Geometrically Selective Synthesis of Functionalized β,β -Disubstituted Vinylic Sulfoxides by Cu-Catalyzed Conjugate Addition of Organozinc Reagents to 1-Alkynyl Sulfoxides

Naoyoshi Maezaki, Hiroaki Sawamoto, Ryoko Yoshigami,
Tomoko Suzuki, and Tetsuaki Tanaka*

Supporting Information

NMR spectra were recorded in CDCl₃ solution at 500 MHz (¹H) and 75 MHz (¹³C). IR absorption spectra (FT: diffuse reflectance spectroscopy) were recorded with KBr powder, and only noteworthy absorptions (cm⁻¹) are listed. Column chromatography was carried out using Merck silica gel 60 (70–230 mesh). All air- or moisture-sensitive reactions were carried out in flame-dried glassware under an atmosphere of Ar. All solvents were dried and distilled according to standard procedures. All organic extracts were dried over anhydrous MgSO₄, filtered, and concentrated with a rotary evaporator under reduced pressure. Allylzinc bromide and *n*-BuZnI were prepared *in situ* according to the literature¹ (allylzinc bromide: reaction temperature 0 °C, reaction time 4 h; *n*-BuZnI: reaction temperature 40 °C, reaction time 4 h), and the concentration was determined by GC analysis of a hydrolyzed reaction aliquot using *n*-decane as an internal standard.²

(*R*)-[(*Z*)-2-Ethyl-1-hexenyl] *p*-Tolyl Sulfoxide [(*Z*)-2a]. Et₂Zn (0.99 M solution in hexane) (0.32 mL, 0.318 mmol) was slowly added to a mixture of 1-alkynyl sulfoxide **1a** (35.0 mg, 0.159 mmol) and CuI (0.6 mg, 3.18 μmol) in THF (0.16 mL) with stirring at –78 °C. The stirring was continued for 15 min at –78 °C and at 0 °C for 2 h. The reaction was quenched with 28% NH₄OH and the mixture was extracted with Et₂O. The extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (3:1) to give (*Z*)-**2a** (38.8 mg, 97%) as a yellow oil. [α]_D²² –181 (*c* 0.51, CHCl₃). ¹H NMR (CDCl₃) δ: 0.96 (t, *J* = 7.3 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H), 1.38–1.51 (m, 3H), 1.56–1.63 (m, 1H), 2.19 (q, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 2.54 (ddd, *J* = 13.4, 9.8, 6.1 Hz, 1H), 2.63 (ddd, *J* = 13.4, 10.4, 5.5 Hz, 1H), 6.00 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H). ¹³C NMR (CDCl₃) δ: 11.5, 13.8, 21.3, 22.7, 29.2, 31.0, 32.2, 124.1 (2C), 129.8 (2C), 130.7, 140.7, 141.8, 158.0. IR: 2960 (CH), 1493 (C=C), 1041 (S=O). MS (FAB) *m/z*: 251 (MH⁺). HRMS (FAB) Calcd C₁₅H₂₃OS (MH⁺): 251.1470. Found: 251.1469.

(*R*)-[(*E*)-2-Butyl-1,4-pentadienyl] *p*-Tolyl Sulfoxide (3a**).** A 0.95 M solution of allylzinc bromide in THF (0.56 mL, 0.535 mmol) was slowly added to a mixture of 1-alkynyl sulfoxide **1a** (58.9 mg, 0.267 mmol) and Cu(OTf)₂ (1.9 mg, 5.35 μmol) in THF (0.27 mL) with stirring at –78 °C. The stirring was continued for 15 min at –78 °C and at 0 °C for 2 h. The reaction was quenched with saturated NH₄Cl and the mixture was extracted with Et₂O. The extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (5:1) to give **3a** (56.8 mg, 81%) as a yellow oil. [α]_D²⁶ –175 (*c* 0.57, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ: 0.96 (t, *J* = 7.3 Hz, 3H), 1.38–1.51 (m, 3H), 1.56–1.64 (m,

(1) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. J. *Org. Chem.* **1988**, *53*, 2390–2392.

(2) Knochel, P.; Rozema, M. J.; Tucker, C. E. In *Organocopper Reagents: A Practical Approach*; Taylor, R. J. K., Ed.; Harwood, L. M.; Moody, S. J., Series Eds.; Oxford University Press: Oxford, 1994, Ch. 4, pp 85–104.

1H), 2.41 (s, 3H), 2.54 (ddd, $J = 13.4, 9.2, 6.1$ Hz, 1H), 2.62 (ddd, $J = 13.4, 9.8, 5.5$ Hz, 1H), 2.89 (d, $J = 6.7$ Hz, 2H), 5.08 (dd, $J = 17.1, 1.8$ Hz, 1H), 5.11 (dd, $J = 9.8, 1.8$ Hz, 1H), 5.71 (ddt, $J = 17.1, 9.8, 6.7$ Hz, 1H), 6.04 (s, 1H), 7.31 (d, $J = 7.9$ Hz, 2H), 7.49 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ : 13.8, 21.3, 22.6, 30.7, 32.1, 40.6, 118.4, 124.1 (2C), 129.9 (2C), 132.6, 133.5, 140.8, 141.6, 154.4. IR (KBr): 2958 (CH), 1493 (C=C), 1039 (S=O). MS (FAB) m/z : 263 (MH^+). HRMS (FAB) Calcd $\text{C}_{16}\text{H}_{23}\text{OS}$ (MH^+): 263.1470. Found: 263.1479.

(R)-[(E)-2-Ethyl-1-hexenyl] *p*-Tolyl Sulfoxide [(E)-2a]. In a similar manner as described for **3** but with using a 0.95 M solution of *n*-BuZnI in THF (0.55 mL, 0.520 mmol), 1-alkynyl sulfoxide **1g** (50.0 mg, 0.258 mmol) was converted into (E)-2a (48.2 mg, 74%). Yellow oil. $[\alpha]_{\text{D}}^{26} -166$ (c 0.80, CHCl_3). ^1H NMR (CDCl_3) δ : 0.88 (t, $J = 7.3$ Hz, 3H), 1.17 (t, $J = 7.3$ Hz, 3H), 1.30 (qt, $J = 7.3, 7.3$ Hz, 2H), 1.39–1.45 (m, 2H), 2.16 (t, $J = 7.3$ Hz, 2H), 2.40 (s, 3H), 2.56 (dq, $J = 14.6, 7.3$ Hz, 1H), 2.65 (dq, $J = 14.6, 7.3$ Hz, 1H), 5.97 (s, 1H), 7.30 (d, $J = 7.9$ Hz, 2H), 7.49 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (CDCl_3) δ : 13.5, 13.7, 21.3, 22.3, 25.5, 29.2, 35.6, 124.0 (2C), 129.8 (2C), 131.0, 140.7, 141.8, 157.8. IR: 2962 (CH), 1493 (C=C), 1039 (S=O). MS (FAB) m/z : 251 (MH^+). HRMS (FAB) Calcd $\text{C}_{15}\text{H}_{23}\text{OS}$ (MH^+): 251.1470. Found: 251.1469.

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