in the presence of Brønsted acid supported on silica gel (silica sulfuric acid [18]).

2. Experimental

All reagents were purchased from Merck and Aldrich and were used without further purification. Silica sulfuric acid was prepared according to the reported procedure [18]. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, ^1H NMR spectra) and melting point. The NMR spectra were recorded on a Bruker Avance DEX 500 MHz instrument. The spectra were measured in $CDCl_3$ relative to TMS (0.00 ppm). IR spectra were recorded on a Perkin–Elmer 781 spectrophotometer. All of the compounds were solid and solid state IR spectra were recorded using the KBr disk technique. Melting points were determined

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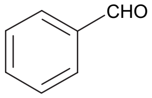
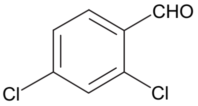
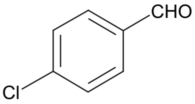
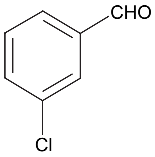
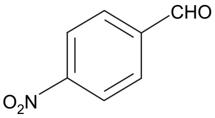
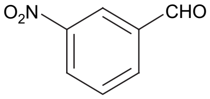
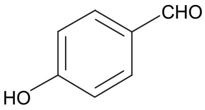
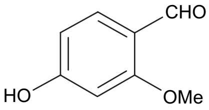
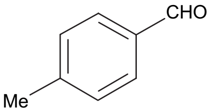
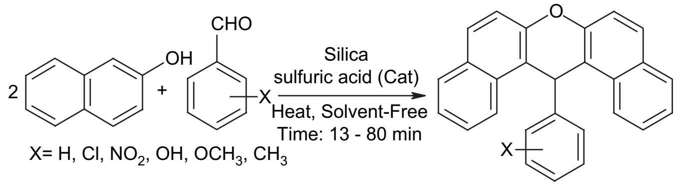
Table 1
Synthesis of aryl 14*H*-dibenzo[*a*,*j*]xanthene derivatives in presence of silica sulfuric acid [18] (0.13 mmol, 0.05 g) as catalyst from β-naphthol and aromatic aldehydes under thermal (bath oil 125 °C) and solvent-free conditions

Entry	Aldehydes	Time (min)	Yield[a] (%)	M.p (°C) (lit. m.p)	References to the known product
1		20	90	181 (183)	[11–17]
2		25	88	227	[16]
3		25	87	289 (287)	[11–17]
4		27	85	174	[16]
5		80	87	317 (312)	[11,13,14,16,17]
6		70	85	215 (213)	[13,14,16,17]
7		17	81	140	[17]
8		13	83	167	–
9		19	91	229 (228)	[11–17]

[a] Yields refer to pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples [11–17].



Scheme 1.

in open capillaries with a Buchi 510 melting point apparatus and are uncorrected. TLC was performed on Silica-gel polygram SIL G/UV 254 plates.

2.1. General procedure for the preparation of 14H-dibenzo[a,j]xanthene derivatives using silica sulfuric acid as catalyst

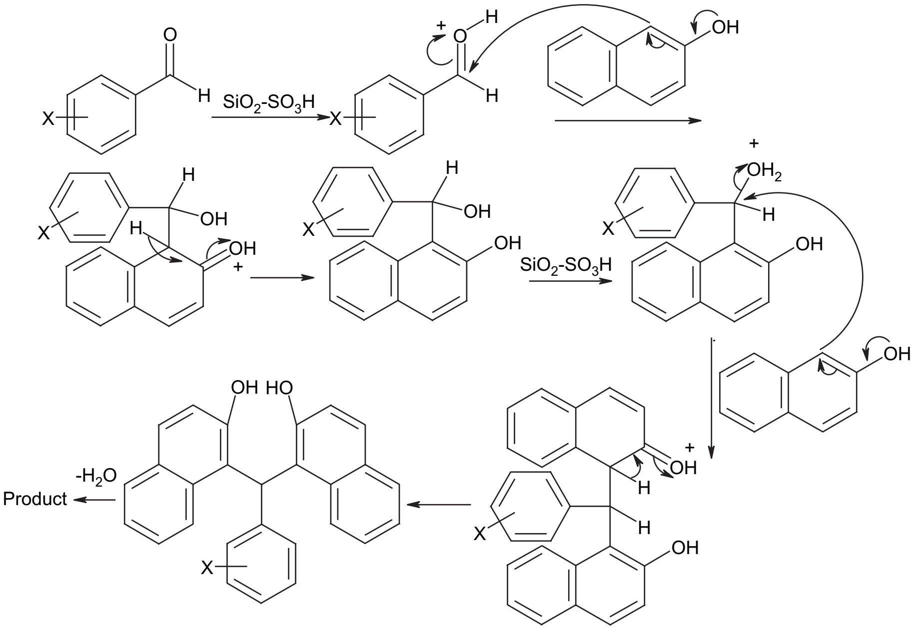
To a mixture of aldehyde (1 mmol) and β-naphthol (2 mmol), silica sulfuric acid [18] (0.13 mmol, 0.05 g) was added and the mixture was heated on an oil bath at 125 °C for the appropriate time (Table 1). Completion of the reaction was indicated by TLC. After completion, the reaction mass was cooled to 25 °C, warm aqueous EtOH (15%) was added and the mixture stirred for 5 min. The solid residue was isolated and dissolved in $CHCl_3$. The silica sulfuric acid was filtered and chloroform was evaporated from the reaction mixture. The solid product was purified by recrystallization in aqueous EtOH (15%). The desired pure product was characterized by comparison of its physical data with that of known benzoxanthenes [11–17]. The spectral data of some representative aryl 14*H*-dibenzo[*a*,*j*]xanthenes are given below.

