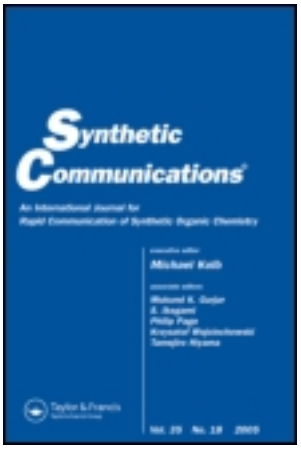

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EFFICIENT ONE-POT SYNTHESIS OF TETRAHYDROBENZO[*c*]XANTHENE-1,11-DIONE DERIVATIVES UNDER MICROWAVE IRRADIATION

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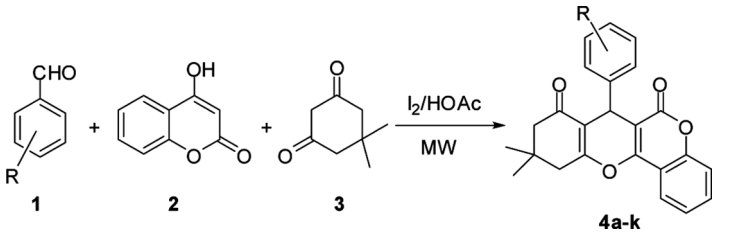
GRAPHICAL ABSTRACT



Abstract *An efficient one-pot condensation of 4-hydroxylcoumarin, aromatic aldehydes, and 5,5-dimethylcyclohexane-1,3-dione has been achieved with molecular iodine as a catalyst via conventional heating and microwave irradiation techniques, and thus a variety of new tetrahydrobenzo[c]xanthene-1,11-dione derivatives were prepared in good yields.*

Keywords 4-Hydroxylcoumarin; microwave irradiation; molecular iodine; one-pot synthesis

INTRODUCTION

Xanthenes and benzoxanthenes have attracted considerable interest because they possess various biological activities such as antibacterial,[1] antiinflammatory,[2] and antiviral activities.[3] These structural motifs have also found a niche as antagonists for paralyzing the action of zoxazolamine[4] and demonstrate efficacy in photodynamic therapy.[5] In addition, these compounds have been employed as dyes[6] and pH-sensitive fluorescent materials for visualization of biomolecular assemblies[7] and utilized in laser technologies.[8] Thus, a broad utility range has made xanthenes prime synthetic candidates, thereby accentuating the need to develop newer synthetic routes for scaffold manipulation of xanthene derivatives.

Recently, the use of molecular iodine[9] has received considerable attention as an inexpensive, nontoxic, readily available catalyst for various organic transformations

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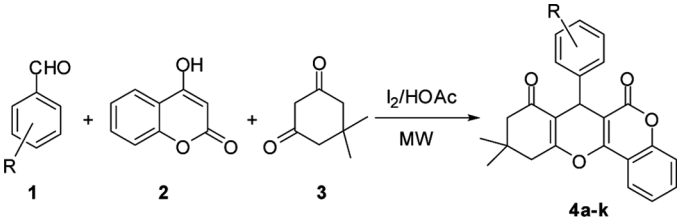


Scheme 1. Synthesis of tetrahydrobenzo[*c*]xanthene-1,11-dione derivatives under microwave irradiation.

to afford the corresponding products in excellent yields. Microwave activation, as a nonconventional energy source, has become an important method in organic synthesis.[10] Now, similar reaction has been synthesized using $KAl(SO_4)_2 \cdot 12H_2O$ as the catalyst.[11] Here we report a rapid and efficient one-pot method for the three-component condensation of 4-hydroxylcoumarin, aromatic aldehyde, and 5,5-dimethylcyclohexane-1,3-dione to synthesize tetrahydrobenzo[*c*]xanthene-1,11-dione derivatives using molecular iodine as the catalyst under microwave irradiation (Scheme 1). To the best of our knowledge, this methodology has not been reported in the literature. These catalysts not only make the synthetic process clean, safe, and inexpensive but also afford the products in excellent yield.

