Gold(III)-chloride Catalyzed Cyclization of α-Hydroxyallenes to 2,5-Dihydrofurans

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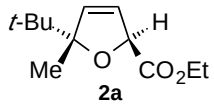
Supplementary Material

General Procedure for the gold(III)-chloride catalyzed cyclization of α-hydroxyallenes to 2,5-dihydrofurans:

Attention: Gold(III)-chloride is hygroscopic; the reaction proceeds sluggishly with material that has been exposed to moisture.

To a solution of the α-hydroxyallene (2.0 mmol) in 5 ml of dry dichlormethane under argon was added 5-10 mol-% of gold(III)-chloride (99%, Aldrich). The reaction mixture was then stirred at room temperature and monitored by TLC. After completion, the solvent was evaporated in vacuo and short flash column chromatography on silica gel with cyclohexane / diethylether (10:1) as eluent afforded the 2,5-dihydrofuran.

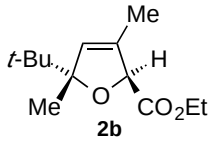
^{1}H and ^{13}C NMR data (signals for the major diastereomer are marked with an asterisk):



2a

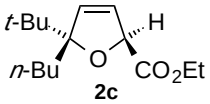
Ethyl 5-*t*-butyl-5-methyl-2,5-dihydrofurancarboxylate 2a (ds 90:10) from **1a** (ds 90:10):

^{1}H NMR (400 MHz, C_6D_6): δ 5.56 (m, 2 H, 3-H, 4-H), 5.13 (m, 1 H, 2-H), 3.91 (m, 2 H, CH_2), 1.41 (s, 3 H, 5-CH_3), 0.91 (m, 12 H, $C(CH_3)_3$), $CH_2C\underline{H}_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 171.0*/170.1 (x, CO), 135.2 (+, C-4), 124.4*/124.2 (+, C-3), 97.7*/97.1 (x, C-5), 85.3*/83.5 (+, C-2), 60.6*/60.5 (-, CH_2), 38.0*/37.1 (x, $\underline{C}(CH_3)_3$), 26.2/25.7* (+, $C(\underline{C}H_3)_3$), 22.6*/21.5 (+, 5-CH_3), 14.1 (+, $CH_2\underline{C}H_3$).



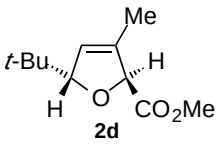
2b

Ethyl 5-*t*-butyl-3,5-dimethyl-2,5-dihydrofurancarboxylate 2b (ds 70:30) from **1b** (ds 70:30):
^{1}H NMR (400 MHz, C_6D_6): δ 5.30*/5.28 (m, 1 H, 4-H), 5.05*/5.03 (m, 1 H, 2-H), 3.92 (q, J = 7.3 Hz, 2 H, CH_2), 1.63*/1.58 (s, 3 H, 3-CH_3), 1.19/1.08* (s, 9 H, $C(CH_3)_3$), 0.94 (s, 3 H, 5-CH_3), 0.90 (t, J = 7.3 Hz, 3 H, CH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 171.1/170.1* (x, CO), 133.3/133.0* (x, C-3), 130.2*/130.0 (+, C-4), 97.1/96.1* (x, C-5), 87.7/85.5* (+, C-2), 60.5/60.4* (-, CH_2), 38.4/37.3 (x, $\underline{C}(CH_3)_3$), 26.3*/25.8 (+, $C(\underline{C}H_3)_3$), 22.5/21.6* (+, 5-CH_3), 14.1 (+, $CH_2\underline{C}H_3$), 12.6*/12.2 (+, 3-CH_3). NOESY: Crosspeak between δ 5.05 (2-H, major diastereomer) and 1.08 ($C(CH_3)_3$, major diastereomer); crosspeak between δ 5.03 (2-H, minor diastereomer) and 0.94 (5-CH_3).



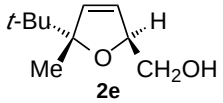
2c

Ethyl 5-*n*-butyl-5-*t*-butyl-2,5-dihydrofurancarboxylate 2c (ds 60:40) from **1c** (ds 60:40):
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 (m, 1 H, 3-H), 5.73 (m, 1 H, 4-H), 5.15 (m, 1 H, 2-H), 4.17 (m, 2 H, OCH_2), 1.84-1.52 (m, 2 H, 5-CH_2), 1.30-1.20 (m, 7 H, CH_2CH_2, $OCH_2C\underline{H}_3$), 0.90 (s, 9 H, $C(CH_3)_3$), 0.83 (t, J = 7.2 Hz, 3 H, $CH_2CH_2C\underline{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6*/170.3 (x, CO), 132.9*/132.5 (+, C-4), 125.0*/124.6 (+, C-3), 100.6*/100.3 (x, C-5), 85.1*/85.0 (+, C-2), 60.8*/60.7 (-, CH_2), 39.3*/37.3 (x, $\underline{C}(CH_3)_3$), 33.5/32.7* (-, 5-CH_2), 26.9/26.2 (-, 5-$CH_2\underline{C}H_2$), 26.4/26.1* (+, $C(\underline{C}H_3)_3$), 22.6*/21.5 (+, 5-CH_3), 14.1/14.1 (2+, $CH_2CH_2\underline{C}H_3$, $OCH_2\underline{C}H_3$).



