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Short communication

The efficient synthesis of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14 (13*H*)-tetraone leuco-dye derivatives

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ABSTRACT

An efficient method for the synthesis of 13-aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone derivatives by the reaction of 2-hydroxynaphthalene-1,4-dione and aldehydes in the presence of a catalytic amount of *p*-toluene sulfonic acid under solvent-free conditions at 100 °C is described.

1. Introduction

It is well known for many years that dyes have been most widely used in dyeing, as well as high technology as such as lasers, liquid crystalline displays, electro-optical devices and ink-jet printers [1,2].

Xanthene derivatives occupy an important position among different families of dyes, owing to a number of reasons related to their photochemical and photophysical properties [3]. Rose Bengal, Eosin, and other xanthene dyes are the most frequently employed dye-sensitizer when a quantitative interpretation of the photodynamic effect is required [4]. In recent years a number of analyte sensors have been designed using these scaffolds via synthesis of new xanthene based dyes [5]. Furthermore, xanthenes and benzoxanthenes have recently received great attention because of their wide range of therapeutic and biological properties, such as antibacterial [6], antiviral [7], and anti-inflammatory activities [8]. The other useful applications of these heterocycles are as leuco-dyes [9] and in laser technologies [10].

Molecules with the napthoquinone structure constitute one of the most interesting classes of compounds in organic chemistry, due to their biological properties, their industrial applications and their potential as intermediates in the synthesis of heterocycles [11]. A series of related napthoquinone pigments (streptocarpone, α-dunnione, dunniol and dunnione) from *Streptocarpus dunnii* have been isolated and characterized [12,13].

Considering the above reports, the development of new and simple synthetic methods for the efficient preparation of new xanthenes containing napthoquinone fragments is therefore an interesting challenge. In continuation of our previous works on synthesis of xanthene derivatives [14–16], herein, we report a simple and efficient method for the preparation of 13-aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone derivatives under solvent-free conditions. To the best of our knowledge, this paper is the first report in the synthesis of some 13-aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraones.

2. Experimental

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. The chemicals used in this work were purchased from Fluka Chemical Company (Buchs, Switzerland). Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer.

2.1. Typical procedure for the preparation of 13-aryl-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone ***3***

A mixture of 2-hydroxynaphthalene-1,4-dione (2 mmol), aldehyde (1 mmol) and *p*-toluene sulfonic acid (*p*-TSA) (0.1 g)

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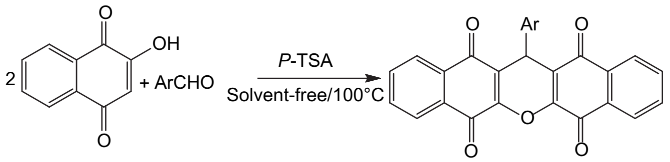


1 2a-g 3a-g

Fig. 1. Synthesis of 13-aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraones.

was heated at 100 °C. The reaction was monitored by TLC. After completion, the reaction mixture was washed with water (15 ml) and residue recrystallized from EtOH to afford the pure product **3**.

Due to very low solubility of the products **3a**–**g**, we cannot report the ^{13}C NMR data for these products.

*2.1.1. 13-Phenyl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (**3a**)*

Red powder, m.p. 305–307 °C; IR (KBr) (ν_{max}, cm^{-1}): 3035, 1660, 1569; ^{1}H NMR (DMSO-d_6): δ_H 5.09 (1H, s, CH), 7.16–8.08 (13H, m, arom.); MS (*m*/*z*, %) 418 (M$^+$, 57), 390 (90), 313 (100). Anal. Calcd (%) for $C_{27}H_{14}O_5$: C, 77.51; H, 3.37. Found: C, 77.64; H, 3.41.

