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The First Example of a Gold-Catalyzed C-S Bond Formation: Cycloisomerization of α-Thioallenes to 2,5-Dihydrothiophenes

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General Information

^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX-400 or DRX-500 spectrometer at room temperature in $CDCl_3$ or C_6D_6 as solvent. Chemical shifts were determined relative to the residual solvent peaks ($CHCl_3$: δ = 7.26 for protons, δ = 77.16 for carbon atoms. C_6H_6: δ = 7.16 for protons, δ = 128.06 for carbon atoms). The signals of the major component of a product mixture are marked with an asterisk (*). GC analyses were carried out with a Carlo Erba GC 8000 gas chromatograph with helium as the carrier gas and an OV-1701 capillary column.

Starting materials (Thioallenes 1a-1e)

1-Methoxy-3,6-dimethylhepta-3,4-diene-2-thiol (1a)

^{1}H NMR ($CDCl_3$, 400 MHz) ; δ 5.23-5.19 (m, 1 H), 3.59-3.55 (m, 1 H), 3.41-3.38 (m 2 H), 3.35 (s, 3 H), 2.32-2.24 (m 1 H), 1.80 (d, J = 6.5 Hz, 1 H), 1.79 (d, J = 2.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.98 (d, J = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) ; δ 199.6, 101.2, 100.7, 76.9, 58.8, 42.6, 28.3, 22.7, 22.5, 17.7.

1-Benzyloxy-3,6-dimethylhepta-3,4-diene-2-thiol (1b)

^{1}H NMR ($CDCl_3$, 400 MHz) ; δ 7.35-7.27 (m, 5 H), 5.26-5.20 (m, 1 H), 4.56 (ABq, J = 11.8 Hz, 2 H), 3.69 (dd, J = 8.5, 5.5 Hz, 1 H), 3.53-3.48 (m, 2 H), 2.33-2.25 (m, 1 H), 1.91 / 1.87* (d, J = 6.5 Hz, 1 H), 1.82* / 1.80 (d, J = 3.0 Hz, 3 H), 1.00* / 0.98 (d, J = 6.5 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz) ; δ 199.7 / 199.6*, 138.2* / 138.2, 128.5 / 128.5*, 127.9 / 127.8*, 127.8 / 127.8*, 101.1* / 101.1, 100.7* / 100.5, 74.5* / 74.4, 73.2, 43.0 / 42.9*, 28.4 / 28.3*, 22.7* / 22.6, 22.5, 17.8* / 17.5.

3,6-Dimethyl-1-(4-trifluoromethylphenoxy)-hepta-3,4-diene-2-thiol (1c)

^{1}H NMR ($CDCl_3$, 500 MHz) ; δ 7.54 (d, J = 8.5 Hz, 2 H), 6.95 (d, J = 8.5 Hz, 2 H), 5.23 (br s, 1 H), 4.18 (dd, J = 9.2, 7.0 Hz, 1 H), 4.05 (dd, J = 9.2, 6.7 Hz, 1 H), 3.64-3.59 (m, 1 H), 2.31-2.25 (m, 1 H), 1.91 (d, J = 7.2 Hz, 1 H), 1.87 (d, J = 2.8 Hz, 3 H), 0.99 (d, J = 6.7 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) ; δ 199.7, 161.1, 127.1, 127.1, 127.1, 127.0, 114.8, 101.3, 100.8, 72.2, 42.1, 28.3, 22.7, 22.5, 17.7.

1-Benzyloxy-3-methylundeca-3,4-diene-2-thiol (1d)

^{1}H NMR ($CDCl_3$, 500 MHz) ; δ 7.35-7.27 (m, 5 H), 5.18 (br s, 1 H), 4.55 (ABq, J = 12.0 Hz, 2 H), 3.71-3.66 (m, 1 H), 3.53-3.47 (m, 2 H), 1.99-1.95 (m, 2 H), 1.88 (d, J = 6.3 Hz, 1 H), 1.79 (d, J = 2.8 Hz, 3 H), 1.40-1.22 (m, 8 H), 0.88 (t, J = 6.5 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) ; δ 201.1, 138.3, 128.5, 127.9, 127.8, 100.2, 93.2, 74.5, 73.2, 43.1, 31.8, 29.2, 29.1, 29.0, 22.8, 17.5, 14.2.

Trideca-2,3,12-triene-1-thiol (1e)

^{1}H NMR ($CDCl_3$, 500 MHz) ; δ 5.81 (ddt, J = 17.0, 10.0, 6.8 Hz, 1 H), 5.30-5.15 (m, 2 H), 4.98 (d, J = 17.0 Hz, 1 H), 4.92 (d, J = 10.3 Hz, 1 H), 3.14-3.11 (m, 2 H), 2.06-1.98 (m, 4 H), 1.55 (t, J = 7.5 Hz, 1 H), 1.45-1.25 (m, 10 H). ^{13}C NMR ($CDCl_3$, 125 MHz) ; δ 203.8, 139.3, 114.3, 93.6, 91.9, 33.9, 29.4, 29.2, 29.2, 29.1, 29.0, 28.9, 24.4.

