

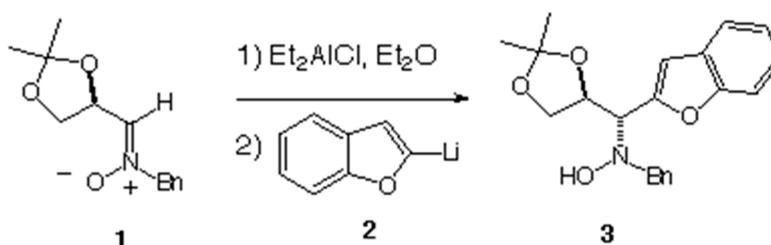
(1R,2S)-N-Benzyl-N-[(2,2-dimethyl-1,3-dioxolan-4-yl)-(2-benzofuryl)methyl] Hydroxylamine

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Scheme

A cooled solution (-90 °C) of benzofuran (0.354 g, 3 mmol) in THF (10 mL) was treated with butyllithium (2 mL of a 1.6 M solution in hexane, 3.2 mmol) under an inert atmosphere. The resulting solution was stirred at -10 °C for 2 h during which time the reaction mixture was cooled to -90 °C and treated via a syringe with a solution of nitron **1** (0.235 g, 1 mmol) in Et₂O (10 mL), previously treated with Et₂AlCl (1 mL of a 1.0 M solution in hexane, 1 mmol) at ambient temperature for 5 min. The rate of addition was adjusted so as to keep the internal temperature below -80 °C. The reaction mixture was stirred for 30 min at -80 °C and then quenched with a 1N aqueous solution of sodium hydroxide (10 mL). The mixture was stirred at ambient temperature for 10 min and diluted with ethyl acetate (15 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with brine and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure to give the crude mixture of diastereomeric hydroxylamines. The NMR analysis of this mixture revealed the presence of a unique diastereomer (ds > 95%) whose absolute configuration was confirmed by X-ray crystallography of the corresponding syn isomer [1]. Purification by column chromatography (hexane/diethyl ether 60:40) on silica gel afforded **3** as a white solid (0.293 g, 83%).

Mp 97-99 °C

TLC (hexane/diethyl ether 60:40) R_f 0.49

$[\alpha]_D^{20} = -22.3$ (c 0.41, CHCl₃)

¹H NMR (CDCl₃) δ 1.32 (s, 3H), 1.34 (s, 3H), 3.81 (d, 1H, J=13.0 Hz), 3.82 (d, 1H, J = 13.0 Hz), 4.01 (d, 1H, J = 8.6 Hz), 4.12 (dd, 1H, J=5.7, 8.7 Hz), 4.20 (dd, 1H, J = 6.1, 8.7 Hz), 4.60 (bs, 1H, ex. D₂O), 4.77 (pseudo dt, 1H, J = 5.8, 8.6 Hz), 6.82 (s, 1H), 7.15-7.43 (m, 9H).

¹³C NMR (CDCl₃) δ 25.5, 26.8, 61.8, 66.2, 67.2, 75.2, 111.4, 121.2, 122.8, 124.1(2C), 127.5, 127.6, 128.3(2C), 128.4, 129.4, 137.1, 153.1.

Anal. Calcd. for C₂₁H₂₃NO₄: C, 71.37; H, 6.56; N, 3.96. Found: C, 71.22; H, 6.38; N, 3.76.

References and Notes

1. Merino, P.; Franco, S.; Martinez, I.; Merchan, F. L.; Tejero, T. *Unpublished results*. Data is available from the authors.

Sample Availability: Available from the authors and MDPI: [MDPI Reg. No. 15811](#).

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