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 (N₂). 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; CDCl₃; Me₄Si) 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 SiO₂ 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 % Et₂O/hexane. (E)-13: δ_H (60 MHz; CDCl₃; Me₄Si) 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 N₂) 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 % Et₂O/hexane. A number of later fractions contained E/Z mixtures. (E)-14: δ_H (200 MHz, CDCl₃, Me₄Si) 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 (2R*,3S*)-3-trimethylsilyloxy-2,3-²H₂-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 ²H₂ (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; CDCl₃, Me₄Si) 0.2 (9H, s), 1.2 (3H, s), 1.4 (9H, s), 2.3 (1H, s); δ_D (30 MHz; CHCl₃; CDCl₃) 2.3 (2D), 4.2 (3D).

*tert*-Butyl (2R*,3S*)-3-tert-butyldimethylsilyloxy-2,3-²H₂-butanoate 16. Reduction of (E)-14 (7.8 g, 29 mmol) with ²H₂ in the presence of Wilkinson’s catalyst (1.06 g, 1.1 mmol) led to 16. 16: δ_H (200 MHz; CDCl₃; Me₄Si) 0.2 (6H, s), 0.9 (9H, s), 1.2 (3H, s), 1.4 (9H, s), 2.2 (s, 1H); δ_D (30 MHz; CHCl₃; CDCl₃) 2.3 (2D), 4.2 (3D).