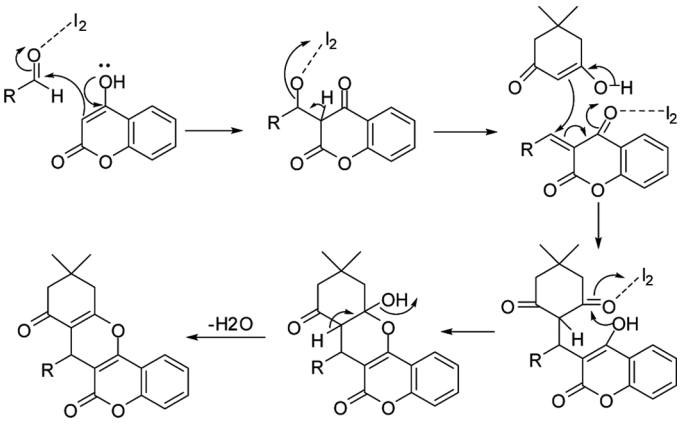
RESULTS AND DISCUSSION

Structural elucidations of **4a**–**k** were accomplished on the basis of their elemental analyses and spectral data. As shown in Table 1, we carried out a comparison of **4a**–**k** syntheses using microwave irradiation and conventional heating. Compared to conventional thermal heating, microwave irradiation greatly reduced the reaction time from 300 min to 6–8 min. It was obvious that yields increased from 70% to 80%. From these data, we conclude that microwave irradiation is a rapid, efficient,

Table 1. Comparison of conventional and microwave-assisted synthesis of **4a**–**k**

		Conventional		Microwave-assisted[a]		
Entry	R	Time (h)	Yield[b] (%)	Time (min)	Yield[b] (%)	Mp (°C)
4a	H	2.5	82	6	93	219–220
4b	4-CH_3	2.5	75	6	85	211–213
4c	4-CH_3O	2.5	64	6	78	191–193
4d	2-Cl	3	77	7	87	228–230
4e	4-Cl	3	78	7	86	236–238
4f	2,4-Cl_2	3	70	7	83	257–259
4g	4-NO_2	4	65	8	74	220–223
4h	4-OH	4	63	8	70	177–179
4i	3,4-(OCH_2O)	3	78	7	84	240–242
4j	3,4-(OCH_3)$_2$	3	66	7	75	181–183
4k	3-CH_3O-4-OH	3	61	7	70	264–266

[a]Microwave power: 100 W, temperature: 120 °C.
[b]Yields of the isolated products.



Scheme 2. Tentative mechanism for the formation of tetrahydrobenzo[*c*]xanthene-1,11-diones.

and environmentally friendly methodology. The results as summarized in Table 1 clearly reveal the scope and generality of the reaction with respect to various substituted aromatic aldehydes and show that reasonable yields of the products were achieved after only 6–8 min irradiation by microwave.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2.

CONCLUSIONS

In summary, we have described an efficient and mild method for the preparation of tetrahydrobenzo[*c*]xanthene-1,11-dione derivatives. This process is efficiently promoted by iodine. The advantages of this method are reduced reaction times, better yields, mild reaction conditions, easy purification, and economic viability of the catalyst. We feel that this economically viable procedure will find practical utility for the one-pot synthesis of novel xanthenes and anthracenes.

EXPERIMENTAL

Melting points were determined in a WRS-1B digital melting-point instrument and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR instrument. ^{1}H NMR and ^{13}C NMR were measured on a Burke 400-MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Mass spectra (MS) were recorded on an LCQ Advantage instrument. Reactions under microwaves were performed in a CEM Discover® monomode microwave reactor. All the reagents are commercially available.

General Procedure for Synthesis of Tetrahydrobenzo[*c*]xanthene-1,11-dione Derivatives 4a–k

Conventional method. Iodine (0.2 mmol) in acetic acid (3 ml) was added to a mixture of aromatic aldehyde (1 mmol), 4-hydroxylcoumarin (1 mmol), and

5,5-dimethylcyclohexane-1,3-dione (1.2 mmol). The mixture was stirred at reflux for the given time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was treated with aqueous $Na_2S_2O_3$ solution and stirred at room temperature for 10 min. The precipitate formed was collected by filtration at the pump, washed with water, and dried. The crude product was recystallized from methanol.

