Golden Times for Allenes: Gold-Catalyzed Cycloisomerization of β -Hydroxyallenes to Dihhydropyrans

Birgit Gockel and Norbert Krause*

Organic Chemistry II, Dortmund University, D-44221 Dortmund, Germany

norbert.krause@uni-dortmund.de

Supporting Information

Typical procedure

To a solution of the β -functionalized allene (0.2 mmol) in 3 mL of dry solvent under argon was added 1-5 mol % of the precatalyst. The mixture was stirred at room temperature and the reaction was monitored by TLC. After completion, the mixture was filtered through celite, the solvent was removed in vacuo and the crude product was purified by flash column chromatography on silica gel with cyclohexane/ethyl acetate (10:1).

2-Butyl-2-methyl-5,6-dihydro-2H-pyran (5)

^1H -NMR (500 MHz, C_6D_6): δ = 5.64-5.61 (m, 1 H, 4-H), 5.45 (dt, $^3J_{\text{HH}}$ = 10.2 Hz, $^4J_{\text{HH}}$ = 1.9 Hz, 1 H, 3-H), 3.68-3.60 (m, 2 H, 6-H), 1.87-1.85 (m, 1 H, 5-H), 1.66-1.60 (m, 1 H, 5-H), 1.57-1.36 (m, 4 H, 1'-H, 2'-H), 1.29 (tq, $^3J_{\text{HH}}$ = 7.3 Hz, $^3J_{\text{HH}}$ = 7.3 Hz, 2 H, 3'-H), 1.20 (s, 3 H, 2-CH₃), 0.90 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 3 H, 4'-H). ^{13}C -NMR (125 MHz, C_6D_6): δ = 135.0 (+, C-3), 123.6 (+, C-4), 73.5 ($\times$, C-2), 59.1 (-, C-6), 41.1 (-, C-1'), 26.2 (-, C-5/C-2'/C-3'), 25.4 (-, C-5/C-2'/C-3'), 25.2 (+, 2-CH₃), 23.6 (-, C-5/C-2'/C-3'), 14.4 (+, C-4').

2-*t*-Butyl-2-methyl-5,6-dihydro-2H-pyran (8a)

^1H -NMR (400 MHz, C_6D_6): δ = 5.67-5.58 (m, 2 H, 3-H, 4-H), 3.69-3.64 (m, 1 H, 6-H), 1.58-1.52 (m, 1 H, 6-H), 2.07-1.98 (m, 1 H, 5-H), 1.43-1.37 (m, 1 H, 5-H), 1.14 (s, 3 H, 2-CH₃), 1.04 (s, 9 H, 2-C(CH₃)₃). ^{13}C -NMR (100 MHz, C_6D_6): δ = 132.7 (+, C-3), 124.5 (+, C-4), 77.7 ($\times$, C-2), 59.3 (-, C-6), 37.9 ($\times$, 2-C(CH₃)₃), 25.4 (+, 2-C(CH₃)₃), 25.3 (-, C-5), 19.0 (+, 2-CH₃).

2-*t*-Butyl-2-butyl-5,6-dihydro-2H-pyran (8b)

^1H -NMR (400 MHz, C_6D_6): δ = 5.84-5.80 (m, 1 H, 4-H), 5.55-5.53 (m, 1 H, 3-H), 3.75-3.66 (m, 2 H, 6-H), 1.88-1.75 (m, 1 H, 5-H), 1.63-1.46 (m, 3 H, 5-H, 1'-H), 1.38-1.20 (m, 4 H, 2'-H, 3'-H), 1.05 (s, 9 H, 2-C(CH₃)₃), 0.92 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 3 H, 4'-H). ^{13}C -NMR (100 MHz, C_6D_6): δ = 131.3 (+, C-3), 125.8 (+, C-4), 79.4 ($\times$, C-2), 61.7 (-, C-6), 39.5 ($\times$, 2-C(CH₃)₃), 35.9 (-, C-1'), 28.2 (-, C-5/C-2'/C-3'), 26.2 (+, 2-C(CH₃)₃), 25.0 (-, C-5/C-2'/C-3'), 24.1 (-, C-5/C-2'/C-3'), 14.5 (+, C-4').

