Molecules **1998**, *3*, M86

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

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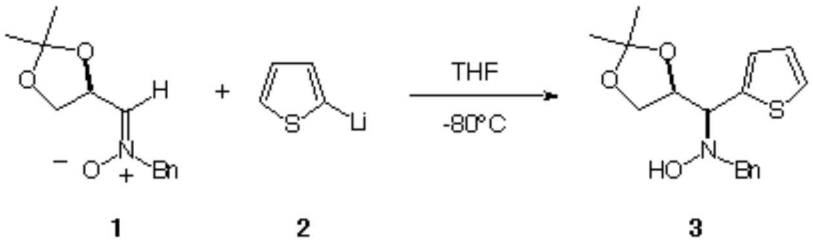
Received: 15 May 1998 / Published: 19 May 1998



Scheme

A cooled solution (-90°C) of thiophene (0.252 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 atmopshere. The resulting solution was stirred at -60 °C for 1 h during which time the reaction mixture was cooled to -90 °C and treated with a solution of nitrone **1** (0.235 g, 1 mmol) in THF (10 mL) added drop by drop. The rate of addition was adjusted so as to keep the internal temperature below -80°C. The reaction mixture was stirred for 1 h at -80 °C and then quenched with saturated aqueous ammonium chloride (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 [1]. Purification by column chromatography (hexane/diethyl ether 60:40) on silica gel afforded **3** as a white solid (0.287 g, 90%).

Mp 117-119°C.

TLC (hexane/diethyl ether 60:40) R_f 0.55.

$[a]_D^{20}$ = -24.9 (c 0.41, $CHCl_3$).

^{1}H NMR ($CDCl_3$) d 1.37 (s, 3H), 1.42 (s, 3H), 3.48 (dd, 1H, J = 5.5, 9.0 Hz), 3.65 (d, 1H, J = 12.7 Hz), 3.75 (dd, 1H, J = 6.5, 9.0 Hz), 3.96 (d, 1H, J = 12.7 Hz), 4.00 (d, 1H, J = 9.4 Hz), 4.72 (ddd, 1H, J = 5.5, 6.5, 9.4 Hz), 5.35 (bs, 1H, ex. D_2O), 6.9-7.4 (m, 8H).

^{13}C NMR ($CDCl_3$) d 25.6, 26.8, 61.4, 67.3, 72.1, 76.6, 110.1, 121.9, 123.8, 126.1, 126.6, 127.4, 128.5, 135.8, 137.0.

Anal. Calcd. for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.39. Found: C, 64.04; H, 6.81; N, 4.22.

References and Notes

1. Merino, P.; Franco, S.; Martinez, I.; Merchan, F.L.; Tejero, T. *Unpublished results*. Data available from the authors and MDPI, MDPI Reg. No. 15818.

Sample Availability: Available from the authors and MDPI.