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Synthesis of 1,3-disubstituted naphthalenes from the Baylis–Hillman acetates with the aid of manganese(III) acetate

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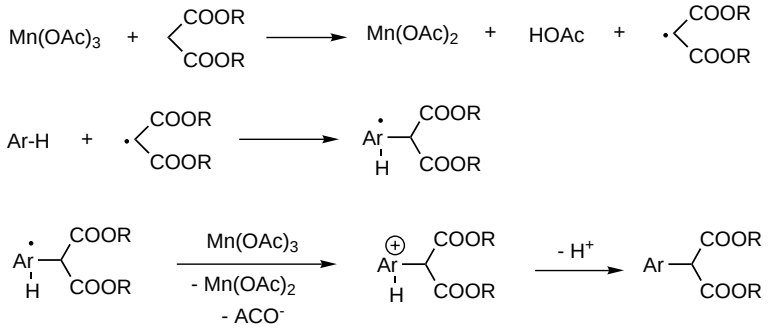
Abstract—1,3-Disubstituted naphthalene derivatives can be easily synthesized from Baylis–Hillman acetates by successive reaction: (1) S_N2' type reaction with diethyl malonate or ethyl nitroacetate; (2) manganese(III) acetate-assisted radical cyclization and (3) aromatization with NaI/O_2 system or elimination of nitrous acid. © 2002 Elsevier Science Ltd. All rights reserved.

The Mn(III)- and Ce(IV)-induced homolytic malonylation[1] or nitroalkylation[2] of aromatic compounds has been studied extensively.[1,2] The reaction might occur as depicted in Scheme 1. The intramolecular version of the reaction can also be carried out. Thus, malonate derivatives with aromatic ring at the δ-position would give tetrahydro- or dihydro-naphthalenes depending on their structure.[1g,1j,1k]

Regioselective synthesis of naphthalene derivatives has been and continues to be of great interest in organic synthesis.[3] A new synthetic procedure is still highly desired due to the abundance of the skeleton in many biologically important natural products.[3,4] Recently we have reported on the synthesis of naphthalenes from the reaction of the Baylis–Hillman acetates derived from *o*-halobenzaldehydes and primary nitro alkanes via the successive S_N2'–S_NAr elimination strategy.[4] In the previous paper there must be a halogen atom at the *ortho* position of the benzaldehyde moiety.

In order to shed more light on the facile synthesis of naphthalenes[4] and to generalize our previous methodology, we focused our attention on the synthesis of naphthalenes from Baylis–Hillman adducts derived from benzaldehydes without a *ortho*-halogen substituent. Thus, we tried the Mn(III)- or Ce(IV)-assisted cyclization of malonate derivatives with aromatic ring at the δ-position, which could be prepared easily from the reaction of diethyl malonate and the Baylis–Hillman acetates of benzaldehydes. As shown in Scheme 2 and in Table 1, the reaction of **1a** and diethyl malonate in the presence of K_2CO_3 in acetonitrile gave **2a** in 81% yield.[5] The reaction of **2a** with $Mn(OAc)_3$ (6 equiv.) in



Scheme 1.

Keywords: Baylis–Hillman acetate; naphthalene; manganese(III) acetate; malonyl radical.
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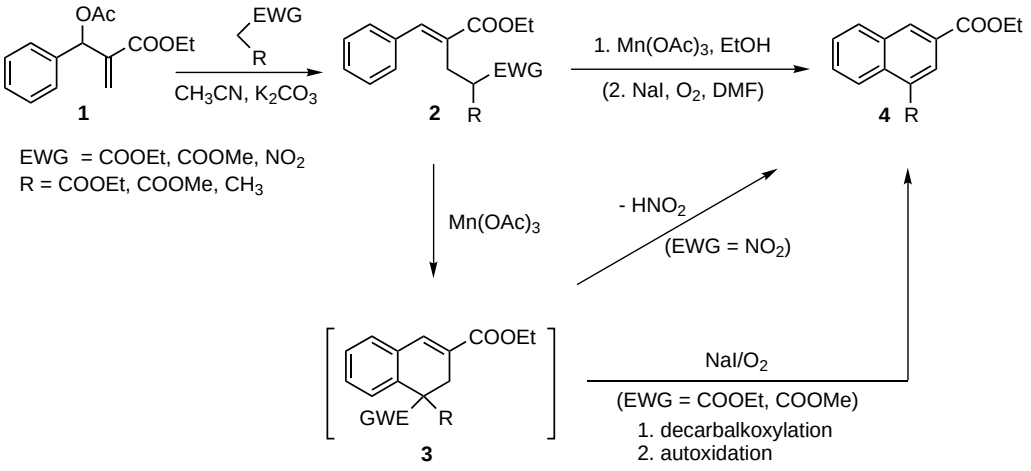

Scheme 2.

ethanol gave the dihydronaphthalene derivative **3a** in 66% isolated yield. The use of CAN (cerium ammonium nitrate) for the conversion of **2a** into **3a** was less effective than the use of $Mn(OAc)_3$ in view of yield and unfavorable formation of many side products. Conversion of **3a** to the naphthalene derivative was carried out with a NaI/O_2 system[1i] in DMF to give **4a** in 70% yield. With these results in hand we extended the reaction toward various combinations and the results are summarized in Table 1. In other cases (entries 2–4) we did not separate the intermediacy dihydronaphthalenes **3**. Crude **3** was used in the next oxidation step without purification. As shown in entry 2, dimethyl malonate derivative **2b** showed similar results.

