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Short communication

An efficient, clean synthesis of 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione) derivatives

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ABSTRACT

A clean, simple and efficient method for the synthesis of 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione) derivatives has been developed which uses the reaction of 2-hydroxynaphthalene-1,4-dione and aromatic aldehydes in the presence of a catalytic amount of LiCl in aqueous media. To the best of our knowledge, this is the first report on such a synthesis of 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione).

1. Introduction

It is well known for many years that dyes have been most widely used in fields such as dyeing textile fiber, biomedical studies, advanced applications in organic synthesis and high-technology areas like lasers, liquid crystalline displays, electro-optical devices, and ink-jet printers [1,2].

2-Hydroxy-1,4-naphthoquinone (HNQ; Lawsone) is the principal natural dye (1.0–1.4%) in the leaves of henna, *Lawsonia inermis*. Henna has been used for more than 4000 years not only as a hair dye, but also as a body paint and tattoo dye. Today, semi-permanent hair dyes containing Henna as well as its pure dye ingredient HNQ are widely used and have become increasingly popular due to their natural origin [3,4].

Naphthoquinones have been the subject of much interest for a number of years due to their various biological activities, their industrial applications and their potential as intermediates in the synthesis of heterocycles [5]. A series of related naphthoquinone pigments (streptocarpone, α-dunnione, dunniol and dunnione) from *Streptocarpus dunnii* have been isolated and characterized [6,7].

Considering the above reports, the development of new and simple synthetic methods for new dyes containing naphthoquinone fragments is an interesting area.

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 (Buchs, Switzerland) chemical company. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer.

*2.1. Typical procedure for the preparation of 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione) (**3**)*

A mixture of 2-hydroxynaphthalene-1,4-dione (2 mmol), aldehyde (1 mmol) and LiCl (1 mmol) in refluxing water (5 ml) was stirred for 12 h (the progress of reaction was monitored by TLC). After completion of reaction, the reaction mixture was filtered and the precipitate washed with water and then with EtOH to afford the pure product **3a**.

*2.1.1. 3,3′-(Phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) (**3a**)*

Yellow powder, m.p. 202–204 °C; IR (KBr) (ν_{max}, cm^{-1}): 3332, 1669, 1576 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 3.84 (bs, OH, overlap with solvent), 6.00 (1H, s, CH), 7.10–7.99 (13H, m, Arom.) ppm; ^{13}C NMR

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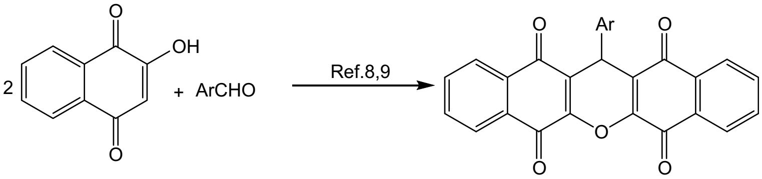


1 2 3

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

(DMSO-d_6): 38.0, 122.2, 123.2, 126.1, 126.5, 129.7, 130.4, 132.6, 133.6, 135.1, 145.9, 150.4, 157.3, 181.6, 183.7 ppm; MS (*m/z*, %) 436 (M^+, 35), 418 (50), 233 (100). Anal. Calcd (%) for $C_{27}H_{16}O_6$: C, 74.31; H, 3.70. Found C, 74.36; H, 3.66.

*2.1.2. 3,3′-((4-Chlorophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) (**3b**)*

Orange powder, m.p. 180–182 °C; IR (KBr) (ν_{max}, cm^{-1}): 3337, 1678, 1576 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 4.00 (bs, OH, overlap with solvent), 5.95 (1H, s, CH), 7.21–7.99 (12H, m, Arom.) ppm; ^{13}C NMR (DMSO-d_6): 37.6, 123.0, 126.0, 126.4, 127.9, 130.3, 130.4, 130.5, 132.6, 133.5, 135.1, 140.5, 156.8, 181.6, 183.9 ppm; MS (*m/z*, %) 470 (M^+, 15), 452 (30), 233 (100). Anal. Calcd (%) for $C_{27}H_{15}ClO_6$: C, 68.87; H, 3.21. Found C, 68.81; H, 3.26.

