Studies Towards the Synthesis of (−)-Euonyminol: An Ireland-Claisen Rearrangement/Lactonization Cascade as a Key Step

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Supporting Information — X-Ray Crystallography

The X-ray crystal structure of 7a.

Crystal data for 7a: C_{16}H_{21}NO_{3}, M = 275.34, monoclinic, P2₁, (no. 4), a = 8.8685(5), b = 7.4720(4), c = 10.7590(8) Å, β = 92.337(2)°, V = 712.36(8)Å³, Z = 2, Dc = 1.284 g cm⁻³, µ(Mo-Kα) = 0.088 mm⁻¹, T = 120 K, colourless fragment, Nonius FR591 Rotating anode, Nonius KappaCCD; 2877 independent measured reflections (R_{int} = 0.0384), F² refinement, R₁(obs) = 0.0447, wR₂(all) = 0.1087, 1384 independent observed reflections [|F_o| > 4σ(|F_o|), 2θ_{max} = 52.74°], 188 parameters. The absolute structure could not be determined from the X-ray diffraction data and so was assigned based on internal reference on C2, C3, C6, C7, C8, C10 and C11. CCDC 819413.

The X-ray crystal structure of 9a.

Crystal data for 9a: C_{23}H_{24}BrNO_{4}, M = 458.34, monoclinic, P2₁, (no. 4), a = 10.8450(1), b = 17.6459(2), c = 11.0083(2)Å, β = 90.12(7)°, V = 2106.65(5)Å³, Z = 4, Dc = 1.445 g cm⁻³, µ(Mo-Kα) = 1.980 mm⁻¹, T = 120 K, colourless prism, Nonius FR591 Rotating anode, Nonius KappaCCD; 8294 independent measured reflections (R_{int} = 0.0563), F² refinement,
\[ R_1(\text{obs}) = 0.0353, \ wR_2(\text{all}) = 0.0872, \ 7649 \text{ independent observed reflections } [|F_o| > 4\sigma(|F_o|)], \ 2\theta_{\text{max}} = 54.74^\circ] \), 529 parameters. The absolute structure of 9a was determined by a combination of \( R \)-factor tests \([R_1^+ = 0.0353, \ R_1^- = 0.0754]\) and by use of the Flack parameter \([x^+ = -0.008(5), \ x^- = +0.991(13)]\), 3840 Friedel pairs. CCDC 819414.

**The X-ray crystal structure of 15b.**

Crystal data for 15b: C\(_{22}\)H\(_{34}\)BrNO\(_3\)Si, \( M = 468.50 \), triclinic, \( P-1 \) (no. 2), \( a = 8.33764(16), \ b = 11.1787(3), \ c = 14.0235(3) \) Å, \( \alpha = 87.990(2), \ \beta = 76.8660(19), \ \gamma = 69.337(2)^\circ, \ V = 1189.51(5) \) Å\(^3\), \( Z = 2, \ \ D_c = 1.308 \) g cm\(^{-3}\), \( \mu(\text{Mo-K\(\alpha\)}) = 1.799 \) mm\(^{-1}\), \( T = 173 \) K, colourless blocky needles, Oxford Diffraction Xcalibur 3 diffractometer; 7568 independent measured reflections \( (R_{\text{int}} = 0.0379) \), \( F^2 \) refinement, \( R_1(\text{obs}) = 0.0330, \ wR_2(\text{all}) = 0.0868, \ 4899 \text{ independent observed absorption-corrected reflections } [|F_o| > 4\sigma(|F_o|), \ 2\theta_{\text{max}} = 65^\circ] \), 253 parameters. CCDC 819415.

**The X-ray crystal structure of 20** (see manuscript footnote 13).

Crystal data for 20: C\(_{17}\)H\(_{25}\)BrO\(_4\), \( M = 373.28 \), monoclinic, \( P2_1 \), (no. 4), \( a = 8.00502(5), \ b = 10.12595(7), \ c = 11.24941(7) \) Å, \( \beta = 110.0133(7)^\circ, \ V = 856.795(10) \) Å\(^3\), \( Z = 2, \ \ D_c = 1.447 \) g cm\(^{-3}\), \( \mu(\text{Cu-K\(\alpha\)}) = 3.399 \) mm\(^{-1}\), \( T = 173 \) K, colourless columnar needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3237 independent measured reflections \( (R_{\text{int}} = 0.0215) \), \( F^2 \) refinement, \( R_1(\text{obs}) = 0.0185, \ wR_2(\text{all}) = 0.0500, \ 3195 \text{ independent observed absorption-corrected reflections } [|F_o| > 4\sigma(|F_o|), \ 2\theta_{\text{max}} = 143^\circ] \), 200 parameters. The absolute structure of 20 was determined by a combination of \( R \)-factor tests \([R_1^+ = 0.0185, \ R_1^- = 0.0340]\) and by use of the Flack parameter \([x^+ = +0.000(11), \ x^- = +1.007(11)]\). CCDC 819416.
**Figure 1.** The molecular structure of 7a showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level and hydrogen atoms are displayed as spheres of arbitrary radius.
Figure 2. View of the crystal packing of 7a down the c-axis of the unit cell.

Figure 3. Stereochemistry assignment from crystallography for 9a. Flack parameter = 0.000(5). The two independent molecules in the asymmetric unit have different ring conformations but same stereochemistry.
Figure 4. The molecular structure of molecule A of 9a showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level and hydrogen atoms are displayed as spheres of arbitrary radius.
**Figure 5.** The molecular structure of molecule B of 9a showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level and hydrogen atoms are displayed as spheres of arbitrary radius.
**Figure 6.** View of the crystal packing of 9a down the c-axis of the unit cell.

**Figure 7.** The molecular structure of 15b.
Figure 8. The molecular structure of 15b (50% probability ellipsoids).

Figure 9. The molecular structure of 20.
Figure 10. The molecular structure of 20 (50% probability ellipsoids).