Highly Regioselective Rearrangement of 2-Substituted Vinylepoxides Catalyzed by Gallium (III) Triflate

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Supporting Information

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General Information. All reactions were carried out under nitrogen atmosphere. *t*-BuOH was distilled over sodium. Toluene was purified by distillation over sodium-benzophenone ketyl prior to use. Dichloromethane was distilled over CaH₂ before use.

1. General procedure for preparation of the vinylepoxides 1a-j¹

To an Schlenk tube was added sequentially tetrahydrothiophene (10 μ L, 0.1 mmol), trimethylsilylallylbromide (579 mg, 3.0 mmol), aldehyde (2.0 mmol), dry K₂CO₃ (powdered, 331 mg, 2.4 mmol) and *t*-BuOH (2.0 ml) under N₂ atmosphere. The resulting mixture was refluxed for 12~24 h, filtered rapidly through a funnel with a thin layer of silica gel and eluted with ethyl acetate. The filtrate was concentrated and the residue was purified by chromatography (hexane/ethyl acetate, 100/1, v/v) on silica gel to afford the desired product.

(1) **1a, 1b, 1c, 1d, 1i, and 1j** please see ref. 1a.

(2) **1e, 1f** please see ref. 1b.

(3)

1g Yield: 99%, trans/cis = 72/28 IR (film) ν/cm^{-1} 3052 (w), 2956 (m), 1616 (w), 1510 (w), 1248 (s), 865 (s), 839 (s), 799 (s), 778 (s). ¹H NMR (300 MHz, CDCl₃/TMS) for a mixture of cis- and trans-isomers (with a ratio of 28 to 72) δ 8.04-7.96 (m, 1H), 7.88-7.76 (m, 2H), 7.54-7.43 (m, 4H), 6.23 (1H), 5.99 (dd, *J* = 7.2, 18.6 Hz, 0.72H), 5.37 (dd, *J* = 7.8, 18.9 Hz, 0.29H), 4.67 (d, *J* = 4.5 Hz, 0.27H), 4.40 (d, *J* = 2.4 Hz, 0.70H), 3.87 (dd, *J* = 4.5, 7.5 Hz, 0.33H), 3.34 (dd, *J* = 2.1, 7.2 Hz, 0.69H), 0.10 (s, 6H), -0.20 (s, 3H). MS (EI, *m/z*, rel. intensity) 268 (M⁺, 31.45), 267 (28.01), 179 (27.81), 178 (70.45), 165 (24.99), 139 (32.23), 75 (19.39), 73 (100.00). HRMS Calcd for C₁₇H₂₀OSi: 268.1283. Found: 291.1176 (M + Na⁺).

¹ (a) Li, K.; Deng, X.-M.; Tang, Y. *Chem. Commun.* **2003**, 2074. (b) Zhou, Y.-G.; Li, A.-H.; Hou, .X.-L.; Dai, L.-X. *Chem. Commun.* **1996**, 1353.

(4)

1h Yield: 26%, dr = 51/49. IR (film) ν/cm^{-1} 2956 (m), 1606 (w), 1512 (s), 1379 (w), 1249 (m), 1232 (m), 872 (m), 838 (s). ^1H NMR (300 MHz, CDCl_3/TMS) for a mixture of cis- and trans-isomers (with a ratio of 49 to 51) δ 7.34-7.28 (m, 2H), 7.24-6.98 (m, 2H), 6.17 (1H), 5.98 (dd, $J = 6.6, 18.3$ Hz, 0.51H), 5.28 (dd, $J = 7.8, 18.3$ Hz, 0.49H), 3.47 (d, $J = 8.1$ Hz, 0.51H), 3.26 (d, $J = 6.3$ Hz, 0.49H), 1.66 (3H), 0.14 (s, 4.59H), -0.08 (s, 4.41H). MS (EI, m/z , rel. intensity) 250 (M^+ , 14.97), 160 (16.89), 122 (53.63), 121 (25.17), 96 (18.21), 75 (26.86), 73 (100.00), 59 (16.01), 43 (27.45). HRMS Calcd for $\text{C}_{14}\text{H}_{19}\text{FOSi}$: 250.1189. Found: 251.1262 ($\text{M} + \text{H}^+$)

2. NMR spectra for all new compounds.

^1H NMR **1g**

¹H NMR 1h

¹H NMR 3a

¹³C NMR 3a

¹H NMR **3b**

¹³C NMR 3b

¹H NMR 2c

¹³C NMR 2c

¹H NMR 2d

¹³C NMR 2d

¹H NMR 2e

¹³C NMR 2e

¹H NMR 2f

¹³C NMR 2f

¹H NMR 2g

¹³C NMR 2g

¹H NMR 2h

¹³C NMR 2h

¹H NMR 4j-E

¹³C NMR 4j-E

¹H NMR 5c

¹³C NMR 5c