Electronic Supplementary Information

A Facile Tetrahydrothiophene-catalyzed Ylide Route to Vinyloxiranes

Kai Li, Xian-Ming Deng, Yong Tang *

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 354 Fenglin Lu, Shanghai 200032, China. E-mail: tangy@mail.sioc.ac.cn

1. General procedure for the preparation of vinyloxiranes.

To a Schlenk tube were added tetrahydrothiophene (5.7 mg, 0.06 mmol), allylbromide (1.68 ml, 19.4 mmol), 4-chlorobenzaldehyde (907 mg, 6.5 mmol), dry K_2CO_3 (powdered, 1.07 g, 7.8 mmol) and *t*-BuOH (2 mL, was distilled over sodium) under N_2 atmosphere. The resulting mixture was refluxed for 12 hours, and then filtered rapidly through a short silica gel column (ethyl acetate as the eluent). The filtrate was concentrated and the residue was purified by chromatography (hexane/ethyl acetate, 200/1, v/v) on silica gel to afford the desired product. Yield: 1.09 g, (94%).

1-(4-Chlorophenyl)-1,2-epoxy-3-butene[1] (**3a**, R = 4-ClC_6H_4, R^1 = H). *Cis/trans* = 36/64；yield：0.81 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *trans*-isomer: δ 3.32 (dd, J_1 =1.9 Hz, J_2 = 7.3 Hz, 1H), 3.74 (d, J = 2.0 Hz, 1H), 5.33 (d, J = 10.2 Hz, 1H), 5.54 (d, J = 17.0 Hz, 1H), 5.73 (m, 1H), 7.30 (m, 4H); for *cis*-isomer: δ 3.57 (m, 1H), 4.12 (d, J = 4.5 Hz, 1H), 5.48 (m, 1H), 5.26 (m, 1H), 5.64 (m, 1H), 7.23 (m, 4H).

1,2-Epoxy-1-phenyl-3-butene[1] (**3b**, R = C_6H_5， R^1 = H). *Cis/trans* = 33/67；yield：0.81g (85%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *cis*-isomer: δ 3.66 (dd, J_1 = 7.8 Hz, J_2 = 4.2 Hz, 1H), 4.25 (d, J = 4.2 Hz, 1H), 5.25-5.5 9 (m, 3H), 7.33 (m, 5H); for *trans*-isomer: δ 3.37 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 3.78 (d, J = 1.8 Hz, 1H), 5.34 (dd, J_1 = 10.2 Hz, J_2 = 1.2 Hz, 1H), 5.53 (dd, J_1 = 17.4 Hz, J_2 = 1.5 Hz, 1H), 5.72 (m, 1H), 7.34 (m, 5H).

1,2-Epoxy-1-(4-nitrophenyl)-3-butene[1] (**3c**, R = 4-$NO_2C_6H_4$， R^1 = H). *Cis/trans* = 38/62； yield：1.11 g (96%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *cis*-isomer: δ 3.50 (m, 1H), 4.06 (d, J = 4.2 Hz, 1H), 5.20 (m, 3H), 7.25 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H); for *trans*-isomer: δ 3.03 (dd, J_1 = 6.3 Hz, J_2 = 2.1 Hz, 1H), 3.60 (d, J = 2.2 Hz, 1H), 5.21 (m, 3H), 7.25 (d, J = 8.3 Hz, 2H), 7.94 (d， J = 8.4 Hz, 2H).

1,2-Epoxy-1-(4-methoxylphenyl)-3-butene[1] (**3d**, R = 4-$CH_3OC_6H_4$, R^1 = H). *Cis/trans* = 30/70； yield：0.97 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *cis*-isomer: δ 3.63 (dd, J_1 = 7.8 Hz, J_2 = 4.2 Hz, 1H), 3.80 (s, 3H), 4.20 (d, J = 4.2 Hz, 1H), 5.50 (m, 3H), 6.87 (d, J = 9.3 Hz, 2H), 7.26 (d, J = 9.3 Hz, 2H); for *trans*-isomer: δ 3.36 (m, 1H), 3.73 (d, J = 2.1 Hz, 1H), 3.80 (s, 3H), 5.50 (m, 3H), 6.87 (d, J = 9.3 Hz, 2H), 7.26 (d, J = 9.3 Hz, 2H).

