Gold Catalysis in Organic Synthesis: Efficient Cycloisomerization of α -Aminoallenes to 3-Pyrrolines

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Supporting Information

General Information

NMR spectra were recorded with a Bruker WM 400 spectrometer at 400 MHz (^1H) and 100.6 MHz (^{13}C) in CDCl_3 as solvent. 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.

Typical procedure

20 μL (2 mol%) of a solution of AuCl_3 in CH_3CN (0.165 M) was added to a solution of the α -aminoallene **4a** (42 mg, 0.17 mmol) in 5 ml of dry CH_2Cl_2 at room temperature under argon. After 5 days (the reaction was monitored by thin layer chromatography), the solvent was removed in vacuo and the crude product submitted to SiO_2 column chromatography ($\text{MeOH}/\text{CH}_2\text{Cl}_2$, 1/10) to give 3-pyrroline **5a** (31 mg, 74%).

2-Benzyloxymethyl-5-isopropyl-3-methyl-2,5-dihydro-1H-pyrrole (**5a**)

^1H -NMR δ 7.35-7.27 (m, 5H), 5.46 (d, J = 1.5 Hz, 1H), 4.57 (ABq, J = 12.0 Hz, 2H), 4.10-4.09 (m, 1H), 3.88-3.83 (m, 1H), 3.63 (dd, J = 9.8, 3.5 Hz, 1H), 3.45 (dd, J = 9.8, 5.8 Hz, 1H), 1.99 (br s, 1H), 1.70 (s, 3H), 0.94 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H). ^{13}C -NMR δ 138.3, 137.6, 128.5, 127.9, 127.7, 125.7, 73.3, 71.2, 70.6, 67.3, 33.7, 19.4, 19.0, 13.7.

2-Benzyloxymethyl-5-isopropyl-1-methanesulfonyl-3-methyl-2,5-dihydro-1H-pyrrole (**5b**)

^1H -NMR δ 7.37-7.27 (m, 5H), 5.43 (d, J = 1.5 Hz, 1H), 4.53 (ABq, J = 12.0 Hz, 2H), 4.41-4.39 (m, 1H), 4.38-4.34 (m, 1H), 4.24 (dd, J = 11.0, 2.2 Hz, 1H), 3.52 (dd, J = 11.0, 2.0 Hz, 1H), 2.92 (s, 3H), 2.63-2.55 (m, 1H), 1.67 (d, J = 0.8 Hz, 3H), 0.90 (d, J =

7.3 Hz, 3H), 0.78 (d, $J = 6.8$ Hz, 3H). ^{13}C -NMR δ 137.6, 136.3, 128.6, 128.0, 127.9, 121.1, 73.2, 71.9, 70.8, 66.3, 39.3, 31.1, 19.5, 15.1, 13.6.

2-Benzylloxymethyl-5-isopropyl-3-methyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole (5c)

^1H -NMR δ 7.75 (d, $J = 8.3$ Hz, 2H), 7.35-7.10 (m, 7H), 5.37 (d, $J = 1.5$ Hz, 1H), 4.52-4.49 (m, 1H), 4.48-4.44 (m, 1H), 4.17 (ABq, $J = 12.0$ Hz, 2H), 4.01 (dd, $J = 10.6$, 2.8 Hz, 1H), 3.55 (dd, $J = 10.6$, 2.0 Hz, 1H), 2.73-2.67 (m, 1H), 2.33 (s, 3H), 1.66 (s, 3H), 0.90 (d, $J = 7.0$ Hz, 3H), 0.64 (d, $J = 6.5$ Hz, 3H). ^{13}C -NMR δ 142.6, 139.4, 138.2, 136.5, 129.3, 128.3, 127.6, 127.5, 126.8, 120.9, 72.8, 72.6, 70.4, 67.4, 30.7, 21.5, 19.6, 15.2, 13.8.

1-(2-Benzylloxymethyl-5-isopropyl-3-methyl-2,5-dihydro-pyrrol-1-yl)-ethanone (5d)

^1H -NMR δ 7.34-7.22 (m, 5H), 5.43 / 5.38* (d, $J = 1.2$ Hz, 1H), 4.68-4.63 / 4.55-4.50* (m, 1H), 4.49* (ABq, $J = 12.3$ Hz, 2H), 4.49 (s, 2H), 4.49-4.45* / 4.40-4.35 (m, 1H), 4.24 / 3.59* (dd, $J = 10.0$, 3.0 Hz, 2H), 2.90-2.82 / 2.22-2.15* (m, 1H), 2.06* / 2.00 (s, 3H), 1.78 / 1.74* (s, 3H), 0.93* / 0.89 (d, $J = 7.0$ Hz, 3H), 0.67* / 0.56 (d, $J = 6.8$ Hz, 3H). ^{13}C -NMR δ 169.7*, 169.3, 138.7*, 137.9*, 137.8, 136.4, 128.6*, 128.4*, 128.0, 127.8, 127.6*, 127.6, 121.7, 119.8*, 73.4, 73.2*, 70.9, 70.1*, 70.0, 68.6, 68.1*, 65.8*, 32.0*, 26.5, 22.9*, 19.5, 19.4*, 15.0, 14.8*, 14.2, 13.9*.