*2.1.2. 13-(4-Chlorophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (**3b**)*

Orange powder, m.p. 330–332 °C; IR (KBr) (ν_{max}, cm^{-1}): 3028, 1663, 1610; ^{1}H NMR (DMSO-d_6): δ_H 5.10 (1H, s, CH), 7.26–8.07 (12H, m, arom.); MS (*m*/*z*, %) 452 (M$^+$, 5), 424 (60), 313 (100). Anal. Calcd (%) for $C_{27}H_{13}ClO_5$: C, 71.61; H, 2.89. Found: C, 71.56; H, 3.93.

*2.1.3. 13-(4-Bromophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (**3c**)*

Yellow powder, m.p. 333–335 °C; IR (KBr) (ν_{max}, cm^{-1}): 3088, 1663, 1657, 1608; ^{1}H NMR (DMSO-d_6): δ_H 5.17 (1H, s, CH), 7.43–8.16 (12H, m, arom.); MS (*m*/*z*, %) 498 (M$^+$, 30), 470 (95), 313 (100). Anal. Calcd (%) for $C_{27}H_{13}BrO_5$: C, 65.21; H, 2.63. Found: C, 65.27; H, 2.67.

*2.1.4. 13-(4-Fluorophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (**3d**)*

Coffee-brown powder, m.p. 270–272 °C; IR (KBr) (ν_{max}, cm^{-1}): 3028, 1663, 1610; ^{1}H NMR (DMSO-d_6): δ_H 5.11 (1H, s, CH), 7.04–8.10 (12H, m, arom.); MS (*m*/*z*, %) 436 (M$^+$, 100), 408 (95), 313 (70). Anal. Calcd (%) for $C_{27}H_{13}FO_5$: C, 74.31; H, 3.00. Found: C, 74.36; H, 2.94.

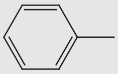
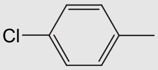
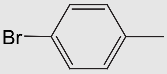
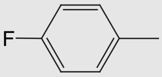
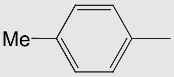
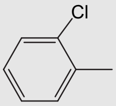
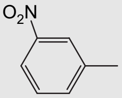
*2.1.5. 13-*p*-Tolyl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (**3e**)*

Brick-red powder, m.p. 304–307 °C; IR (KBr) (ν_{max}, cm^{-1}): 3088, 1663, 1608; ^{1}H NMR (DMSO-d_6): δ_H 2.21 (3H, s, CH_3), 5.09 (1H, s, CH), 7.07–8.12 (12H, m, H-arom.); MS (*m*/*z*, %): 432 (M$^+$, 45), 404 (100), 313 (65). Anal. Calcd (%) for $C_{28}H_{16}O_5$: C, 77.77; H, 3.73. Found: C, 77.68; H, 3.66.

*2.1.6. 13-(2-Chlorophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (**3f**)*

Dark green powder, m.p. 307–309 °C; IR (KBr) (ν_{max}, cm^{-1}): 3037, 1667, 1598; ^{1}H NMR (DMSO-d_6): δ_H 5.45 (1H, s, CH), 7.17–8.10 (12H,

Table 1
Synthesis of aryl-5*H*-dibenzo[*b*,*i*]xanthene-tetraone

Product **3**	Ar	Time (h)	Yield[a] (%)	M.p. (°C)
a		3	81	305–307
b		2.5	80	330–332
c		3	78	333–335
d		2.5	75	270–272
e		4	78	304–307
f		3	76	307–309
g		2.5	90	340–342

[a] Isolated yields.