1,2-Epoxy-1-nonyl-3-butene[1] (**3e**, R = *n*-C_9H_{19}, R^1 = H). *Cis/trans* = 55/45； yield：1.32 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *cis*-isomer: δ 0.87 (t, J = 6.9 Hz, 3H), 1.40 (m, 16H), 3.18 (m, 1H), 3.40 (dd, J_1 = 6.3 Hz, J_2 = 4.4 Hz, 1H), 5.50 (m, 3H); for *trans*-isomer: δ 0.87 (t, J = 6.9 Hz, 3H), 1.25-1.59 (m, 16H), 2.82 (m, 1H), 3.09 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz 1H), 5.24-5.54 (m, 3H).

1-(4-Chlorophenyl)-1,2-epoxy-2-trimethylsilyl-3-butene[2] (**3f**, R = 4-ClC_6H_4, R^1 = TMS). Tetrahydrothiophene as the catalyst. *Cis/trans* = 25/75； yield：1.33 g (83%). ^{1}H NMR (300 MHz $CDCl_3$, TMS) for *trans*-isomer: δ 0.10 (s, 9H), 3.30 (dd, J_1 = 4.2 Hz, J_2 = 8.1 Hz, 1H), 3.76 (d, J = 2.1 Hz, 1H), 5.83 (dd, J_1 = 8.1 Hz, J_2 = 18.0 Hz, 1H), 6.22 (d, J = 18.0 Hz, 1H), 7.31 (m, 4H); for *cis*-isomer: δ －0.02 (s, 9H), 3.65 (dd, J_1 = 4.2 Hz, J_2 = 8.1 Hz, 1H), 4.19 (d, J = 8.0 Hz, 1H), 5.50 (dd, J_1 = 8.0 Hz, J_2 = 16.2 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 7.30 (s, 4H).

Compound 4 as the catalyst. *Cis/trans* = 40/60； yield：40%; 37% ee for *trans*-**3f** (Determined by HPLC: AD, *i*-PrOH/hexane = 1/100, 0.6 mL/min, 205 nm; t_r (major) = 8.17 min, t_r (minor) = 11.48 min).

1,2-Epoxy-1-phenyl-2-trimethylsilyl-3-butene[2] (**3g**, R = C_6H_5, R^1 = TMS). *Cis/trans* = 24/76; yield: 1.24 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *trans*-isomer: δ

0.12 (s, 9H), 3.37 (dd, J_1 = 1.8 Hz, J_2 = 7.2 Hz, 1H), 3.80 (d, J = 1.8 Hz, 1H), 5.88 (dd, J_1 = 7.2 Hz, J_2 = 18.3 Hz, 1H), 6.24 (d, J = 18.3 Hz, 1H), 7.35 (m, 5H); for *cis*-isomer: δ 0.02 (s, 9H), 3.73 (dd, J_1 = 3.3 Hz, J_2 = 7.8 Hz, 1H), 4.31 (d, J = 3.3 Hz, 1H), 5.68 (dd, J_1 = 7.8 Hz, J_2 = 18.9 Hz, 1H), 6.12 (d, J = 18.9 Hz, 1H), 7.35 (m, 5H).

1,2-Epoxy-1-(4-nitrophenyl)-2-trimethylsilyl-3-butene[2] (**3h**, R = 4-$NO_2C_6H_4$, R^1 = TMS). *Cis/trans* = 30/70； yield：1.42 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *trans*-isomer: δ 0.16 (s, 9H), 3.38 (dd, J_1 = 1.2 Hz, J_2 = 8.7 Hz, 1H), 3.95 (d, J = 1.5 Hz, 1H), 5.90 (dd, J_1 = 1.2 Hz, J_2 = 18.6 Hz, 1H), 6.32 (d, J = 18.6 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 8.26 (d, J = 8.4 Hz, 2H); for *cis*-isomer: δ 0.01 (s, 9H), 3.81 (dd, J_1 = 4.2 Hz, J_2 = 7.5 Hz, 1H) 4.35 (d, J = 4.5 Hz, 1H), 5.51 (dd, J_1 = 7.5 Hz, J_2 = 18.9 Hz, 1H), 6.35 (d, J = 19.2 Hz, 1H), 7.58 (d, J = 8.7 Hz, 2H), 8.27 (d, J = 8.7 Hz, 2H).