Microwave irradiation method. A 10-mL process vial was charged with a mixture of aromatic aldehyde (1 mmol), 4-hydroxylcoumarin (1 mmol), 5,5-dimethylcyclohexane-1,3-dione (1.2 mmol), iodine (0.2 mmol), and acetic acid (3 mL) and sealed with a cap containing a septum. The loaded vial was then placed into the cavity of the microwave reactor and heated at 100 W, 120 °C for 6–8 min (as indicated by thin-layer chromatography, TLC). After completion of the reaction, the mixture was treated with aqueous $Na_2S_2O_3$ solution and stirred at room temperature for 10 min. The formed precipitate was collected by filtration at the pump, washed with water, and dried. The crude product was recystallized from methanol.

Selected Data

Compound 4a. Mp 219–220 °C; IR (KBr, cm^{-1}): 3062, 2957, 2871, 1714, 1663, 1608, 1456, 1365, 1190, 1051, 759. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, $J = 8.0$ Hz, 1H), 7.59–7.55 (m, 1H), 7.39–7.24 (m, 6H), 7.17 (m, 1H), 4.98 (s, 1H), 2.74 (d, $J = 17.6$ Hz, 1H), 2.67 (d, $J = 17.6$ Hz, 1H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.27 (d, $J = 16.4$ Hz, 1H), 1.18 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 195.9, 161.9, 160.5, 153.9, 152.6, 142.5, 132.2, 128.6, 128.3, 127.0, 124.2, 122.4, 116.8, 115.2, 113.7, 106.8, 50.8, 40.9, 33.4, 32.3, 29.1, 27.6. MS (ESI): $m/z = 373$ $[M + H]^+$. Anal. calcd. for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.33: H, 5.60.

Compound 4b. Mp 211–213 °C, IR (KBr, cm^{-1}): 3128, 2960, 2869, 1727, 1665, 1614, 1362, 1190, 1055, 759. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.58–7.54 (m, 1H), 7.38–7.28 (m, 4H), 7.07 (d, $J = 8.0$ Hz, 2H), 4.94 (s, 1H), 2.73 (d, $J = 17.6$ Hz, 1H), 2.66 (d, $J = 17.6$ Hz, 1H), 2.33 (d, $J = 16.4$ Hz, 1H), 2.25 (d, $J = 16.4$ Hz, 1H), 2.29 (s, 3H), 1.18 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 195.9, 161.8, 160.6, 153.8, 152.6, 139.7, 136.6, 132.1, 129.0, 128.5, 124.2, 122.4, 116.8, 115.3, 113.8, 106.9, 50.8, 40.9, 33.0, 32.3, 32.2, 29.1, 27.6, 21.1. MS (ESI): $m/z = 387$ $[M + H]^+$. Anal. calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.53; H, 5.66.

Compound 4c. Mp 191–193 °C; IR (KBr, cm^{-1}): 2960, 1728, 1662, 1609, 1508, 1363, 1179, 758. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, $J = 7.6$ Hz, 1H), 7.58–7.55 (m, 1H), 7.38–7.31 (m, 4H), 6.79 (d, $J = 8.8$ Hz, 2H), 4.93 (s, 1H), 3.75 (s, 3H), 2.72 (d, $J = 17.6$ Hz, 1H), 2.66 (d, $J = 17.6$ Hz, 1H), 2.33 (d, $J = 16.4$ Hz, 1H), 2.27 (d, $J = 16.4$ Hz, 1H), 1.18 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 195.9, 161.7, 160.6, 158.6, 153.7, 152.6, 134.9, 132.1, 129.6, 124.4, 124.2, 122.4, 116.9, 115.3, 113.8, 113.7, 107.0, 55.2, 50.8, 40.9, 32.6, 32.3, 29.1, 27.6. MS (ESI): $m/z = 425$ $[M + Na]^+$. Anal. calcd. for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51. Found: C, 74.52; H, 5.65.