*2.1.3. 3,3′-((4-Bromophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) (**3c**)*

Brown powder, m.p. 216–218 °C; IR (KBr) (ν_{max}, cm^{-1}): 3332, 1660, 1585 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 4.10 (bs, OH, overlap with solvent), 5.93 (1H, s, CH), 7.18–8.07 (12H, m, Arom.) ppm; ^{13}C NMR (DMSO-d_6): 38.1, 122.2, 123.2, 126.1, 126.5, 129.7, 130.4, 132.5, 133.6, 135.1, 145.9, 150.3, 157.1, 181.5, 183.7 ppm; MS (*m/z*, %) 516 (M^+, 10), 514 (M^+, 10), 498 (45), 342 (100). Anal. Calcd (%) for $C_{27}H_{15}BrO_6$: C, 62.93; H, 2.93. Found C, 62.87; H, 2.89.

*2.1.4. 3,3′-(p-Tolylmethylene)bis(2-hydroxynaphthalene-1,4-dione) (**3d**)*

Yellow powder, m.p. 170–172 °C; IR (KBr) (ν_{max}, cm^{-1}): 3347, 1661, 1596 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 2.23 (3H, s, CH_3), 4.20 (bs, OH, overlap with solvent), 5.95 (1H, s, CH), 6.97–7.98 (12H, m, H-Arom.) ppm; ^{13}C NMR (DMSO-d_6): 21.0, 37.7, 123.7, 126.0, 126.4, 128.5, 128.6, 130.3, 132.6, 133.5, 134.7, 135.1, 138.2, 156.7, 181.7, 184.0 ppm; MS (*m/z*, %): 450 (M^+, 15), 265 (80), 231 (100). Anal. Calcd (%) for $C_{28}H_{18}O_6$: C, 74.66; H, 4.03. Found C, 74.71; H, 4.08.

*2.1.5. 3,3′-((4-Methoxyphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) (**3e**)*

Yellow powder, m.p. 220–222 °C; IR (KBr) (ν_{max}, cm^{-1}): 3399, 3245, 1668, 1637 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 3.69 (3H, s, OCH_3), 3.79 (bs, OH, overlap with solvent), 5.92 (1H, s, CH), 6.75 (2H, d, $J = 8.8$ Hz, H-Arom.), 7.14 (2H, d, $J = 8.9$ Hz, H-Arom.), 7.74–7.99 (8H, m, H-Arom.) ppm; ^{13}C NMR (DMSO-d_6): 37.5, 55.3, 113.4, 123.9, 126.0, 126.4, 129.6, 130.2, 132.6, 133.1, 133.5, 135.1, 156.4, 157.7, 181.7, 184.0 ppm; MS (*m/z*, %): 466 (M^+, 20), 448 (40), 233 (100). Anal. Calcd (%) for $C_{28}H_{18}O_7$: C, 72.10; H, 3.89. Found C, 72.17; H, 3.95.

*2.1.6. 3,3′-((4-Hydroxyphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) (**3f**)*

Orange powder, m.p. 175–177 °C; IR (KBr) (ν_{max}, cm^{-1}): 3392, 3390, 1669, 1582 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 5.89 (1H, s, CH), 6.59 (2H, d, $J = 9.1$ Hz, H-Arom.), 7.01 (2H, d, $J = 9.1$ Hz, H-Arom.), 7.48–9.09 (8H, m, H-Arom.), 9.06 (1H, bs, OH) ppm; ^{13}C NMR (DMSO-d_6): 37.4, 114.9, 124.1, 125.9, 126.4, 129.6, 130.2, 131.1, 132.6, 133.8, 135.0, 155.6, 156.5, 181.7, 184.1 ppm; MS (*m/z*, %): 452 (25), 233 (100). Anal. Calcd (%) for $C_{27}H_{16}O_7$: C, 71.68; H, 3.56. Found C, 71.63; H, 3.51.

*2.1.7. 3,3′-((4-Nitrophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) (**3g**)*

Orange powder, m.p. 177–179 °C; IR (KBr) (ν_{max}, cm^{-1}): 3347, 1658, 1588 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 4.32 (bs, OH, overlap with solvent), 6.07 (1H, s, CH), 7.52–8.08 (12H, m, H-Arom.) ppm; ^{13}C NMR (DMSO-d_6): 38.1, 122.2, 123.2, 126.1, 126.5, 129.7, 130.4, 132.5, 133.6, 135.1, 145.9, 150.4, 157.1, 181.5, 183.7 ppm; MS (*m/z*, %): 481 (25), 463 (30), 233 (100). Anal. Calcd (%) for $C_{27}H_{15}NO_8$: C, 67.36; H, 3.14; N, 2.91. Found C, 67.30; H, 3.18; N, 2.98.