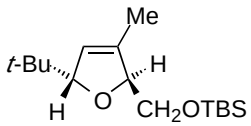
2d

Methyl 5-*t*-butyl-3-methyl-2,5-dihydrofurancarboxylate 2d (ds 50:50) from **1d** (ds 50:50):
^{1}H NMR (400 MHz, C_6D_6): δ 5.26 (m, 1 H, 4-H), 5.01 (m, 1 H, 2-H), 4.75/4.44 (m, 1 H, 5-H), 3.32/3.30 (s, 3 H, OCH_3), 1.58 (s, 3 H, 3-CH_3), 1.00/0.86 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 171.4/170.7 (x, CO), 135.7/135.4 (x, C-3), 125.1/124.8 (+, C-4), 95.6 (+, C-5), 87.3/86.5 (+, C-2), 51.3/51.1 (+, OCH_3), 35.3/35.0 (x, $\underline{C}(CH_3)_3$), 26.0/25.6 (+, $C(\underline{C}H_3)_3$), 12.6*/12.2 (+, 3-CH_3).



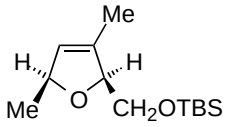
2e

5-*t*-Butyl-2-hydroxymethyl-5-methyl-2,5-dihydrofuran 2e (ds 85:15) from **1e** (ds 85:15):
^{1}H NMR (400 MHz, C_6D_6): δ 5.57/5.52* (dd, J = 6.0/2.4 Hz, 1 H, 3-H), 5.40/5.36* (dd, J = 6.0/1.1 Hz, 1 H, 4-H), 4.76/4.67* (m, 1 H, 2-H), 3.57-3.40 (m, 2 H, CH_2), 2.19 (s, 1 H, OH), 1.19*/1.15 (s, 3 H, 5-CH_3), 0.92*/0.90 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 134.7/134.1* (+, C-4), 126.5*/126.3 (+, C-3), 95.5*/95.2 (x, C-5), 88.1*/85.5 (+, C-2), 66.0*/65.4 (-, CH_2), 38.5*/36.4 (x, $\underline{C}(CH_3)_3$), 26.2/25.8* (+, $C(\underline{C}H_3)_3$), 23.5*/21.1 (+, 5-CH_3).



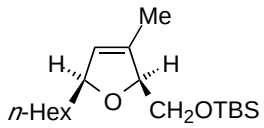
2f

5-*t*-Butyl-2-(*t*-butyldimethylsilyloxymethyl)-3-methyl-2,5-dihydrofuran 2f (ds 60:40) from **1f** (ds 60:40):
^{1}H NMR (400 MHz, C_6D_6): δ 5.29*/5.24 (dd, J = 3.0/1.5 Hz, 1 H, 4-H), 4.64/4.59* (m, 1 H, 2-H), 4.49*/4.42 (m, 1 H, 5-H), 3.74-3.60 (m, 2 H, CH_2), 1.62/1.61* (d, J = 0.5 Hz, 3 H, 3-CH_3), 0.98-0.94 (m, 18 H, 5-$C(CH_3)_3$, $SiC(CH_3)_3$), 0.08-0.05 (m, 6 H, $Si(CH_3)_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 139.0/138.4* (x, C-3), 123.4/123.3 (+, C-4), 94.0+/93.5 (+, C-5), 88.9*/88.1 (+, C-2), 66.4/65.5* (-, CH_2), 35.9*/34.5 (x, 5-$\underline{C}(CH_3)_3$), 26.1/25.3 (2+, 5-$C(\underline{C}H_3)_3$, $SiC(\underline{C}H_3)_3$), 18.5/18.4 (x, $Si\underline{C}(CH_3)_3$), 13.0/12.8* (+, 3-CH_3), -5.2/-5.3 (+, $Si(CH_3)_2$).