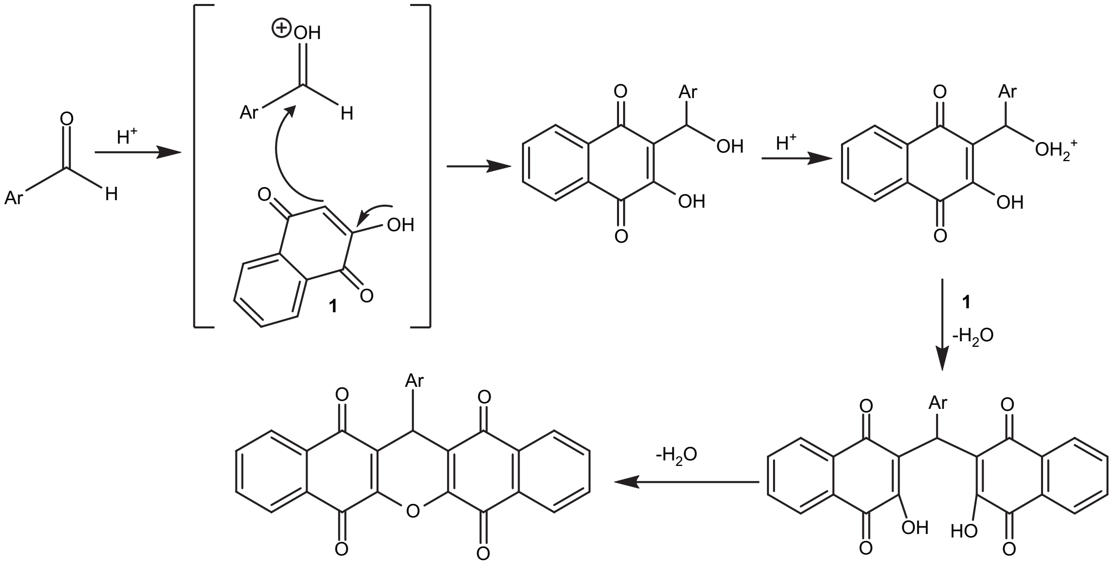


Fig. 2. Mechanism of the reaction.

m, H-arom.); MS (m/z, %): 454 ($M^+ + 2$, 20), 417 (100), 313 (50). Anal. Calcd (%) for $C_{27}H_{13}ClO_5$: C, 71.61; H, 2.89. Found: C, 71.55; H, 2.94.

*2.1.7. 13-(3-Nitrophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14 (13*H*)-tetraone (**3g**)*

Orange powder, m.p. 340–3342 °C; IR (KBr) (ν_{max}, cm^{-1}): 3035, 1662, 1605; ^1H NMR (DMSO-d_6): δ_H 5.47 (1H, s, CH), 7.11–8.13 (12H, m, H-arom.); MS (m/z, %): 463 (25), 418 (40), 313 (100). Anal. Calcd (%) for $C_{27}H_{13}NO_7$: C, 69.98; H, 2.83; N, 3.02. Found: C, 69.91; H, 2.78; N, 3.09.

3. Results and discussion

After some preliminary experimentation, it was found that a mixture of 2-hydroxynaphthalene-1,4-dione **1** and benzaldehyde **2a** in the presence of a catalytic amount of *p*-toluene sulfonic acid (*p*-TSA) at 100 °C for 3 h under solvent-free conditions afforded 13-phenyl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone **3a** in 81% yield (Fig. 1).

To explore the scope and limitations of this reaction further, we have extended the reaction of 2-hydroxynaphthalene-1,4-dione **1** with a range of other aromatic aldehydes **2b**–**g** under similar conditions (*p*-TSA/100 °C), furnishing the respective 13-aryl-5 *H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraones **3b**–**g** in good yields. The optimized results are summarized in Table 1. Good yields were obtained using aromatic aldehydes carrying electron-donating or electron-withdrawing substituents. Aliphatic aldehyde reacted poorly under the same conditions (<20%).

Finally, it should be mentioned when reactions were carried out in the absence of catalyst for long period of time (6–8 h) and in solvent-free condition at 100 °C the yields of products were low (<30%).

We have not established an exact mechanism for the formation of aryl-5*H*-dibenzo[*b*,*i*]xanthene-tetraone **3**, however, a reasonable possibility is shown in Fig. 2.

4. Conclusion

We have developed a simple, efficient and green methodology for the synthesis of new aryl-5*H*-dibenzo[*b*,*i*]xanthene-tetraone derivatives under solvent-free conditions. The simple experimental procedure, solvent-free reaction conditions, and good yields are the advantages of the present method.

Acknowledgements

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