Typical procedure: Cycloisomerization

AuCl (3 mg, 13 μmol) was added to a stirred solution of α-thioallene **1a** (50 mg, 0.27 mmol) in CH_2Cl_2 (5 mL) at room temperature under argon, and the mixture was stirred for 90 min at room temperature (the reaction was monitored by TLC). The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (30 : 1) as eluent to afford 2,5-dihydrothiophene **2a** (44 mg, 88%) as a yellow oil.

Products (2,5-Dihydrothiophenes 2a-2e)

5-Isopropyl-2-methoxymethyl-3-methyl-2,5-dihydrothiophene (2a)

^{1}H NMR ($CDCl_3$, 400 MHz) ; δ 5.45 (br s, 1 H), 4.13-4.08 (m, 1 H), 4.07-4.01 (m, 1 H),

3.64 (dd, J = 9.3, 4.8 Hz, 1 H), 3.44 (dd, J = 9.3, 6.8 Hz, 1 H), 3.39 (s, 3 H), 1.81-1.73 (m, 1 H), 1.79 (s, 3 H), 0.94 (d, J = 6.8 Hz, 3 H), 0.91 (d, J = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) ; δ 139.1, 128.2, 76.6, 61.0, 59.2, 56.2, 34.5, 20.6, 19.4, 15.9.

2-Benzyloxymethyl-5-isopropyl-3-methyl-2,5-dihydrothiophene (2b)

^{1}H NMR ($CDCl_3$, 400 MHz) ; δ 7.35-7.27 (m, 5 H), 5.44* / 5.42 (br d, J = 1.5 Hz, 1 H), 4.58* / 4.57 (s, 2 H), 4.16-4.12 (m, 1 H), 4.05-4.01* / 4.00-3.95 (m, 1 H), 3.75 / 3.73* (dd, J = 9.3, 5.3 Hz, 1 H), 3.51* / 3.48 (dd, J = 9.3, 6.8 Hz, 1 H), 1.78 (s, 3 H), 1.80-1.73 (m, 1 H), 0.95 (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.6 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) ; δ 139.3* / 139.1, 138.4, 128.5, 128.2* / 128.0, 127.8* / 127.7, 127.7* / 127.7, 75.1 / 74.5*, 73.4* / 73.3, 61.3 / 60.9*, 56.2* / 56.1, 34.6 / 34.6*, 20.7 / 20.6*, 20.0 / 19.4*, 16.4 / 16.1*.

5-Isopropyl-3-methyl-2-(4-trifluoromethyl-phenoxymethyl)-2,5-dihydrothiophene (2c)

^{1}H NMR ($CDCl_3$, 400 MHz) ; δ 7.54 (d, J = 8.5 Hz, 2 H), 6.96 (d, J = 8.5 Hz, 2 H), 5.52 (br s, 1 H), 4.34-4.27 (m, 1 H), 4.21 (dd, J = 9.0, 5.8 Hz, 1 H), 4.12-4.08 (m, 1 H), 4.05 (dd, J = 9.0, 6.5 Hz, 1 H), 1.86 (s, 3 H), 1.85-1.78 (m, 1 H), 0.97 (d, J = 6.5 Hz, 3 H), 0.94 (d, J = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) ; δ 161.2, 138.7, 129.1, 127.1, 127.1, 127.0, 127.0, 114.7, 72.6, 61.2, 55.3, 36.2, 20.6, 19.4, 16.2.

2-Benzyloxymethyl-5-hexyl-3-methyl-2,5-dihydrothiophene (2d)

^{1}H NMR ($CDCl_3$, 400 MHz) ; δ 7.35-7.26 (m, 5 H), 5.43 (br s, 1 H), 4.58 (s, 2 H), 4.20-4.15 (m, 1 H), 4.15-4.08 (m, 1 H), 3.71 (dd, J = 9.5, 5.3 Hz, 1 H), 3.52 (dd, J = 9.5, 6.5 Hz, 1 H), 1.78 (s, 3 H), 1.73-1.66 (m, 1 H), 1.54-1.43 (m, 1 H), 1.40-1.25 (m, 8 H), 0.88 (t, J = 6.3 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) ; δ 138.5, 138.4, 129.8, 128.5, 127.7, 127.6, 74.5, 73.4, 56.4, 53.6, 38.6, 31.9, 29.3, 27.9, 22.7, 16.1, 14.2.

2-Non-8-enyl-2,5-dihydrothiophene (2e)

^{1}H NMR (C_6D_6, 400 MHz) ; δ 5.80 (ddt, J = 16.8, 10.0, 6.8 Hz, 1 H), 5.47 (dd, J = 6.2, 2.2 Hz, 1 H), 5.40 (dd, J = 6.2, 2.2 Hz, 1 H), 5.05 (dd, J = 17.0, 1.0 Hz, 1 H), 5.00 (dd, J = 10.3, 1.0 Hz, 1 H), 4.19-4.12 (m, 1 H), 3.48 (d, J = 2.5 Hz, 2 H), 1.98 (q, J = 7.0 Hz, 2 H), 1.65-1.48 (m, 2 H), 1.43-1.20 (m, 10 H). ^{13}C NMR (C_6D_6, 100 MHz) ; δ 139.3, 133.7, 127.7, 114.5, 56.3, 38.9, 38.7, 34.2, 29.9, 29.8, 29.4, 29.3, 28.2.