

Short communication

Iodine catalyzed simple and efficient synthesis of 14-aryl or alkyl-14-*H*-dibenzo[*a,j*]xanthenes[☆]

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Abstract

A simple and facile synthesis of 14-aryl or alkyl-14-*H*-dibenzo[*a,j*]xanthenes has been accomplished by treatment of 2-naphthol with aryl or alkyl aldehydes under neat conditions in the presence of molecular iodine as a catalyst.

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Xanthenes and benzoxanthenes are important biologically active oxygen heterocycles possessing antibacterial [1a], anti-inflammatory [1b] and antiviral properties [1c]. These compounds are also utilized as antagonists for paralyzing action of zoxazolamine [2] and in photodynamic therapy [3]. The other useful applications of these heterocycles are as dyes [4], fluorescent materials for visualization of biomolecules [5] and in laser technologies [6]. Several polycyclic compounds possessing xanthene skeleton have also been reported from natural source [7].

Xanthenes and benzoxanthenes have been prepared by different methods including the reaction of aryloxymagnesium halides with triethylorthoformate [8a], cyclodehydration [8b], trapping of benzynes by phenols [8c], intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones [8d], cyclization of polycyclic aryltriflate esters [8e] and cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone [8f]. Furthermore, 14-*H*-dibenzo[*a,j*]xanthenes and its analogues are prepared by reaction of 2-naphthol with 2-naphthol-1-methanol [9a], formamide [9b], CO [9c], aldehydes [9d,e] and aldehyde acetals [9d]. However, many of these methods suffer from certain drawbacks including longer reaction times, unsatisfactory yields, harsh reaction conditions and necessity of excess of reagents and catalysts.

In continuation of our work [10] on the application of molecular iodine for development of useful synthetic methodologies we have recently observed that it acts as an efficient catalyst for the synthesis of 14-aryl or alkyl-14-*H*-dibenzo[*a,j*]xanthenes by one-pot condensation of 2-naphthol with aldehydes. Initially, we carried out the reaction of 2-naphthol with 3-nitrobenzaldehyde in the presence of this catalyst under different reaction conditions using a solvent or without using any solvent (Table 1). Considering time and yield the best result was obtained when the reaction mixture was heated for 3 h under neat conditions.

The reaction was also tried by grinding a mixture of 2-naphthol, 3-nitrobenzaldehyde and iodine in a mortar with a pestle. However, after 0.5 h the product was formed with an yield of only 6%.

For preparation of a series of 14-aryl or alkyl-14-*H*-dibenzo[*a,j*]xanthenes a mixture of 2-naphthol and an aldehyde along with iodine was heated without using any solvent (Scheme 1).

Table 1

Reaction of 2-naphthol (1 mmol) with 3-nitrobenzaldehyde (0.5 mmol) in the presence of iodine (0.1 mmol) under different conditions

Entry	Solvent	Temperature (°C)	Time (h)	Isolated yield (%)
a	ClCH ₂ CH ₂ Cl	RT	24	26
b	–	RT	15	91
c	ClCH ₂ CH ₂ Cl	90	20	89
d	–	90	3	92

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Table 2
Preparation of 14-aryl or alkyl-14-*H*-dibenzo[*a,j*]xanthenes^a

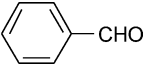
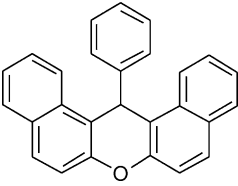
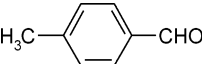
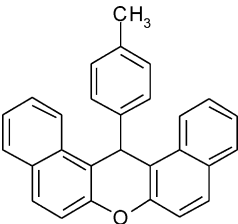
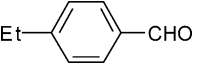
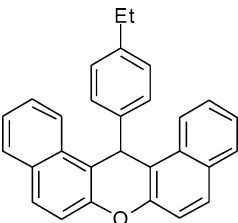
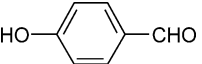
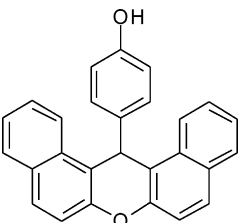
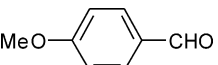
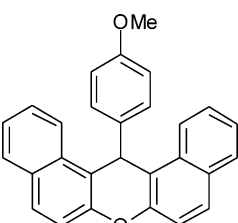
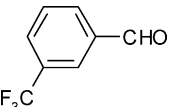
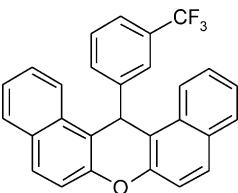
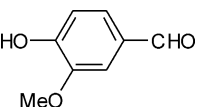
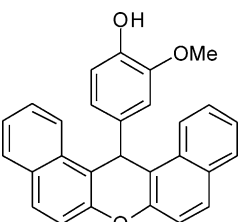
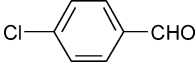
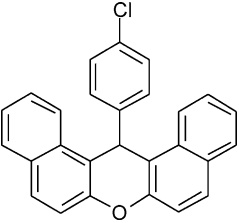
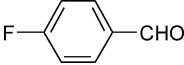
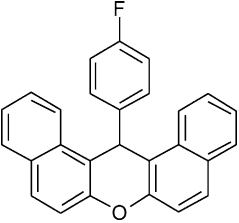
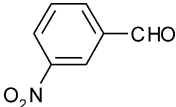
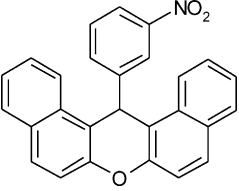
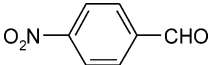
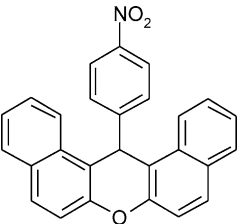
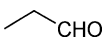
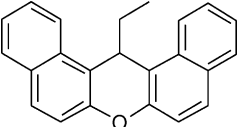