*2.1.8. 3,3′-((3-Bromophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) (**3h**)*

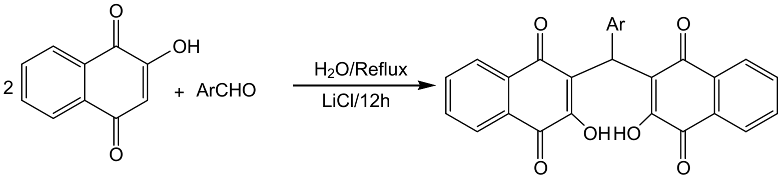
Yellow powder, m.p. 221–223 °C; IR (KBr) (ν_{max}, cm^{-1}): 3311, 1668, 1591 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 4.30 (bs, OH, overlap with solvent), 5.96 (1H, s, CH), 7.16–7.99 (12H, m, Arom.) ppm; ^{13}C NMR (DMSO-d_6): 37.8, 121.8, 122.7, 126.0, 126.4, 127.8, 128.8, 130.1, 130.3, 131.1, 132.6, 133.5, 135.1, 144.4, 156.9, 181.6, 183.8 ppm; MS (*m/z*, %) 516 (M^+, 25), 514 (M^+, 25), 233 (100). Anal. Calcd (%) for $C_{27}H_{15}BrO_6$: C, 62.93; H, 2.93. Found C, 62.99; H, 2.88.

*2.1.9. 3,3′-((3-Methoxyphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) (**3i**)*

Yellow powder, m.p. 185–187 °C; IR (KBr) (ν_{max}, cm^{-1}): 3339, 1669, 1584 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ_H 3.66 (3H, s, OCH_3), 4.24 (bs, OH, overlap with solvent), 5.97 (1H, s, CH), 6.68–7.99 (12H, m, H-Arom.) ppm; ^{13}C NMR (DMSO-d_6): 38.0, 55.2, 110.8, 114.9, 121.1, 123.4, 126.0, 126.4, 128.9, 130.3, 132.6, 133.5, 135.1, 142.8, 156.7, 159.3, 181.6, 183.9 ppm; MS (*m/z*, %): 467 ($M^+ + 1$, 20), 233 (100). Anal. Calcd (%) for $C_{28}H_{18}O_7$: C, 72.10; H, 3.89. Found C, 72.15; H, 3.85.

3. Results and discussion

Very recently, we reported the reaction of 2-hydroxynaphthalene-1,4-dione **1** and aromatic aldehyde **2** (2:1) to form



1 2a-i 3a-i

Fig. 2. Synthesis of 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione).

Table 1
Screening of catalyst.[a]

Entry	Salt	Time (h)	Yield (%)[b]
1	LiCl	12	83
2	$LiNO_3$	12	67
3	NaCl	24	45
4	KCl	24	51
5	NH_4Cl	24	Trace
6	Na_2SO_4	24	Trace
7	*p*-TSA	24	Trace
8	HCl	24	Trace
9	$FeCl_3$	24	58

[a] 2-Hydroxynaphthalene-1,4-dione (2 mmol), benzaldehyde (1 mmol) and cat. (0.1 g).
[b] Isolated yields.

13-aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraones **3** under solvent-free conditions [8,9] (Fig. 1). In this context, herein, we have explored the reaction of 2-hydroxynaphthalene-1,4-dione **1** with aromatic aldehydes **2** employing water as the reaction medium.

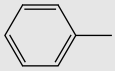
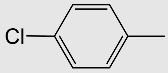
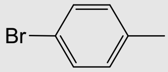
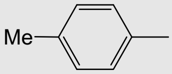
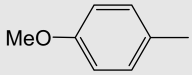
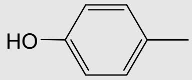
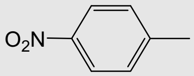
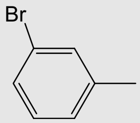
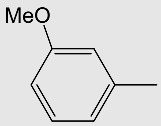
In a pilot experiment, a mixture of 2-hydroxynaphthalene-1,4-dione **1** and benzaldehyde **2a** in the presence of a catalytic amount of LiCl in refluxing water afforded 3,3′-(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) **3a** as a yellow solid in 83% yield for 12 h (Fig. 2).

The product was characterized by spectroscopic analysis. In the IR spectrum of **3a**, the hydroxy and carbonyl absorption was seen at 3332 and 1669 cm^{-1}, respectively. The ^1H NMR spectrum of compound **3a** exhibited a multiplet at δ 7.10–7.99 for the 13 aromatic hydrogens and a singlet at δ 6.00 for the methine proton. The ^{13}C NMR spectrum of compound **3a** showed 15 signals in agreement with the structure, and the mass spectrum shows the expected molecular ion peak.