The reaction mechanism for the formation of dihydronaphthalene **3a** and its conversion to naphthalene **4a** is depicted in Scheme 3. Generation of malonyl radical **I**, addition to aromatic ring and coupling with acetoxy radical to give **II**, elimination of acetic acid furnished **3a**. Successive decarbalkoxylation and autoxidation[6] of **3a** gave the naphthalene **4a**.[1i,6] It is uncertain at this stage which step proceeds first, decarbalkoxylation or autoxidation. Further studies on the reaction mechanism for the conversion of **3a** to **4a** are in progress.

We extended the reaction with primary nitro alkane derivatives, which were known to undergo the Mn(III)-assisted radical coupling to arenes.[2a,b] In these cases naphthalene derivatives were obtained directly in good yields (entries 5–9). The aromatization step was not necessary when we used nitro compounds. Elimination of nitrous acid from the intermediacy dihydronaphthalenes might occur in the reaction conditions directly, as depicted in Scheme 2.

A typical procedure for the synthesis of **5a** and the selected spectroscopic data was mentioned in Ref. 5. Extension of this methodology to the synthesis of various heterocycles by using the Baylis–Hillman acetates derived from heterocyclic aldehydes is currently underway.

Acknowledgements

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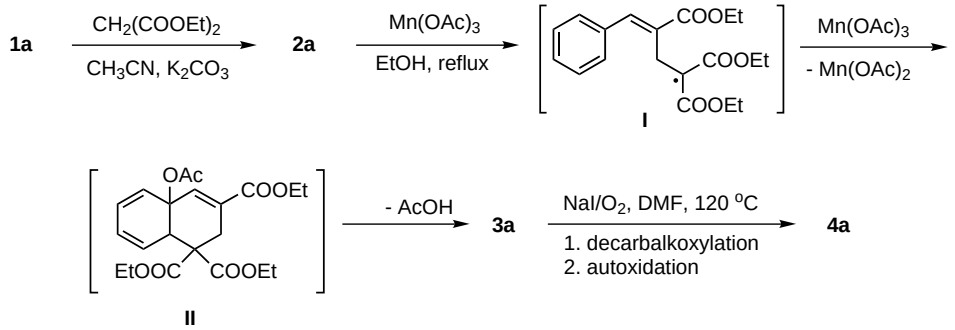
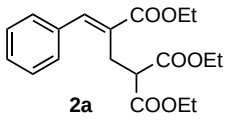
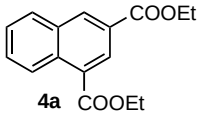
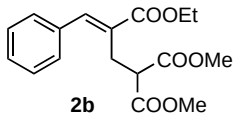
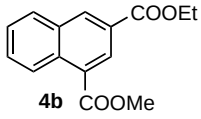
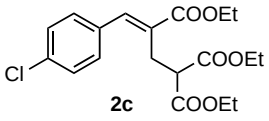
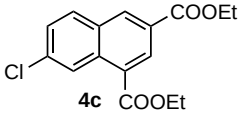
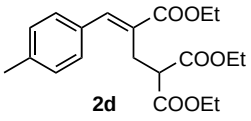
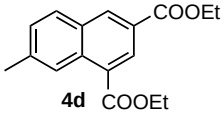
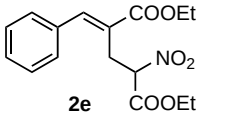
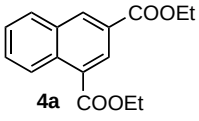
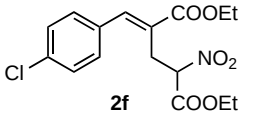
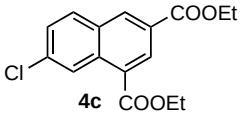
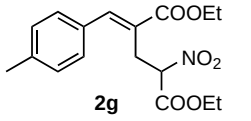
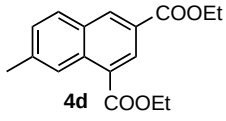
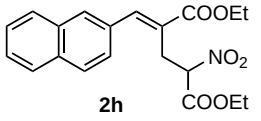
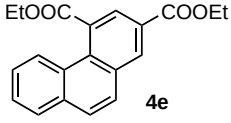
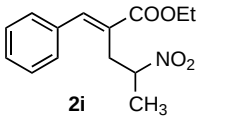
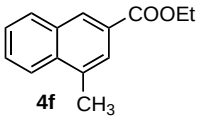


Scheme 3.

