

Michael Additions

Synthesis of Functionalized Arenopyrans and Arenylsulfanes via Reaction of Nitroallylic Acetates with Arenols and Arenethiols

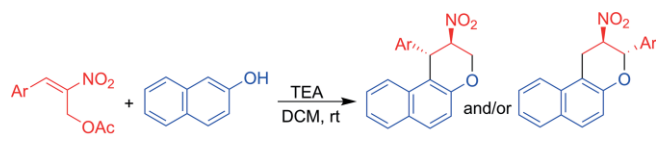
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We have noticed several errors in our previous manuscript^[1] and would like to provide corrections:

1. Abstract, line 5: "involving an S_N2' reaction" should read "involving an S_N2/S_N2' reaction"

2. Page 2, column 2, paragraph 2: The description of entries 3–6 in Table 2 should read:

Besides dihydronaphthopyran **3a** bearing a furyl group which was synthesized in excellent yield (86 %, entry 1), dihydronaphthopyran **3b** was synthesized in moderate yield by treating β-naphthol **2a** with appropriate MBH acetate **1b** (entry 2). In the case of MBH acetates **1c–f**, a reversal of regioselectivity leading to S_N2 products **3'** as the major or exclusive products was observed (entries 3–6). In the case of **1c** and **1d**, the minor S_N2' products (< 20 %) **3c** and **3d**, respectively, could be isolated and characterized (entries 3–4). Moreover, the reaction in Table 2 and footnote are updated:

Table 2. Scope of MBH-acetate.^[a]

Entry	Ar	1	Time /h	% Yield (3) ^[b]	% Yield (3') ^[b]
1	2-Furyl	1a	12	86 ^[c]	— ^[e]
2	4-OMeC ₆ H ₄	1b	2.5	61 ^[d]	— ^[e]
3	4-MeC ₆ H ₄	1c	10	15	53 ^[d]
4	C ₆ H ₅	1d	9	18	50 ^[d]
5	3-OMeC ₆ H ₄	1e	4	— ^[e]	36 ^[d]
6	3,4-(OCH ₂ O)-C ₆ H ₃	1f	4	— ^[e]	48 ^[d]
7	2-NO ₂ C ₆ H ₄	1g	9	— ^[f]	— ^[f]
8	4-Br-C ₆ H ₄	1h	6	— ^[f]	— ^[f]
9	4-Cl-C ₆ H ₄	1i	6	— ^[f]	— ^[f]

[a] 2-Naphthol **2a** (0.36 mmol), MBH-acetate **1** (0.4 mmol, 1.1 equiv.), NEt₃ (1.08 mmol, 3 equiv.) in DCM (6 mL). [b] After silica gel column chromatography, *dr* ≥ 95:05 (*trans/cis*) except in the case of **3a**. [c] *dr* = 90:10 (*trans/cis*). [d] 5–10 % of 2-naphthol was recovered. [e] Formation 10–20 % of this regioisomer was observed which could not be isolated in pure form. [f] Complex mixture.

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3. Page 4, column 2, paragraph 1, line 5: Scheme 2 should read: Scheme 2, Path A,

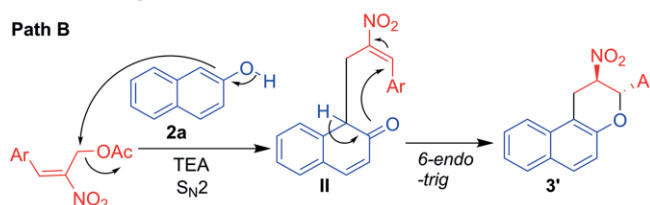
followed by the sentence:

In the alternative pathway (Path B), the carbon-centred nucleophile reacts with the hard centre of the electrophile in an S_N2 fashion.

In addition, **Path B** should be added to the original Scheme 2 as follows:

Path A. Existing Scheme 2

Path B



Scheme 2. Proposed mechanistic outline for the formation of arenopyrans.

4. Experimental Section

Following are the experimental data for minor products **3c** and **3d** (Table 2, Entries 3–4):

2-Nitro-1-(p-tolyl)-2,3-dihydro-1H-benzo[f]chromene (3c): Pinkish white solid; yield 10 mg, 15 %; m.p. 61–63 °C; IR (neat, cm⁻¹) 2923 (w), 1625 (w), 1551 (s), 1511 (w), 1470 (w), 1355 (w), 1241 (m), 1226 (m), 815 (m), 747 (m); ¹H (500 MHz, CDCl₃) δ = 7.76–7.78 (m, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.48–7.51 (m, 1H), 7.30–7.33 (m, 2H), 7.09–7.16 (m, 5H), 5.45–5.47 (unresolved m, 1H), 4.89 (dt, *J* = 12.3, 2.0 Hz, 1H), 4.84–4.86 (m, 1H), 4.35 (dd, *J* = 12.3, 1.6 Hz, 1H), 2.31 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ = 21.2, 40.1, 61.7, 84.1, 111.0, 118.5, 123.0, 124.0, 127.1, 128.6, 128.8, 129.9, 130.1, 130.2, 132.4, 137.8, 138.7, 151.6; HRMS (ES⁺) calcd for C₂₀H₁₇NO₃Na (MNa⁺) 342.1101, found 342.1106.

2-Nitro-1-phenyl-2,3-dihydro-1H-benzo[f]chromene (3d):^[28] Pinkish white solid; yield 11 mg, 18 %; m.p. 132–134 °C (lit.^[28] Not reported); IR (neat, cm⁻¹) 2922 (w), 1625 (m), 1551 (s), 1470 (w), 1355 (w), 1226 (m), 747 (m), 704 (m); ¹H (500 MHz, CDCl₃) δ = 7.77–7.79 (m, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.46–7.50 (m, 1H), 7.32–7.35 (m, 2H), 7.31 (t, *J* = 3.2 Hz, 2H), 7.27–7.30 (m, 1H), 7.21–7.23 (m, 2H), 7.15 (d, *J* = 9.0 Hz, 1H), 5.50–5.51 (unresolved m, 1H), 4.90 (dt, *J* =

12.0, 2.2 Hz, 1H), 4.87–4.89 (m, 1H), 4.36 (dd, $J = 12.0, 1.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) $\delta = 40.5, 61.7, 84.0, 110.8, 118.5, 123.0, 124.0, 127.1, 128.0, 128.7, 128.8, 129.5, 130.0, 130.1, 132.3, 141.7, 151.7$.

Keywords: Arenopyrans · Arenylsulfanes · Diastereoselectivity · Michael addition · Nucleophilic substitution

The Authors

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