6-Butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran (8c)

^1H -NMR (400 MHz, C_6D_6): δ = 5.66-5.61 (m, 1 H, 4-H), 5.48 (dd, $^3J_{\text{HH}}$ = 10.3 Hz, $^4J_{\text{HH}}$ = 1.3 Hz, 1 H, 3-H), 1.90-1.85 (m, 1 H, 5-H), 1.69-1.64 (m, 1 H, 5-H), 1.61-1.29 (m, 6 H, 1'-H, 2'-H, 3'-H), 1.26 (s, 3 H, 2-CH₃), 1.24 (s, 3 H, 6-CH₃), 1.21 (s, 3 H, 6-CH₃), 0.92 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 3 H, 4'-H). ^{13}C -NMR (100 MHz, C_6D_6): δ = 133.43 (+, C-3), 121.9 (+, C-4), 73.7 ($\times$, C-2), 70.0 ($\times$, C-6), 43.6 (-, C-1'), 36.1 (-, C-5), 30.9 (+, 2-CH₃), 28.6 (-, 6-CH₃), 28.2 (+, 6-CH₃), 26.3 (-, C-2'/C-3'), 23.5 (-, C-2'/C-3'), 14.5 (+, C-4').

Ethyl 6-butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran-3-carboxylate (8d)

^1H -NMR (400 MHz, C_6D_6): δ = 5.94*/5.78 (2dd, $^3J_{\text{HH}}$ = 3.8 Hz/10.3 Hz, 1 H, 4-H), 5.64/5.46* (2dd, $^3J_{\text{HH}}$ = 2.8 Hz/10.3 Hz, 1 H, 4-H), 3.98-3.84 (m, 2 H, OCH₂CH₃), 3.08-3.07*/3.01-2.99 (2m, 1 H, 5-H), 1.52*/1.41 (2s, 3 H, 6-CH₃), 1.33-1.24 (m, 6 H, 1'-H, 2'-H, 3'-H), 1.21*/1.18 (2s, 3 H, 2-CH₃), 0.95-0.87 (m, 6 H, 4'-H, OCH₂CH₃). ^{13}C -NMR (100 MHz, C_6D_6): δ = 172.0*/171.6 (2 $\times$, OC(O)CH₃), 135.0/133.3* (2+, C-3), 121.6*/120.0 (2+, C-4), 74.0*/73.7 (2 $\times$, C-6), 72.5*/72.2 (2 $\times$, C-2), 60.4*/60.3 (2-, OCH₂CH₃), 50.4*/50.3 (2+, C-5), 43.7*/42.0 (2-, C-1'), 30.7/30.6* (2+, 2-CH₃), 27.7*/27.4 (2+, 6-CH₃), 26.4/26.2* (2-, C-2'), 26.0/24.9* (2+, 6-CH₃), 23.7/23.4* (2-, C-3'), 14.5*/14.4 (2+, C-4'), 14.3/14.2* (2+, OCH₂CH₃).

1-Hydroxy-3,6,6-trimethylhepta-3,4-dien-2-yl acetate (9a)

^1H -NMR (400 MHz, C_6D_6): δ = 5.41 (m, 1 H, 2-H), 5.15 (m, 1 H, 5-H), 3.70-3.69 (m, 2 H, 1-H), 1.79 (m, 3 H, OC(O)CH₃), 1.66 (d, $^5J_{\text{HH}}$ = 2.3 Hz, 3 H, 3-CH₃), 0.98 (s, 9 H, C(CH₃)₃). ^{13}C -NMR (100 MHz, C_6D_6): δ = 199.4 ($\times$, C-4), 170.5 ($\times$, OC(O)CH₃), 105.2 (+, C-5), 99.1 ($\times$, C-3), 75.7 (+, C-2), 63.7 (-, C-1), 32.2 ($\times$, C-6), 30.2 (+, C(CH₃)₃), 20.8 (+, OC(O)CH₃), 16.5 (+, 3-CH₃).

Cis-6-*t*-Butyl-4-methyl-3,6-dihydro-2*H*-pyran-3-yl acetate (10a)

¹H-NMR (400 MHz, C₆D₆): δ = 5.56 (m, 1 H, 3-H), 4.91 (m, 1 H, 5-H), 4.11-4.08 (m, 1 H, 6-H), 3.39-3.35 (m, 2 H, 2-H, 6-H), 1.66 (s, 3 H, OC(O)CH₃), 1.61 (s, 3 H, 4-CH₃), 0.96 (s, 9 H, C(CH₃)₃).

