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RESEARCH ARTICLE

A GREENER APPROACH TOWARDS THE SYNTHESIS OF ARYL-14H-DIBENZO [A.J] XANTHENES USING AMBERLYST-15

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ABSTRACT

A convenient and green approach was developed for the synthesis of 14H-dibenzo[a,j]xanthenes (**3a-k**) by the condensation of various aromatic aldehydes (**1a-k**) with 1-naphthol (**2**) using Amberlyst-15 as a re-usable catalyst in a solvent-free media at 80 °C. This method gives high yield without any chromatographic purification.

Key words:

Amberlyst-15, Aldehyde, 1-naphthol, dibenzoxanthenes, solvent-free.

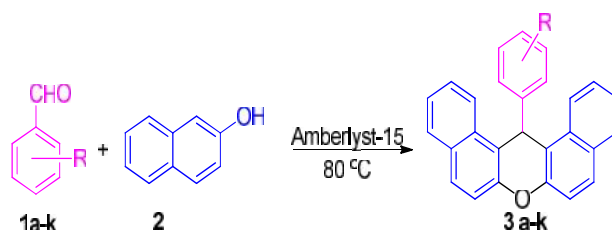
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INTRODUCTION

Due to the enormous applications in organic as well as medicinal chemistry, xanthenes, especially benzoxanthenes, has attracted the attention of organic chemists (Hideo *et al*, 1981). Many researchers were reported the synthesis of xanthenes and benzoxanthenes, they involve cyclodehydrations (Bekert *et al*, 1992), alkylations to the heteroatoms (Vazquez *et al*, 1994), trapping of benzyne by phenol (Knight *et al*, 1998), cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone (Jha *et al*, 2005), the reaction of 1-naphthol with aldehydes (Lingaiah *et al* 2007) or acetals under acidic conditions and intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones (Kuo *et al*, 2001). In addition, 14H-dibenzo [a,j] xanthenes and related products are prepared by reaction of 1-naphthol with formamide (Papini *et al*, 1947) 2-naphthol-1-methanol (Sen *et al*, 1925), carbon monoxide (Ota *et al*, 1976) and sulfonic acid (Rajitha *et al*, 2005).

Herein we report the usage of Amberlyst-15 as reusable catalyst for the synthesis of 14H-dibenzo [a,j] xanthenes (**3a-n**) by the

condensation of various aromatic aldehydes (**1a-k**) with 1-naphthol (**2**) using Amberlyst-15 as a green and reusable catalyst in a solvent-free media at 80 °C. (Scheme 1).



Scheme 1

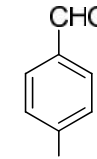
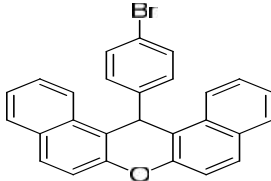
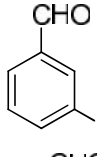
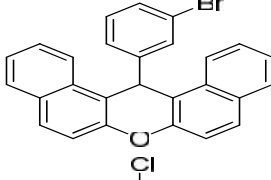
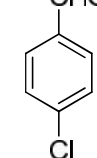
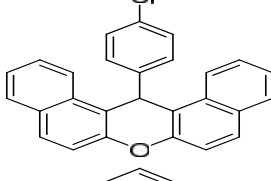
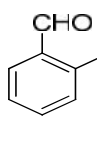
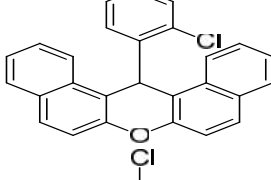
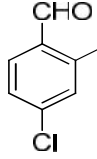
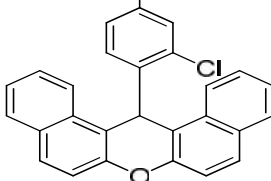
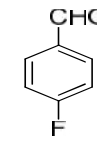
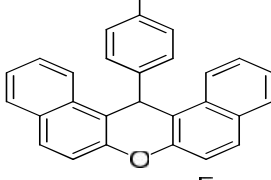
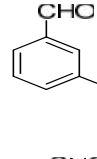
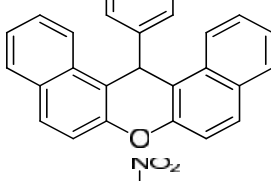
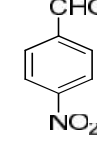
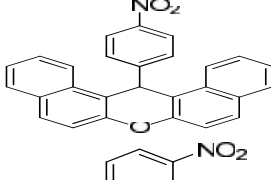
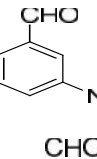
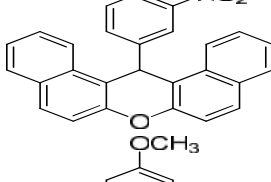
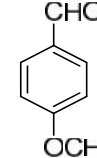
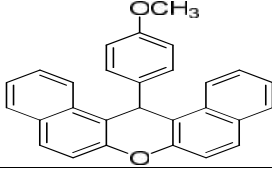
Experimental