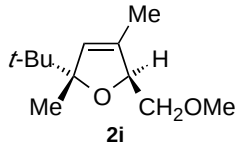
2g

2-(*t*-Butyldimethylsilyloxymethyl)-3,5-dimethyl-2,5-dihydrofuran 2g (ds 90:10) from **1g** (ds 90:10):
^{1}H NMR (400 MHz, C_6D_6): δ 5.20/5.16 (m, 1 H, 4-H), 4.91/4.83* (m, 1 H, 5-H), 4.64/4.59* (m, 1 H, 2-H), 3.69-3.59 (m, 2 H, CH_2), 1.56 (s, 3 H, 3-CH_3), 1.23 (d, J = 6.3 Hz, 3 H, 5-CH_3), 0.97-0.93 (m, 9 H, $C(CH_3)_3$), 0.06-0.03 (m, 6 H, $Si(CH_3)_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 136.6 (x, C-3), 127.4/127.2* (+, C-4), 88.6*/88.2 (+, C-2), 81.5/81.3* (+, C-5), 65.9*/65.3 (-, CH_2), 26.1 (+, $C(\underline{C}H_3)_3$), 23.0*/22.5 (+, 5-CH_3), 18.5 (x, $\underline{C}(CH_3)_3$), 12.7 (+, 3-CH_3), -5.2/-5.3 (+, $Si(CH_3)_2$). NOESY: Crosspeak between δ 4.83 (5-H, major diastereomer) and 4.59 (2-H, major diastereomer).



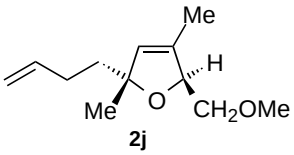
2h

2-(*t*-Butyldimethylsilyloxymethyl)-5-hexyl-3-methyl-2,5-dihydrofuran 2h (ds 75:25) from **1h** (ds 75:25):
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.43 (m, 1 H, 4-H), 4.74/4.67* (m, 1 H, 5-H), 4.55 (m, 1 H, 2-H), 3.68-3.65 (m, 2 H, OCH_2), 1.72 (s, 3 H, 3-CH_3), 1.26 (m, 10 H, $(CH_2)_5$), 0.99-0.94 (m, 12 H, $CH_2C\underline{H}_3$, $C(CH_3)_3$), 0.06-0.03 (m, 6 H, $Si(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7/136.6* (x, C-3), 125.5/125.4* (+, C-4), 88.1*/87.9 (+, C-2), 85.5/85.4* (+, C-5), 65.7*/65.1 (-, CH_2), 37.2*/36.6 (-, 5-CH_2), 31.9*/31.9, 29.7*/29.7, 29.4/29.4*, 22.7*/22.6 (4-, $(CH_2)_4$), 25.8 (+, $C(\underline{C}H_3)_3$), 18.3 (x, $\underline{C}(CH_3)_3$), 14.1 (+, $CH_2\underline{C}H_3$), 12.8 (+, 3-CH_3), -5.4/-5.5 (+, $Si(CH_3)_2$).



2i

5-*t*-Butyl-3,5-dimethyl-2-methoxymethyl-2,5-dihydrofuran 2i (ds 80:20) from **1i** (ds 80:20):
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.46 (m, 1 H, 4-H), 4.69/4.61* (m, 1 H, 2-H), 3.52-3.37 (m, 2 H, CH_2), 3.38/3.37* (s, 3 H, OCH_3), 1.70*/1.68 (s, 3 H, 3-CH_3), 1.23*/1.18 (s, 3 H, 5-CH_3), 0.95/0.89 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.6 (x, C-3), 128.7/128.4* (+, C-4), 94.4*/94.0 (x, C-5), 87.5*/85.0 (+, C-2), 75.1*/74.9 (-, CH_2), 59.3*/59.2 (+. OCH_3), 38.5 (x, $\underline{C}(CH_3)_3$), 26.1/25.6* (+, $C(\underline{C}H_3)_3$), 22.9*/21.3 (+, 5-CH_3), 12.4 (+, 3-CH_3).



2j

5-(3-Buten-1-yl)-3,5-dimethyl-2-methoxymethyl-2,5-dihydrofuran 2i (ds >95:<5) from **1i** (ds >95:<5):
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddt, J =17.0/10.2/6.6 Hz, 1 H, $C\underline{H}=CH_2$), 5.37 (m, 1 H, 4-H), 4.97 (dd, J = 17.0/2.0 Hz, $CH=C\underline{H}_2$), 4.89 (dd, J = 10.2/2.0 Hz, $CH=C\underline{H}_2$), 4.68 (m, 1 H, 2-H), 3.53-3.37 (m, 2 H, OCH_2), 3.40 (s, 3 H, OCH_3), 2.16-1.95 (m, 2 H, $H_2C=CHC\underline{H}_2$), 1.75-1.53 (m, 2 H, 5-CH_2), 1.71 (s, 3 H, 3-CH_3), 1.30 (s, 3 H, 5-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2 (+, $\underline{C}H=CH_2$), 134.9 (x, C-3), 129.3 (+, C-4), 113.8 (-, $CH=\underline{C}H_2$), 89.3 (x, C-5), 86.9 (+, C-2), 75.2 (-, OCH_2), 59.3 (+. OCH_3), 40.6 (-, 5-CH_2), 28.8 (-, $H_2C=CH\underline{C}H_2$), 22.9 (+, 5-CH_3), 12.4 (+, 3-CH_3).