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Tin(II)chloride Mediated Synthesis of Aryl-14H-dibenzo[a.*j*] xanthenes

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ABSTRACT

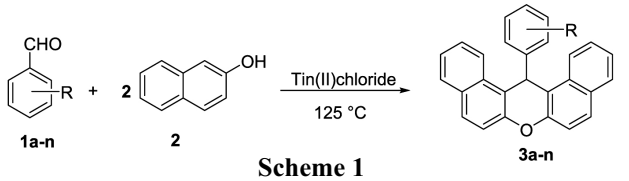
An alternative method have been developed for the synthesis of 14*H*-dibenzo[*a.j*]xanthenes (**3a-n**) by the condensation of various aromatic aldehydes (**1a-n**) with β-naphthol (**2**) using Tin(II)chloride as a catalyst in a solvent-free media at 125 °C.

Key words: Tin(II)chloride, dibenzoxanthenes, solvent-free.

Introduction

The synthesis of xanthenes, especially benzoxanthenes, has attracted the attention of organic chemists due to their wide range of biological and therapeutic properties[1]. Many procedures have been reported for the synthesis of xanthenes and benzoxanthenes, they involve cyclodehydrations[2], alkylations γ to the heteroatoms[3], trapping of benzynes by phenol[4], cyclocondenzation between 2-hydroxyaromatic aldehydes and 2-tetralone[5], the reaction of β-naphthol with aldehydes[6,7] or acetals under acidic conditions and intrmolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones[8]. In addition, 14*H*-dibenzo[*a.j*]xanthenes and related products are prepared by reaction of β-naphthol with formamide[9] 2-naphthol-1-methanol[10], carbon monoxide[11] and sulfomic acid[12].

In this paper we describes our results on the use of Tin(II)chloride as a catalyst for the synthesis of 14*H*-dibenzo[*a.j*]xanthenes (**3a-n**) by the condensation of various aromatic aldehydes (**1a-n**) with β-naphthol (**2**) using Tin(II)chloride as a catalyst in a solvent-free media at 125 °C. (Scheme 1).



Scheme 1

Experimental

All the commercial 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 precoated silica gel 60F254 plates (Merck). Compounds were visualized with UV light at 254 nm and 365 nm, I2 and heating plates after dipping in 2% phosphomolybdic acid in 15% aq. H2SO4 soln. IR spectra were recorded on a Perkin-Elmer 683 or a 1310 FT-IR spectrometers with KBr pellets. NMR spectra were recorded on a Varian Unity-400 MHz and BRUKER AMX 300 spectrometers using TMS as an internal standard. Mass spectra were recorded on a VG. Micromass 7070H and a Finnigan Mat 1020B mass spectrometers operating at 70eV.

Typical procedure for aryl-14*H*-dibenzo[*a.j*]xanthenes by conventional heating: To a mixture of the aromatic aldehydes **1a-n** (1 mmol) and β-naphthol (**6,** 2 mmol), the catalyst SnCl2.2H2O (10 mmol) was added and the reaction mixture was stirred at 125 °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 76-96% yields.

Representative Spectral data:

14-(Phenyl)-14*H*-dibenzo[*a.j*]xanthene (7a): Yield: 92%, white crystalline solid, m.p. 182–184 °C. 1H NMR (200 MHz, CDCl3): δ 8.41 (d, *J* = 8.57 Hz, 2H), 7.79 (t, *J* = 8.59 Hz, 9.28 Hz, 4H) 7.59-7.36 (m, 8H), 7.18 (t, *J* = 7.85 Hz, *J* = 7.85 Hz, 2H), 6.95 (t, *J* = 7.14 Hz, *J* = 7.14 Hz, 1H), 6.45 (s,