Table 1. Synthesis of 1,3-disubstituted naphthalenes **4a–f**

entry	substrate	conditions	product	yield (mp)
1	 **2a**	1. $Mn(OAc)_3$ (6 equiv) EtOH, reflux, 48 h (66%) 2. O_2/NaI, DMF 120 °C, 24 h (70%)	 **4a**	46% (38-39 °C)
2	 **2b**	1. $Mn(OAc)_3$ (6 equiv) EtOH, reflux, 48 h 2. O_2/NaI, DMF 120 °C, 6 h	 **4b**	49% (46-47 °C)
3	 **2c**	1. $Mn(OAc)_3$ (6 equiv) EtOH, reflux, 48 h 2. O_2/NaI, DMF 120 °C, 24 h	 **4c**	51% (87-88 °C)
4	 **2d**	1. $Mn(OAc)_3$ (6 equiv) EtOH, reflux, 48 h 2. O_2/NaI, DMF 120 °C, 24 h	 **4d**	37% (oil)
5	 **2e**	$Mn(OAc)_3$ (4 equiv) EtOH, reflux, 48 h	 **4a**	64%
6	 **2f**	$Mn(OAc)_3$ (4 equiv) EtOH, reflux, 48 h	 **4c**	60%
7	 **2g**	$Mn(OAc)_3$ (4 equiv) EtOH, reflux, 48 h	 **4d**	80%
8	 **2h**	$Mn(OAc)_3$ (4 equiv) EtOH, reflux, 48 h	 **4e**	47%[a] (108-109 °C)
9	 **2i**	$Mn(OAc)_3$ (6 equiv) EtOH, reflux, 48 h	 **4f**	67% (51-52 °C)

[a]Trace amounts (3%) of diethyl 2,4-anthracene dicarboxylate was isolated.

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5. Typical procedure for the synthesis of **2a**, **3a** and **5a** and their selected spectroscopic data are as follows: To a stirred solution of Baylis–Hillman acetate **1a** (1.0 g, 4.0 mmol) and diethyl malonate (710 mg, 4.4 mmol) in acetonitrile (10 mL) was added potassium carbonate (620 mg, 4.5 mmol). The reaction mixture was stirred at room temperature for 20 h. After usual workup and column chromatographic purification process (hexane/ether, 8:1) **2a** was obtained as an oil (1.13 g, 81%). The stereochemistry of **2a** is *E* as in the previous report.[4] Trace amounts (ca. 5%) of the corresponding *Z* form were contaminated. A stirred mixture of **2a** (100 mg, 0.287 mmol) and manganese(III) acetate dihydrate (115 mg, 0.43 mmol) in dry ethanol (4 mL) was heated to reflux for 48 h. Additional manganese(III) acetate (115 mg×3, 1.29 mmol) was added three times during the reaction. The reaction mixture was filtered through a Celite pad and washed with ethanol. After usual workup and column chromatographic purification process (hexane/ether, 8:1) **3a** was obtained as an oil (66 mg, 66%). A stirred solution of **3a** (66 mg, 0.19 mmol) and sodium iodide (86 mg, 0.57 mmol) in DMF (3 mL) was heated to 120°C under an oxygen atmosphere for 24 h. After usual workup and column chromatographic purification process (hexane/ether, 8:1) **5a** was obtained as a white solid (36 mg, 70%).
2a: 81%; clear oil; ^{1}H NMR ($CDCl_3$) δ 1.15 (t, $J=7.2$ Hz, 6H), 1.34 (t, $J=7.2$ Hz, 3H), 3.20 (d, $J=7.8$ Hz, 2H), 3.79 (t, $J=7.8$ Hz, 1H), 3.98–4.15 (m, 4H), 4.27 (q, $J=7.2$ Hz, 2H), 7.25–7.38 (m, 5H), 7.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.79, 14.13, 26.15, 50.42, 60.87, 61.18, 127.83, 128.14, 128.46, 129.01, 134.92, 141.44, 167.32, 168.72.
3a: 66%; clear oil; IR (KBr) 1733, 1713, 1634 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, $J=7.1$ Hz, 6H), 1.35 (t, $J=7.1$ Hz, 3H), 3.34 (d, $J=1.5$ Hz, 2H), 4.19–4.32 (m, 6H), 7.26–7.37 (m, 4H), 7.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.99, 14.30, 29.89, 59.17, 60.89, 62.09, 126.95, 127.84, 128.56, 128.88, 129.87, 131.98, 132.91, 135.60, 166.30, 170.36.
5a: 70%; white solid, mp 38–39°C; IR (KBr) 2984, 2937, 1721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.47 (t, $J=7.1$ Hz, 3H), 1.49 (t, $J=7.1$ Hz, 3H), 4.51 (q, $J=7.1$ Hz, 2H), 4.48 (q, $J=7.1$ Hz, 2H), 7.60–7.75 (m, 2H), 8.01 (d, $J=8.2$ Hz, 1H), 8.73 (s, 1H), 8.75 (s, 1H), 8.93 (d, $J=8.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.31 (2C), 61.26, 61.32, 125.86, 126.56, 126.83, 127.93, 129.21, 129.81, 129.88, 133.10, 133.14, 135.34, 165.84, 166.92.
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