X = H in Scheme 1, Table 1, Entry 1: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.41$ (2H, d, $J = 8.5$ Hz), 7.83 (2H, d, $J = 7.9$ Hz), 7.79 (2H, d, $J = 8.8$ Hz), 7.59 (2H, t, $J = 7.7$ Hz), 7.54 (2H, d, $J = 7.5$ Hz), 7.50 (2H, d, $J = 8.8$ Hz), 7.42 (2H, t, $J = 7.5$ Hz), 7.16 (2H, t, $J = 7.5$ Hz), 7.00 (1H, t, $J = 7.5$ Hz), 6.50 (1H, s) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 148.8$, 145.0, 131.5, 131.1, 128.8, 128.5, 128.2 126.8, 126.5, 126.4, 124.2, 122.7, 118.0, 117.4, 38.1 ppm; IR (KBr, cm^{-1}): 3074, 3020, 2887, 1620, 1591, 1512, 1489, 1457, 1402, 1253, 1079, 1026, 964, 827, 744, 700.

X = 2,4-dichloro in Scheme 1, Table 1, Entry 2: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.65$ (2H, d, $J = 8.5$ Hz), 7.83 (2H, d, $J = 7.9$ Hz), 7.80 (2H, d, $J = 8.8$ Hz), 7.63 (2H, t, $J = 7.5$ Hz), 7.48 (2H, d, $J = 8.8$ Hz), 7.45 (2H, t, $J = 7.4$ Hz), 7.31 (1H, d, $J = 8.6$ Hz), 7.27 (1H, s), 6.88 (1H, d, $J = 6.8$ Hz), 6.75 (1H, s) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 148.9$, 142.2, 132.8, 132.6, 131.6, 130.9, 130.6, 129.3, 129.1, 128.7, 128.4, 127.0, 124.5, 123.1, 118.0, 117.4, 34.3 ppm; IR (KBr, cm^{-1}): 3057, 2920, 1619, 1592, 1558, 1514, 1458, 1404, 1240, 1208, 1141, 1101, 1041, 960, 863, 836, 808, 742, 699, 607.

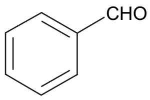
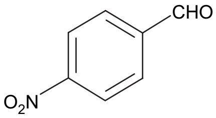
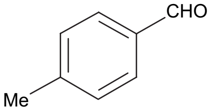
X = 3-chloro in Scheme 1, Table 1, Entry 4: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.33$ (2H, d, $J = 8.4$ Hz), 7.84 (2H, d, $J = 8.6$ Hz), 7.80 (2H, d, $J = 9.0$ Hz), 7.61 (2H, t, $J = 7.0$ Hz), 7.49 (2H, d, $J = 8.9$ Hz), 7.47–7.41 (4H, m), 7.09 (1H, t, $J = 8.0$ Hz), 6.98 (1H, d, $J = 8.7$ Hz), 6.45 (1H, s) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 148.7$, 146.9, 134.4, 131.2, 131.0, 129.6, 129.1, 128.9, 128.3, 126.9, 126.7, 126.4, 124.4, 122.4, 118.0, 116.5, 37.7 ppm; IR (KBr, cm^{-1}): 2922, 1621, 1590, 1509, 1456, 1431, 1397, 1245, 1065, 959, 812, 775, 746, 691.