tert-Butyl 2-benzylloxymethyl-5-isopropyl-3-methyl-2,5-dihydro-pyrrole-1-carboxylate (5e)

^1H -NMR δ 7.35-7.24 (m, 10H), 5.40 (d, $J = 1.2$ Hz, 1H), 5.36 (d, $J = 1.3$ Hz, 1H), 4.55 (ABq, $J = 12.3$ Hz, 2H), 4.50 (s, 2H), 4.49-4.46 (m, 1H), 4.40-4.35 (m, 1H), 4.34-4.31 (m, 1H), 4.28-4.25 (m, 1H), 4.16 (dd, $J = 10.0$, 3.2 Hz, 1H), 3.83 (dd, $J = 10.0$, 4.0 Hz, 1H), 3.65-3.59 (m, 2H), 2.82-2.74 (m, 1H), 2.53-2.45 (m, 1H), 1.75 (s, 3H), 1.74 (s, 3H), 1.50 (s, 9H), 1.41 (s, 9H), 0.89 (d, $J = 7.0$ Hz, 3H), 0.88 (d, $J = 7.0$ Hz, 3H), 0.64 (d, $J = 6.8$ Hz, 3H), 0.62 (d, $J = 6.8$ Hz, 3H). ^{13}C -NMR δ 153.9, 153.3, 138.9, 138.5, 137.2, 137.1, 128.5, 128.4, 127.7, 127.6, 127.5, 121.1, 120.8, 79.3, 79.2, 73.5, 73.3, 69.6, 69.3, 68.9, 67.9, 67.6, 66.6, 29.8, 28.7, 27.5, 27.0, 19.5, 19.3, 15.1, 15.0, 14.2, 14.0,

2-Benzylloxymethyl-3,5-dimethyl-2,5-dihydro-1H-pyrrole (7a)

^1H -NMR δ 7.36-7.27 (m, 5H), 5.40 (br s, 1H), 4.59 (ABq, $J = 11.8$ Hz, 2H), 4.40-4.32 (m, 1H), 4.30-4.26 (m, 1H), 3.71 (dd, $J = 10.0$, 3.3 Hz, 1H), 3.54 (dd, $J = 10.0$, 5.3 Hz,

1H), 1.69 (s, 3H), 1.36 (d, J = 6.6 Hz, 3H). ¹³C-NMR δ 138.0, 135.8, 128.5, 128.0, 127.8, 127.7, 73.4, 69.1, 66.9, 60.4, 20.5, 13.4.

2-(*tert*-Butyl-dimethyl-silanyloxymethyl)-5-hexyl-3-methyl-2,5-dihydro-1*H*-pyrrole (7b)

¹H-NMR δ 5.43 (br s, 1H), 4.08-4.00 (m, 2H), 3.82 (dd, J = 10.6, 3.7 Hz, 1H), 3.65 (dd, J = 10.6, 4.3 Hz, 1H), 1.71 (s, 3H), 1.62-1.52 (m, 2H), 1.39-1.25 (m, 8H), 0.90-0.85 (m, 3H), 0.87 (s, 9H), 0.07, 0.05 (2 s, 6H). ¹³C-NMR δ 137.1, 126.9, 68.6, 64.6, 63.4, 31.9, 29.4, 26.6, 26.0, 22.8, 18.4, 14.2, 13.7, -5.2, -5.4.

2-(*tert*-Butyl-dimethyl-silanyloxymethyl)-3-methyl-5-phenyl-2,5-dihydro-1*H*-pyrrole (7c)

¹H-NMR δ 7.30-7.22 (m, 5H), 5.50 (br s, 1H), 5.04 (br s, 1H), 4.05 (br s, 1H), 3.74 (dd, J = 8.0, 3.4 Hz, 1H), 3.62 (dd, J = 8.0, 4.6 Hz, 1H), 1.81 (s, 3H), 0.91 (s, 9H), 0.09 (s, 6H). ¹³C-NMR δ 145.2, 139.1, 128.6, 127.8, 127.2, 127.0, 69.5, 67.8, 65.9, 26.0, 18.4, 13.9, -5.2, -5.3.