All the reagents and solvents were used without further purification unless otherwise stated. Melting points were recorded on a Buchi 535 melting point apparatus and are uncorrected. All the reactions were monitored by thin layer chromatography performed on pre-coated silica gel F₂₅₄ plates (Merck). Compounds were visualized with UV light at 254 nm and 365 nm. NMR spectra were recorded on a Varian Unity-400 MHz using TMS as an internal standard. Mass spectra were recorded on Finnigan Mat 1020B mass spectrometer.

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Table 1 Synthesis of aryl-14H-dibenzo[a,j]xanthenes using Amberlyst-15

Entry	Aldehyde (1)	Product (3)	Yield
a			94
B			91
C			96
D			94
E			92
F			89
G			87
H			92
I			93
J			96

Typical procedure for aryl-14h-dibenzo [a,j]xanthenes

To a mixture of the aromatic aldehydes **1a-k** (1 mmol) and -naphthol (**2**, 2 mmol), Amberlyst-15 (10 mol%) was added and the reaction mixture was stirred at 80 °C. On the completion of reaction as indicated by TLC, the reaction mixture was cooled to 25 °C, ethyl acetate (20 mL) was added and the mixture stirred for 10 min, filtered to separate catalyst, catalyst was washed with ethyl acetate (2 x 10 mL). The combined organic extracts were washed with water (2 x 10 mL), dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue obtained was recrystallized from ethyl alcohol to provide corresponding xanthenes **3a-n** as solids in 86-96% yields.

REPRESENTATIVE SPECTRAL DATA

14-(4-Chlorophenyl)-14 Hdibenzo [A.J] Xanthene (7c)

Yield: 90%, white crystalline solid, m.p. 300-302 °C. IR (KBr.) 3026, 2914, 1621, 1590, 1241, 829, 805, 740 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 8.29 (d, *J* = 8.59 Hz, 2H), 7.80 (t, *J* = 6.250 Hz, 9.35 Hz, 4H) 7.61-7.35 (m, 8H), 7.11 (d, *J*=8.59 Hz, 2H), 6.44(s, 1H).

¹³C NMR: 147.81, 130.79, 130.62, 130.50, 129.51, 129.08, 128.49, 128.20, 126.89, 124.45, 123.11, 117.53, 116.77, 35.69. ESIMS (*m/z*) 393 (M+H)⁺.

14-(4-Fluorophenyl)-14h-Dibenzo [A.J] Xanthene (7f)

Yield: 90%, white crystalline solid, m.p. 264-266 °C. ¹H NMR (400 MHz, CDCl₃): 8.28 (d, *J* = 8.59 Hz, 2H), 7.78 (t, *J* = 7.87, 6.25 Hz, 4H) 7.58-7.33 (m, 8H), 6.80 (t, *J*=8.59 Hz, 2H), 6.42 (s, 1H). ESIMS (*m/z*) 377 (M+H)⁺.

14-(4-Nitro Phenyl)-14hdibenzo [A.J]Xanthene (7l)

Yield: 86%, white crystalline solid, m.p. 309-310 °C. ¹H NMR (200 MHz, CDCl₃): 8.24 (d, *J* = 7.81 Hz, 2H), 8.04-7.24 (m, 14H), 6.56 (s, 1H). ESIMS (*m/z*) 404(M+H)⁺.

CONCLUSIONS

In conclusion, a convenient and efficient process for the synthesis of aryl-14H-dibenzo [a,j] xanthenes is described in this section. The condensation of various aromatic aldehydes with -naphthol using Amberlyst-15 as a catalyst (10 mol %) in a solvent-free media at conventional heating at 80 °C has been developed.

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