X = 4-NO_2 in Scheme 1, Table 1, Entry 5: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.29$ (2H, d, $J = 8.4$ Hz), 7.99 (2H, d, $J = 8.7$ Hz), 7.86 (2H, d, $J = 4.1$ Hz), 7.82 (2H, d, $J = 5.4$ Hz), 7.67 (2H, d, $J = 8.8$ Hz), 7.61 (2H, t, $J = 5.6$ Hz), 7.51 (2H, d, $J = 8.9$ Hz), 7.44 (2H, t, $J = 7.9$ Hz), 6.60 (1H, s) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 152.6$, 148.1, 145.9, 135.1, 130.8, 130.7, 129.6, 128.7, 127.2, 124.7, 123.6, 123.1, 117.7, 116.2, 36.4 ppm; IR (KBr, cm^{-1}): 3070, 2930, 1621, 1591, 1614, 1457, 1400, 1340, 1200, 1140, 1105, 1013, 964, 851, 827, 808, 742, 690.



Scheme 2.

Table 2
Comparison result of silica sulfuric acid with toluenesulfonic acid [13], sulfamic acid [14], potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}.3H_2O$) [16] and iodine [17] in the synthesis of aryl 14*H*-dibenzo[*a*,*j*]xanthene derivatives

Entry	Substrate	Catalyst	Substrate/β-naphthol/catalyst[a]	Condition	Yield[b] (%)
1		Iodine [17]	1/2/0.2(0.05 g)	Solvent-free, heat (90 °C), time: 2.5 h	90
		p-Toluenesulfonic acid [13]	A: 1/2/0.1	1,2-Dichloroethane as solvent, reflux, time: 20.0 h	91
			B: 1/2/0.02	Solvent-free, heat (125 °C), time: 4.0 h	89
		Sulfamic acid [14]	1/2/0.1	Solvent-free, heat (125 °C), time: 8.0 h	93
		Potassium dodecatungstocobaltate trihydrate [16]	1/2/0.01(0.064 g)	Solvent-free, heat (125 °C), time: 2.0 h	91
		Silica sulfuric acid	0.5/1.0/0.13(0.05 g)	Solvent-free, heat (125 °C), time: 20.0 min	90
2		Iodine [17]	1/2/0.2(0.05 g)	Solvent-free, heat (90 °C), time: 2.5 h	85
		p-Toluenesulfonic acid [13]	A: 1/2/0.1	1,2-Dichloroethane as solvent, reflux, time: 20.0 h	93
			B: 1/2/0.02	Solvent-free, heat (125 °C), time: 2.5 h	90
		Sulfamic acid [14]	1/2/0.1	Solvent-free, heat (125 °C), time: 11.0 h	94
		Potassium dodecatungstocobaltate trihydrate [16]	1/2/0.01(0.064 g)	Solvent-free, heat (125 °C), time: 1.0 h	97
		Silica sulfuric acid	0.5/1.0/0.13(0.05 g)	Solvent-free, heat (125 °C), time: 80.0 min	87
3		Iodine [17]	1/2/0.2(0.05 g)	Solvent-free, heat (90 °C), time: 3.0 h	88
		p-Toluenesulfonic acid [13]	A: 1/2/0.1	1,2-Dichloroethane as solvent, reflux, time: 18.0 h	90
			B: 1/2/0.02	Solvent-free, heat (125 °C), time: 3.0 h	92
		Sulfamic acid [14]	1/2/0.1	Solvent-free, heat (125 °C), time: 11.0 h	92
		Potassium dodecatungstocobaltate trihydrate [16]	1/2/0.01(0.064 g)	Solvent-free, heat (125 °C), time: 2.0 h	96
		Silica sulfuric acid	1/2/0.2(0.05 g)	Solvent-free, heat (125 °C), time: 19.0 min	91

[a] Molar ratio.

[b] Yields refer to pure isolated products.

X = 4-hydroxy in Scheme 1, Table 1, Entry 7: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.37$ (2H, d, $J = 8.4$ Hz), 7.83 (2H, d, $J = 8.1$ Hz), 7.79 (2H, d, $J = 5.1$ Hz), 7.58 (2H, t, $J = 7.4$ Hz), 7.48 (2H, d, $J = 8.85$ Hz), 7.43 (2H, d, $J = 7.5$ Hz), 7.38 (2H, t, $J = 10.9$ Hz), 6.59 (2H, d, $J = 8.4$ Hz), 6.43 (1H, s), 5.19 (1H, br s) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 153.7$, 148.6, 137.5, 131.3, 131.0, 129.3, 128.7, 126.7, 126.5, 124.2, 122.6, 118.0, 117.4, 115.3, 37.0 ppm; IR (KBr, cm^{-1}): 3393, 3058, 2928, 1628, 1596, 1514, 1464, 1437, 1404, 1257, 1188, 958, 818, 748.