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1H). ESIMS (*m/z*) 359 (M+H)+. **14-(4-Chlorophenyl)-14*H*-dibenzo[*a.j*]xanthene (7d):** Yield: 90%, white crystalline solid, m.p. 300-302 °C. IR (KBr,) 3026, 2914, 1621, 1590, 1241, 829, 805, 740 cm-1. 1H NMR (200 MHz, CDCl3): δ 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)-14*H*-dibenzo[*a.j*]xanthene (7g):** Yield: 90%, white crystalline solid, m.p. 264-266 °C. 1H NMR (200 MHz, CDCl3): δ 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)-14*H*-dibenzo[*a.j*]xanthene (7k):** Yield: 86%, white crystalline solid, m.p. 309-310 °C. 1H NMR (200 MHz, CDCl3): δ 8.24 (d, *J* = 7.81 Hz, 2H), 8.04-7.24 (m, 14H), 6.56 (s, 1H). ESIMS (*m/z*) 404(M+H)+.

Results and Discussion

We initially investigated the catalytic activity of Tin(II)chloride for the condensation reaction between *p*-chlorobenzaldehyde and β-naphthol in 1:2 ratio. The catalyst, Tin(II)chloride was studied at 10 mmol concentration in a solvent- free media using conventional heating at 125 °C. We found that under these reaction conditions in the presence of 10 mmol of Tin(II)chloride, complete conversion of the reactants to 14-(4-chlorophenyl)-14*H*-dibenzo[*a.j*]xanthene was observed in 2 h with 90% yield. We also investigated the catalytic activity of Tin(II)chloride by varying the concentration of catalyst (10-50 mmol) to increase the yield of xanthenes formation. However we found that, the excess use of the catalyst, Tin(II)chloride up to 5% concentration did not increased the yield. Therefore, the parameters such as 10 mmol catalyst, temperature of 125 °C were found to be optimal for xanthene formation. These parameters were extended for the condensation of β-naphthol with different substituted aromatic aldehyde for the synthesis of xanthene. The effects of various substituent (electron withdrawing and electron donating groups) of aromatic aldehyde were studied for this one-pot condensation reaction with Tin(II) chloride and some of the results are discussed here (**Table 1**). The condensation reaction of β-naphthol with different substituted aromatic aldehyde proceeded smoothly under the optimized conditions. The nature of the functional group on the aromatic ring of the aldehyde exerted a strong influence on the reaction time. An increase in the rate of reaction was observed with arylaldehyde bearing electron-withdrawing group at the *para* position (**Table 1**, entry **10**), in comparison to electron donating group. The xanthene **7d** was obtained by the condensation of 4-chloro benzaldehyde (**5d**, 1.0 mmol) and β-naphthol (2 mmol) in the presence catalyst Tin(II) chloride (10 mmol) 125 °C for a period of 2 h. The xanthene **7d** was obtained in 90% as colorless solid. The formation of compound **7d** was confirmed from 1H NMR by appearance of peaks at δ 6.42 (s, 1H), 7.10 (d, *J* = 9.6 Hz, 2H), 7.62-7.30 (m, 12H), 8.30 (d, *J* = 9.4 Hz, 2H). The compound 14-(2,4-dichlorophenyl)-14*H*-dibenzo[*a.j*]xanthene (**Table 1**, entry **7f**) was prepared from 2,4-dichlorobenzaldehyde and β-naphthol. The formation of the **7f** was confirmed from the 1H NMR spectrum by the appearance of peaks at δ 6.71 (s, 1H), 6.90 (d, *J* = 9.5 Hz, 1H), 7.23-7.82 (m, 12H), 8.60 (d, *J* = 9.5 Hz, 2H) and with a melting point of 251-253 °C.