After screening a number of catalysts such as LiCl, $LiNO_3$, NaCl, KCl, NH_4Cl, Na_2SO_4, *p*-TSA, and HCl it has been found that LiCl promotes the reaction of 2-hydroxynaphthalene-1,4-dione **1** and benzaldehyde **2a** to afford the 3,3′-(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) **3a** in very good yield while other catalysts formed the product in low yield (Table 1). This indicates LiCl is required for this reaction.

The reaction was found to be general with respect to various aromatic aldehydes **2a**–**i**, and the 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione) derivatives **3a**–**i** were obtained in good yields by allowing the reaction to proceed for 12 h. The results are summarized in Table 2. Good yields were obtained using

Table 2
Synthesis 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione).

Product **3**	Ar	Yield (%)[a]	M.P. (°C)
a		83	202–204
b		91	180–182
c		84	216–218
d		91	170–172
e		81	220–222
f		88	175–177
g		80	177–179
h		80	221–223
i		83	185–187

[a] Isolated yields.

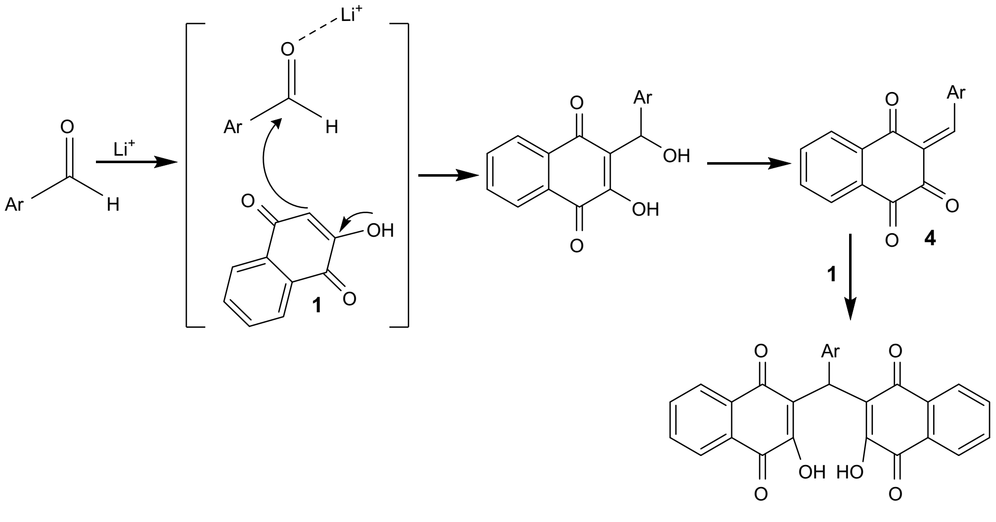


Fig. 3. Proposed mechanism of the reaction.

Table 3
UV/visible data for compound **3** in DMSO.

Entry	Compound **3**	λ_{max} (nm)	Molar absorptivity (log ϵ)
1	**a**	222, 269	3.81, 3.98
2	**b**	221, 267	3.73, 4.01
3	**c**	220, 268	3.86, 3.99
4	**d**	222, 269	3.67, 4.08
5	**e**	222, 266	3.91, 4.02
6	**f**	221, 265	3.86, 4.02
7	**g**	221, 269	3.78, 4.01
8	**h**	221, 270	3.67, 3.85
9	**i**	222, 266	3.90, 4.00

aromatic aldehydes carrying electron-donating or electron-withdrawing substituents (Table 2). When this reaction was carried out with an aliphatic aldehyde such as butanal or propanal, TLC and ^{1}H NMR spectra of the reaction mixture showed a combination of starting materials and numerous products, the yield of the expected product was very low.

Finally, it should be mentioned that when the reactions were carried out in the absence of LiCl for long period of time (48 h) in refluxing water, the yields of products were low (<20%).

According to the results, and as in numerous reports [10–13], it is thought that compound **3** results from initial addition of 2-hydroxynaphthalene-1,4-dione **1** to the aldehyde **2** to yield intermediate **4**, which reacted further with another molecule of **1** to afford the corresponding product **3** (Fig. 3).

Compounds **3a**–**i** are stable solids whose structures are fully supported by IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Electronic absorption spectra of 5×10^{-5} M solutions of **3a**–**i** in DMSO were measured. Data are summarized in Table 3.

4. Conclusion

We have reported a simple and clean methodology for the synthesis of new 3,3′-(arylmethylene)bis(2-hydroxynaphthalene-1,4-dione) derivatives in aqueous media. The simple experimental procedure and purification and good yields are the advantages of the present method.

Acknowledgements

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