X = 4-hydroxy-2-methoxy in Scheme 1, Table 1, Entry 8: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.40$ (2H, d, $J = 8.2$ Hz), 7.83 (2H, d, $J = 7.8$ Hz), 7.79 (2H, d, $J = 8.7$ Hz), 7.58 (2H, t, $J = 7.2$ Hz), 7.48 (2H, d, $J = 8.7$ Hz), 7.42 (2H, t, $J = 7.2$ Hz), 7.15 (1H, d, $J = 8.0$ Hz), 6.85 (1H, s), 6.73 (1H, d, $J = 8.0$ Hz), 6.44 (1H, s), 5.34 (1H, s), 3.65 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 148.7$, 146.7, 144.1, 137.1, 131.4, 131.1, 128.8, 128.7, 126.7, 124.2, 122.7, 121.0, 117.9, 117.5, 113.7, 110.7, 55.6, 37.5 ppm; IR (KBr, cm^{-1}): 3477, 2963, 1591, 1509, 1458, 1430, 1401, 1240, 1032, 959, 805, 781, 749.

X = 4-methyl in Scheme 1, Table 1, Entry 9: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.39$ (2H, d, $J = 8.4$ Hz), 7.83 (2H, d, $J = 8.9$ Hz), 7.78 (2H, d, $J = 8.9$ Hz), 7.57 (2H, t, $J = 8.4$ Hz), 7.48 (2H, d, $J = 8.8$ Hz), 7.43–7.38 (4H, m), 6.95 (2H, d, $J = 7.8$ Hz), 6.46 (1H, s), 2.13 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 147.9$, 147.8, 142.5, 135.9, 130.8, 128.8, 128.4, 127.7, 126.7, 124.3, 123.3, 117.5, 117.4, 117.3, 37.1, 20.2 ppm; IR (KBr, cm^{-1}): 3073, 2913, 1625, 1595, 1513, 1462, 1435, 1405, 1258, 1123, 1086, 966, 841, 813, 785, 744.

3. Results and discussion

Silica sulfuric acid has been used as a Brønsted acid, supported on silica gel, for various acid catalyzed reactions, such as the deprotection of acetals and ketals [19], nitration of phenols [20], oxidation of alcohols [21], methoxylation of alcohols [22], synthesis of acylals from aldehydes [23], deprotection of acylals [23], synthesis of trisubstituted imidazoles [24] and the preparation of β-acetamidoketones [25].

The reagent is safe, easy to handle, environmentally benign and presents few disposal problems. Silica sulfuric acid as a reusable solid acid catalyst was prepared from the reaction of silica gel with chlorosulfonic acid [18]. In the present paper, we wish to describe a new protocol for the rapid preparation of 14*H*-dibenzo[*a*,*j*]xanthene derivatives using a catalytic amount of silica sulfuric acid as a recyclable catalyst under thermal conditions (Scheme 1).

As summarized in Table 1, several different aromatic aldehydes and β-naphthol were reacted in the presence of silica sulfuric acid [18] (0.13 mmol, 0.05 g) as catalyst under solvent-free conditions, to yield the corresponding aryl 14*H*-dibenzo[*a*,*j*]xanthene in good/high yield (Scheme 1 and Table 1). The condensation reaction of ketones with β-naphthol did not occur as reported in the literature [8–17].

In a typical experiment, when reaction was complete, chloroform was poured into the cooled reaction mixture until the solid crude product had dissolved. Then, the silica sulfuric acid catalyst was isolated from the mixture by simple filtration. The catalyst was purified by washing the solid residue with ethyl acetate followed by drying in an oven at 100 °C for 30 min. In every experiment more than 95% of the silica sulfuric acid was thus recovered from the reaction mixture. The catalytic activity of the recovered catalyst was the same as that of fresh silica sulfuric acid. In the development of the procedure, chloroform was evaporated from the reaction mixture and 15% aqueous ethanol was added to the crude product; the ensuing precipitate was separated and recrystallized, twice, using 15% aqueous ethanol.

The suggested mechanism of the silica sulfuric acid catalyzed transformation is shown in Scheme 2.

In comparison of the results obtained in this work using silica sulfuric acid with those achieved using toluenesulfonic acid [13], sulfamic acid [14], potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}\cdot 3H_2O$) [16] and iodine [17] in the synthesis of aryl 14*H*-dibenzo[*a*,*j*]xanthene derivatives, Table 2 shows that silica sulfuric acid acts as effective catalyst with respect to reaction times, yields and products.

4. Conclusions

Silica sulfuric acid is a new, efficient and heterogeneous catalyst for the one-pot synthesis of a variety of aryl 14*H*-dibenzo[*a*,*j*]xanthene derivatives using aryl aldehydes and β-naphthol under solvent-free conditions. This simple method is important from both environmental and economic viewpoints as it produces little waste and also the catalyst can be recovered from the reaction mixtures and reused.

Acknowledgements

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