Table 1

Synthesis of aryl-14H-dibenzo[a.j]xanthenes using Tin(II)chloride

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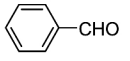
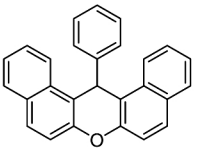
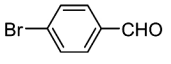
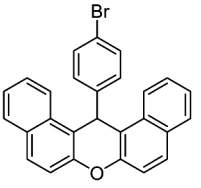
a		
b		

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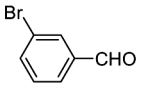
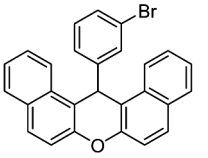
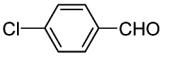
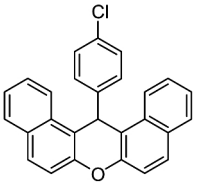
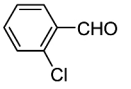
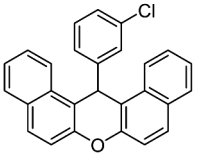
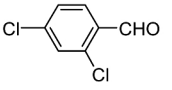
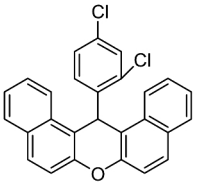
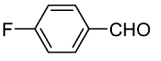
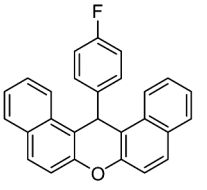
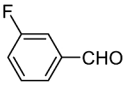
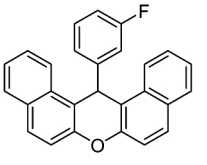
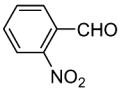
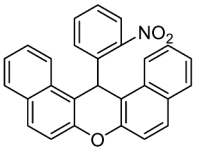
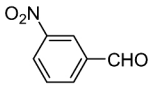
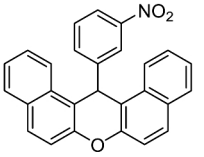
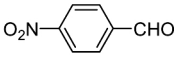
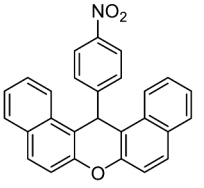
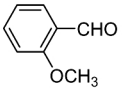
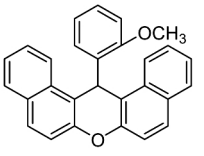
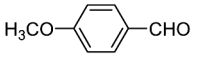
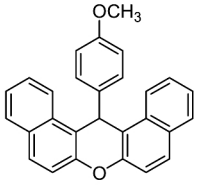
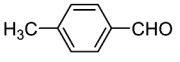
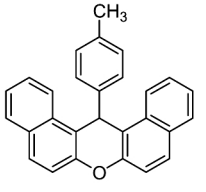
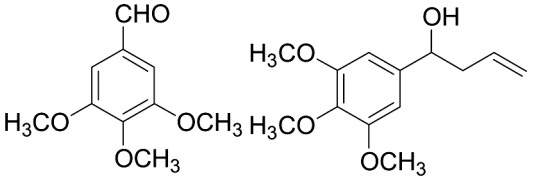
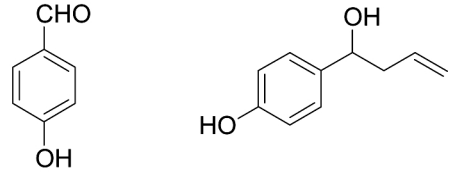
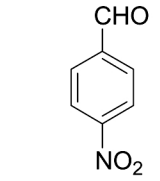
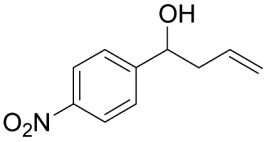
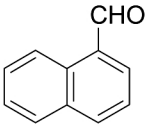
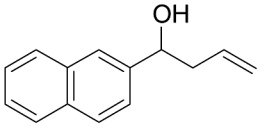
c		
d		
e		
f		
g		
h		
i		

Entry	Aldehyde **5**	Product **7**
j		
k		
l		
m		
n		

g		2	83
h		3	85

i			2	88
j			3	80

Conclusions

In conclusion, a convenient and efficient process for the synthesis of aryl-14*H*-dibenzo[*a.j*]xanthenes is described in this section. The condensation of various aromatic aldehydes with β-naphthol using Tin(II)chloride as a catalyst (10 mmol) in a solvent-free media at conventional heating at 125 °C has been developed.

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