Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Stereochemistry of 1,2-Elimination Reactions at the E2-E1cB Interface − *tert*-Butyl 3-Tosyloxybutanoate and its Thioester

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Electronic Supplementary Information

***tert*-Butyl 3-trimethylsilyloxy-2-butenoate 13.** *tert*-Butyl acetoacetate (44 mL, 0.265 mol) and triethylamine (6 mL) were mixed together and 1-trimethylsilylimidazole (40 mL, 0.273 mol) was added (N_2). The reaction mixture became warm and was stirred for 1 h at 40 °C. Filtration and vacuum distillation (bp 42-45 °C at 0.4 mm Hg) led to **13** (36.5 g, 60% including unreacted starting material). **13**: δ_H (200 MHz; $CDCl_3$; Me_4Si) 5.01 [(*Z*)-**13** vinyl proton], 5.06 [(*E*)-**13** vinyl proton]; 1:9 ratio. The silyl enol ether of *tert*-butyl acetoacetate was quite moisture sensitive and very unstable in the presence of acids. It was also unstable in the presence of silica gel, even in the presence of triethylamine; this made SiO_2 chromatography impossible.

13 (4.94 g) was chromatographed on 125 g of Florisil (dried overnight at 120 °C). The (*E*)-isomer (>99.5%, 2.32 g, 47%) eluted in 2-4 % Et_2O/hexane. (*E*)-**13**: δ_H (60 MHz; $CDCl_3$; Me_4Si) 0.2 (9H, s), 1.4 (9H, s), 2.1 (3H, s), 4.9 (1H, s). Later fractions contained *E*/*Z* mixtures.

***tert*-Butyl 3-*tert*-butyldimethylsilyloxy-2-butenoate 14.** To a solution (under N_2) of *tert*-butyldimethylsilyl chloride (14.35 g, 0.095 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (6.15 g, 0.106 mol) in 172 mL of benzene (distilled from Na) was added *tert*-butyl acetoacetate (14.3 g, 0.090 mol), and the mixture was refluxed for 30 min. The benzene was removed by distillation, and the silyl enol ether was distilled (62-72 °C at 0.3 mm Hg), (17.8 g, 73%), *E*/*Z* 5.3:1. **14** (3.82 g) was chromatographed on 175 g of Florisil (dried overnight at 120 °C). (*E*)-**14** (>99.5%, 2.3 g, 60%) eluted in 3-6 % Et_2O/hexane. A number of later fractions contained *E*/*Z* mixtures. (*E*)-**14**: δ_H (200 MHz, $CDCl_3$, Me_4Si) 0.2 (6H, s), 0.9 (9H, s), 1.4 (9H, s), 2.2 (3H, s), 5.06 (1H, s); (*Z*)-**14**: δ_H 4.98 (1H, s).

***tert*-Butyl (2*R**,3*S**)-3-trimethylsilyloxy-2,3-$^2H_2$-butanoate 15**. (*E*)-**13** (4.2 g, 18 mmol) and Wilkinson's catalyst (0.68 g. 0.73 mmol) in 75 mL benzene were reacted with $^2H_2$ (200 psi) at 50 °C for 5 days. **15** (2.1 g, 50%) was recovered by short-path vacuum distillation. **15**: δ_H (200 MHz; $CDCl_3$, Me_4Si) 0.2 (9H, s), 1.2 (3H, s), 1.4 (9H, s), 2.3 (1H, s); δ_D (30 MHz; $CHCl_3$; CDCl3) 2.3 (2D), 4.2 (3D).

***tert*-Butyl (2*R**,3*S**)-3-*tert*-butyldimethylsilyloxy-2,3-$^2H_2$-butanoate 16.** Reduction of (*E*)-**14** (7.8 g, 29 mmol) with $^2H_2$ in the presence of Wilkinson's catalyst (1.06 g, 1.1 mmol) led to **16**. **16**: δ_H (200 MHz; $CDCl_3$; Me_4Si) 0.2 (6H, s), 0.9 (9H, s), 1.2 (3H, s), 1.4 (9H, s), 2.2 (s, 1H); δ_D (30 MHz; $CHCl_3$; $CDCl_3$) 2.3 (2D), 4.2 (3D).