Compound 4d. Mp 228–230 °C; IR (KBr, cm^{-1}): 3069, 2958, 2871, 1731, 1667, 1612, 1464, 1360, 1191, 1054, 751. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, $J = 7.6$ Hz, 1H), 7.59–7.53 (m, 2H), 7.38–7.13 (m, 5H), 5.23 (s, 1H), 2.70 (d, $J = 17.6$ Hz, 1H), 2.65 (d, $J = 17.6$ Hz, 1H), 2.32 (d, $J = 16.4$ Hz, 1H), 2.26 (d, $J = 16.4$ Hz, 1H), 1.18 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 196.0, 162.6, 160.3, 154.6, 152.8, 138.3, 133.8, 133.4, 132.3, 130.3, 128.4, 126.5, 124.2, 122.6, 116.9, 113.4, 113.2, 104.6, 50.7, 40.8, 33.3, 32.1, 29.1, 27.5. MS(ESI): $m/z = 407$ $[M + H]^+$. Anal. calcd. for $C_{24}H_{19}ClO_4$: C, 70.85; H, 4.71. Found: C, 70.73; H, 4.76.

Compound 4e. Mp 236–238 °C; IR (KBr, cm^{-1}): 3102, 2961, 1722, 1664, 1609, 1490, 1361, 1189, 1056, 762. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.61–7.57 (m, 1H), 7.39–7.21 (m, 6H), 4.95 (s, 1H), 2.73 (d, $J = 17.6$ Hz, 1H), 2.67 (d, $J = 17.6$ Hz, 1H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.26 (d, $J = 16.4$ Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 195.8, 162.0, 160.5, 154.0, 152.7, 141.1, 133.0, 132.4, 130.0, 128.8, 128.5, 127.9, 124.3, 122.5, 116.9, 114.9, 113.6, 106.4, 50.7, 40.9, 33.0, 32.3, 29.1, 27.5. MS (ESI): $m/z = 407$ $[M + H]^+$. Anal. calcd. for $C_{24}H_{19}ClO_4$: C, 70.85; H, 4.71. Found: C, 70.59; H, 4.86.

Compound 4f. Mp 257–259 °C, 90.9%, IR (KBr, cm^{-1}): 2958, 1722, 1667, 1615, 1466, 1361, 1193, 1058, 759. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, $J = 7.6$ Hz,1H), 7.61–7.58 (m, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.28–7.19 (m, 2H), 5.19 (s, 1H), 2.73 (d, $J = 17.6$ Hz, 1H), 2.67 (d, $J = 17.6$ Hz, 1H), 2.26 (d, $J = 16.4$ Hz, 1H), 2.21 (d, $J = 16.4$ Hz, 1H), 1.18 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 196.1, 162.8, 160.3, 154.8, 152.8, 137.0, 134.4, 133.6, 132.5, 129.9, 126.9, 124.3, 122.6, 116.9, 113.3, 112.9, 104.1, 50.7, 40.8, 33.1, 32.2, 32.0, 29.1, 27.5. MS (ESI): $m/z = 442$ $[M + H]^+$. . Anal. calcd. for $C_{24}H_{18}Cl_2O_4$: C, 65.32; H, 4.11. Found: C, 65.23; H, 4.25.

Compound 4g. Mp 220–223 °C; IR (KBr, cm^{-1}): 3075, 2960, 2603, 1722, 1657, 1606, 1517, 1347, 1188, 767. ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, $J = 8.8$ Hz, 1H), 8.12 (d, $J = 8.8$ Hz, 2H), 7.69–7.34 (m, 5H), 5.05 (s, 1H), 2.76 (d, $J = 18.0$ Hz, 1H), 2.71 (d, $J = 18.0$ Hz, 1H), 2.36 (d, $J = 16.4$ Hz, 1H), 2.27 (d, $J = 16.4$ Hz, 1H), 1.19 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 195.8, 162.6, 160.4, 154.5, 152.8, 149.7, 146.9, 143.4, 132.8, 129.7, 127.6, 124.5, 123.8, 122.6, 116.8, 114.2, 113.3, 105.4, 50.6, 40.9, 33.8, 32.4, 29.1, 27.5. MS (ESI): $m/z = 418$ $[M + H]^+$. Anal. calcd. for $C_{24}H_{19}NO_6$: C, 69.06; H, 4.59; N, 3.36. Found: C, 69.53; H, 4.42; N, 3.30.