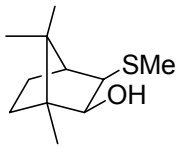
1-(2-Chlorophenyl)-1,2-epoxy-2-trimethylsilyl-3-butene (**3i**, R = 2-ClC_6H_4, R^1 = TMS). *Cis/trans* = 27/73； yield：1.36 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *trans*-isomer: δ 0.18 (s, 9H), 3.30 (d, J = 7.5 Hz, 1H), 4.22 (s, 1H), 5.95 (dd, J_1 = 7.2 Hz, J_2 = 18.6 Hz, 1H), 6.35 (d, J = 17.4 Hz, 1H), 7.43 (m, 4H); for *cis*-isomer: δ 0.01 (s, 9H), 3.84 (dd, J_1 = 4.2 Hz, J_2 = 7.2 Hz, 1H), 4.41 (d, J = 3.9 Hz, 1H), 5.50 (dd, J_1 = 7.5 Hz, J_2 = 18.9 Hz, 1H), 6.37 (d, J = 18.6 Hz, 1H), 7.46 (s, 4H); IR ν/cm^{-1} 2956, 1617, 1516, 1248, 839; MS (EI, m/z, rel intensity) 252 ($[M]^+$, 3.20%), 254 ($[M]^+$, 1.18%); HRMS(EI) Calcd. for $C_{13}H_{17}ClOSi$: 252.07516; Found: 252.07659.

1,2-Epoxy-1-nonyl-2-trimethylsilyl-3-butene[2] (**3j**, R = *n*-C_9H_{19}, R^1 = TMS). *Cis/trans* = 42/58; yield: 1.50 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *trans*-isomer: δ 0.08 (s, 9H), 0.88 (t, J = 6.9 Hz, 3H), 1.45 (m, 16H), 2.85 (m, 1H), 3.08 (dd, J_1 = 2.1 Hz, J_2 = 4.8 Hz, 1H), 5.70 (dd, J_1 = 7.2 Hz, J_2 = 18.6 Hz, 1H), 6.15 (d, J = 18.6 Hz, 1H); for *cis*-isomer: δ 0.08 (s, 9H), 0.88 (t, J = 6.6 Hz, 3H), 1.44 (m, 16H), 3.08 (m, 1H), 3.40 (m, 1H), 5.85 (dd, J_1, = 7.2 Hz, J_2 = 18.9 Hz, 1H), 6.20 (d, J = 18.6 Hz, 1H).

1-Cyclohexyl-1,2-epoxy-2-trimethylsilyl-3-butene[2] (**3k**, R = *cyclo*-C_6H_{11}, R^1 = TMS). *Cis/trans* = 50/50； yield：1.11 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS)

for *trans*-isomer: δ 0.03 (s, 9H), 1.15 (m, 6H), 1.28 (m, 4H), 1.86 (d, J = 3.3 Hz, 1H), 2.66 (dd, J_1 = 0.6 Hz, J_2 = 2.7 Hz, 1H), 3.14 (dd, J_1 = 0.6 Hz, J_2 = 2.4 Hz, 1H), 5.71 (dd, J_1 = 3.6 Hz, J_2 = 6.9 Hz, 1H), 6.09 (d, J = 6.3 Hz, 1H); for *cis*-isomer: δ 0.05 (s, 9H) 1.29 (m, 6H), 1.73 (m, 4H), 1.97 (m, 1H), 2.80 (dd, J_1 = 1.5 Hz, J_2 = 8.4 Hz, 1H), 3.40 (dd, J_1 = 4.2 Hz, J_2 = 6.9 Hz, 1H), 5.88 (dd, J_1 = 6.9 Hz, J_2 = 18.6 Hz, 1H), 6.18 (d, J = 18.6 Hz, 1H).

2. Preparation of chiral catalysts



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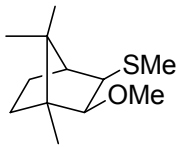

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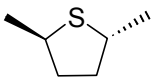

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Compound **4** was prepared according to the literature. [3]

Compound **5** was prepared according to the literature. [4]

Compound **6** was prepared according to the literature. [5]

3. Reference

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