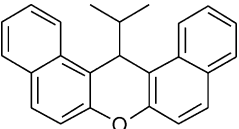
Entry	Aldehyde	Product	Time (h)	Isolated yield (%)	Ref.
a			2.5	90	[9e]
b			3	88	[9e]
c			3	91	–
d			3	93	–
e			4	89	[9e]
f			2	95	–
g			4	92	–

Table 2 (Continued)

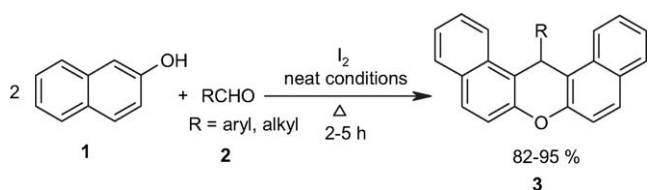
Entry	Aldehyde	Product	Time (h)	Isolated yield (%)	Ref.
h			3	90	[9e]
I			2.5	93	[9e]
j			3	92	[9e]
k			2.5	85	[9e]
l			5	84	[9e]
m			4.5	82	–

^a All the products were characterized from spectral (IR, ¹H NMR and MS) data.

Both aromatic and aliphatic aldehydes were utilized in the present case to form the corresponding benzoxanthenes **3** in high yields (Table 2). The aromatic aldehydes containing electron-donating as well as electron-withdrawing groups

underwent the conversion equally. However, the reaction conducted with phenol instead of 2-naphthol, could not afford any product. The experimental procedure of the present reaction is simple and the conversion was completed within a short period of time (2–5 h). The structures of the products were settled from their spectral (IR, ¹H NMR and MS) data.

In conclusion, we have developed a convenient and efficient method for the synthesis of 14-aryl or alkyl-14-*H*-dibenzo[*a,j*]xanthenes by single-pot condensation of 2-naphthol with aromatic or aliphatic aldehydes in the presence of molecular iodine. The simple experimental procedure, solvent-free



Scheme 1.

reaction conditions, utilization of an inexpensive and readily available catalyst, short period of conversion and excellent yields are the advantages of the present method.

1. Experimental

1.1. General procedure for the preparation of 14-aryl or alkyl-14-H-dibenzo[*a,j*]xanthenes

A mixture of 2-naphthol (1 mmol), aldehyde (0.5 mmol) and I₂ (0.1 mmol) was heated at 90 °C. The reaction was monitored by TLC. After completion, the mixture was treated with aqueous Na₂S₂O₃ solution and extracted with EtOAc (3 × 10 ml). The extract was concentrated and the residue was subjected to column chromatography over silica gel using hexane as eluent to afford pure 14-aryl or alkyl-14-H-dibenzo[*a,j*]xanthenes.

The spectral (IR, ¹H NMR and MS) data of some representative compounds are given below:

Compound **3c**—IR (CHCl₃): 1639, 1617, 1561, 1416, 1217 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 8.34 (2H, d, *J* = 8.0 Hz), 7.88–7.72 (4H, m), 7.60–7.32 (8H, m), 6.93 (2H, d, *J* = 8.0 Hz), 6.42 (1H, s), 2.42 (2H, q, *J* = 7.0 Hz), 1.04 (3H, t, *J* = 7.0 Hz); EIMS: *m/z* 386 (M⁺).

Compound **3d**—IR (KBr): 3428, 1632, 1560, 1475, 1229 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 8.13 (2H, d, *J* = 8.0 Hz), 7.82–7.68 (4H, m), 7.56–7.30 (8H, m), 6.55 (2H, d, *J* = 8.0 Hz), 6.38 (1H, s), 4.32 (1H, brs); EIMS: *m/z* 374 (M⁺).

Compound **3f**—IR (KBr): 1621, 1592, 1515, 1398, 1244 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 8.27 (1H, d, *J* = 8.0 Hz), 7.84–7.75 (4H, m), 7.62–7.33 (9H, m), 7.28–7.15 (2H, m), 6.50 (1H, m); EIMS: *m/z* 426 (M⁺).

Compound **3g**—IR (KBr): 1629, 1525, 1475, 1288 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 8.37 (2H, d, *J* = 8.0 Hz), 7.82–7.75 (4H, m), 7.59–7.52 (2H, m), 7.48–7.37 (4H, m), 7.12 (1H, dd, *J* = 8.0, 2.0 Hz), 6.78 (1H, d, *J* = 2.0 Hz), 6.70 (1H, d, *J* = 2.0 Hz), 6.38 (1H, s), 5.28 (1H, s), 3.63 (3H, s); EIMS: *m/z* 404 (M⁺).

Compound **3m**—IR (CHCl₃): 1622, 1591, 1515, 1457, 1240 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 8.26 (2H, d, *J* = 8.0 Hz), 7.90–7.72 (4H, m), 7.61–7.49 (2H, m), 7.43–7.32 (4H, m), 5.42 (1H, d, *J* = 7.0 Hz), 2.28 (1H, m), 0.81 (6H, d, *J* = 7.0 Hz); EIMS: *m/z* 324 (M⁺).

Acknowledgements

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