Compound 4h. Mp 177–179 °C, IR (KBr, cm^{-1}): 3639, 3379, 2961, 1695, 1661, 1613, 1513, 1364, 1191, 1055, 765. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, $J = 7.6$ Hz, 1H), 7.59–7.56 (m, 1H), 7.38–7.21 (m, 4H), 6.67 (d, $J = 8.8$ Hz, 2H), 4.91 (s, 1H), 3.51 (s, 1H), 2.73 (d, $J = 17.6$ Hz, 1H), 2.66 (d, $J = 17.6$ Hz, 1H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.28 (d, $J = 16.4$ Hz, 1H), 1.18 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 196.3, 161.8, 160.7, 154.7, 153.8, 152.6, 132.1, 129.8, 124.2, 122.4, 116.9, 115.4, 115.3, 113.8, 107.0, 50.8, 40.9, 32.6, 32.4, 29.1, 27.6. MS (ESI): $m/z = 411$ $[M + Na]^+$. Anal. calcd. for $C_{24}H_{20}O_5$: C, 74.21; H, 5.19. Found: C, 74.32; H, 5.05.

Compound 4i. Mp 240–242 °C, IR (KBr, cm^{-1}): 3067, 2958, 2876, 1724, 1665, 1607, 1486, 1363, 1186, 1048, 760. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, $J = 7.6$ Hz, 1H), 7.59–7.56 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 6.88–6.68 (m, 3H), 5.88 (s, 2H), 4.89 (s, 1H), 2.72 (d, $J = 17.6$ Hz, 1H), 2.65 (d, $J = 17.6$ Hz, 1H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.29 (d, $J = 16.4$ Hz, 1H), 1.18 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 196.0, 161.8, 160.6, 153.8, 152.6, 147.6, 146.6, 136.6, 132.2, 124.2, 122.4, 121.9, 116.9, 115.2, 113.7, 109.3, 108.1, 106.8, 100.9, 50.8, 40.9, 33.0, 32.3, 29.0, 27.7. MS (ESI): $m/z = 439$ $[M + Na]^+$. Anal. calcd. for $C_{25}H_{20}O_6$: C, 72.11; H, 4.84. Found C, 72.03, H, 5.01.

Compound 4j. Mp 181–183 °C; IR (KBr, cm^{-1}): 2954, 2836, 1723, 1662, 1608, 1513, 1362, 1190, 1056, 762. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, $J = 7.6$ Hz, 1H), 7.59–7.55 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.05 (s, 1H), 6.82–6.75 (m, 2H), 4.93 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 2.73 (d, $J = 17.6$ Hz, 1H), 2.67 (d, $J = 17.6$ Hz, 1H), 2.35 (d, $J = 16.4$ Hz, 1H), 2.29 (d, $J = 16.4$ Hz, 1H), 1.19 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 196.0, 161.8, 160.7, 153.7, 152.6, 148.8, 148.2, 135.4, 132.1, 124.2, 122.4, 120.3, 116.9, 115.3, 113.8, 112.9, 111.2, 106.9, 56.0, 55.8, 50.8, 40.9, 32.8, 32.3, 29.2, 27.5. MS (ESI): $m/z = 455$ $[M + Na]^+$. Anal. calcd. for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.12; H, 5.61.

Compound 4k. Mp 264–266 °C; IR (KBr, cm^{-1}): 3434, 3130, 2949, 1713, 1665, 1606, 1514, 1363, 1183, 1036, 774. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, $J = 7.6$ Hz, 1H), 7.59–7.55 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.14 (s, 1H), 6.77–6.63 (m, 2H), 5.52 (s, 1H), 4.90 (s, 1H), 3.93 (s, 3H), 2.73 (d, $J = 17.6$ Hz, 1H), 2.66 (d, $J = 17.6$ Hz, 1H), 2.34 (d, $J = 16.4$ Hz, 1H), 2.29 (d, $J = 16.4$ Hz, 1H), 1.19 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 196.1, 161.8, 160.7, 153.7, 152.6, 146.1, 144.7, 134.8, 132.1, 124.2, 122.4, 120.3, 116.9, 115.3, 114.1, 113.8, 112.6, 107.0, 56.0, 50.8, 40.9, 32.9, 32.3, 29.2, 27.5. MS (ESI): $m/z = 441$ $[M + Na]^+$. Anal. calcd. for $C_{25}H_{22}O_6$: C, 71.76; H, 5.30. Found: C, 71.55; H, 5.46.

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