

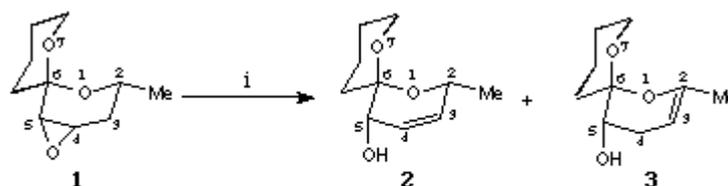
*Molecules* **1997**, *2*, M15

## [2R\*,5S\*,6S\*]-2-Methyl-1,7-dioxaspiro[5.5]undec-3-en-5-ol

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Received: 16 June 1997 / Published: 20 June 1997



*Reagents and Conditions:* (i) lithium diethylamide (1.0 equiv), solvent (see table 1), -35 °C → room temp., 18h. (For yields and product ratios, see table 1).

**Table 1:** Product ratios for allylic and homoallylic alcohols (2) and (3).

<i>Epoxide</i>	<i>Solvent</i>	<i>Product Ratio</i> <i>Allylic: Homoallylic</i>	<i>Overall Yield</i>
<b>1</b>	THF	1.0 : 1.3	73%
<b>1</b>	Ether/Hexane (2:1)	1.4 : 1.0	74%
<b>1</b>	Hexane	4.0 : 1.0	79%

Isomerisations of epoxides to allylic alcohols have been effected by strong non-nucleophilic bases such as lithium dialkylamides. The formation of allylic alcohols from the reaction of epoxides with lithium amide bases appears to proceed via a b-elimination pathway when the reaction is performed in relatively non-polar solvents [1].

To a solution of dry diethylamine (0.085 ml, 0.82 mmol) in dry hexane (40 ml) under a nitrogen atmosphere at -35 deg.C, was added n-butyllithium (1.3 ml of a 1.7 mol L solution in hexane, 7.93 mmol) dropwise, and the resultant suspension stirred for 0.5 h. To this was added [2R\*,4S\*,5S\*,6S\*]-4,5-epoxy-2-methyl-1,7-dioxaspiro[5.5]undecane (**1**) (126 mg, 0.68 mmol) via a closed solid addition tube, the suspension allowed to warm to room temperature and stirred for an additional 16 h. After quenching with sodium dihydrogen phosphate solution (10 ml, 10% w/v), the reaction mixture was extracted with ethyl acetate (3x 50 ml). The combined extracts were washed with water (20 ml) and dried over sodium sulphate. Removal of the solvent under reduced pressure gave an orange oil, that was purified by flash chromatography using hexane-ethyl acetate (6:4) as eluent to afford [2R\*,5S\*,6S\*]-2-Methyl-1,7-dioxaspiro[5.5]undec-3-en-5-ol (**2**, 80 mg, 63%) as colourless needles [2].

M.p. 82-83 deg.C.

IR (Nujol)  $\text{cm}^{-1}$  3640-3200 (br, s, OH), 1650 (w, C=C), 1019 (C-O), 890 (m, C-O).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) 1.28 (3H, d,  $J_{\text{Me},2}$  7.0 Hz, Me), 1.47-2.04 (7H, m, 9- $\text{CH}_2$ , 10- $\text{CH}_2$ , 11- $\text{CH}_2$  and OH), 3.51 (1H, dd,  $J_{5,4}$  5.0 and  $J_{5,3}$  1.8 Hz, 5-H), 3.67 (1H, ddd,  $J_{8\text{ax},8\text{eq}}$  11.2,  $J_{8\text{ax},9\text{ax}}$  11.2 and  $J_{8\text{ax},9\text{eq}}$  3.2 Hz, 8ax-H), 3.73-3.77 (1H, m, 8eq-H), 4.24 (1H, ddq,  $J_{2,\text{Me}}$  7.0,  $J_{2,3}$  3.4 and  $J_{2,4}$  1.5 Hz, 2-H), 5.84 (1H, dd,  $J_{3,4}$  10.2 and  $J_{3,2}$  3.4 Hz, 3-H), 5.91 (1H, ddd,  $J_{4,3}$  10.2,  $J_{4,5}$  5.0 and  $J_{4,2}$  1.5 Hz, 4-H).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) 18.3, 25.0, 30.8 ( $\text{CH}_2$ , C-9, C-10 and C-11), 20.5 ( $\text{CH}_3$ , Me), 62.9 ( $\text{CH}_2$ , C-8), 64.6 ( $\text{CH}$ , C-2), 66.6 ( $\text{CH}$ , C-5), 97.1 (quat, C-6), 124.2, 133.8 (C-3 and C-4).

CI-MS 185, (M+H, 40%), 167 (M+H-H $_2$ O, 100), 101 (50), 84 (20).

Anal. calc. for  $\text{C}_{10}\text{H}_{16}\text{O}_3$  C, 65.11; H, 8.56%,  $\text{M}^+\text{H}$  (CI,  $\text{NH}_3$ ) 185.1180 found C, 65.20; H, 8.75%;  $\text{M}^+\text{H}$ , 185.1177.

*Acknowledgment:* The authors gratefully acknowledge financial support from the Australian Research Council and The University of Sydney.

## References and Notes

1. Crandall, J. K. *Org. React.* **1983**, 346.
2. Another product (**3**, a colourless oil, 20 mg, 16%) will be reported in the following short note. Brimble, M. A.; Johnston, A. D. *Molecules* **1997**, 2, M16.

*Sample Availability:* Available from MDPI, MDPI 11861.

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