¹³C-NMR (100 MHz, C₆D₆): δ = 170.5 (×, OC(O)CH₃), 131.1 (×, C-4), 128.0 (+, C-3), 82.0 (+, C-1), 68.4 (-, C-6), 68.4 (+, C-5), 34.6 (×, C(CH₃)₃), 26.0 (+, C(CH₃)₃), 20.7 (+, 4-CH₃/OC(O)CH₃), 20.7 (+, 4-CH₃/OC(O)CH₃).

Trans-2-Acetoxymethyl-5-*t*-butyl-3,5-dimethyl-2,5-dihydrofuran (11a)

¹H-NMR (400 MHz, C₆D₆): δ = 5.23 (m 1, H- 4-H), 4.62-4.61 (m, 1 H, 2-H), 4.59-4.44 (m, 1 H, 5-H), 4.16-4.06 (m, 2 H, 2-CH₂), 1.67 (s, 3 H, OC(O)CH₃), 1.43 (s, 3 H, 3-CH₃), 0.87 (s, C(CH₃)₃).

¹³C-NMR (100 MHz, C₆D₆): δ = 170.1 (×, OC(O)CH₃), 136.6 (×, C-3), 124.3 (+, C-4), 94.1 (+, C-5), 86.3 (+, C-2), 65.5 (-, 2-CH₂), 35.7 (×, C(CH₃)₃), 25.7 (+, C(CH₃)₃), 20.4 (+, OC(O)CH₃), 12.3 (+, 3-CH₃).

Trans-6-*t*-Butyl-4-methyl-3,6-dihydro-2*H*-pyran-3-yl acetate (10b)

¹H-NMR (400 MHz, C₆D₆): δ = 5.55 (m, 1 H, 5-H), 5.50 (m, 1 H, 3-H), 4.25 (dd, ²J_{HH} = 10.4 Hz, ³J_{HH} = 5.9 Hz, 1 H, 6-H), 3.58 (m, 1 H, 2-H), 3.33 (dd, ²J_{HH} = 10.4 Hz, ³J_{HH} = 9.1 Hz, 1 H, 6-H), 1.62 (s, 3 H, OC(O)CH₃), 1.59 (s, 3 H, 4-CH₃), 0.92 (s, 9 H, C(CH₃)₃).

¹³C-NMR (100 MHz, C₆D₆): δ = 169.8 (×, OC(O)CH₃), 133.9 (×, C-4), 125.8 (+, C-3), 82.4 (+, C-2), 67.7 (+, C-5), 66.7 (-, C-6), 35.0 (×, C(CH₃)₃), 25.8 (+, C(CH₃)₃), 20.3 (+, 4-CH₃/OC(O)CH₃), 18.4 (+, 4-CH₃/OC(O)CH₃).

Cis-2-Acetoxymethyl-5-*t*-butyl-3,5-dimethyl-2,5-dihydrofuran (11b)

¹H-NMR (400 MHz, C₆D₆): δ = 5.18 (m, 1 H, 4-H), 4.63-4.62 (m, 1 H, 2-H), 4.39-4.37 (m, 1 H, 5-H), 4.23 (dd, ²J_{HH} = 11.8 Hz, ³J_{HH} = 3.3 Hz, 1 H, 2-CH₂), 4.14 (dd, ²J_{HH} = 11.8 Hz, ³J_{HH} = 5.5 Hz, 1 H, 2-CH₂), 1.66 (s, 3 H, OC(O)CH₃), 1.40 (s, 3 H, 3-CH₃), 0.91 (s, C(CH₃)₃).

¹³C-NMR (100 MHz, C₆D₆): δ = 170.0 (×, OC(O)CH₃), 136.8 (×, C-3), 124.4 (+, C-4), 93.9 (+, C-5), 85.4 (+, C-2), 65.8 (-, 2-CH₂), 34.5 (×, C(CH₃)₃), 26.0 (+, C(CH₃)₃), 20.4 (+, OC(O)CH₃), 12.3 (+, 3-CH₃).

Trans-6-Butyl-4-methyl-3,6-dihydro-2*H*-pyran-3-yl acetate (10c)

¹H-NMR (400 MHz, C₆D₆): δ = 5.39 (m, 1 H, 5-H), 5.31 (m, 1 H, 3-H), 4.08 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 5.0 Hz, 1 H, 6-H), 3.95-3.93 (m, 1 H, 2-H), 3.51 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 6.7 Hz, 1 H,

6-H), 1.64 (s, 3 H, 4-CH₃), 1.59 (s, 3 H, OC(O)CH₃), 1.50-1.37 (m, 2 H, 1'-H), 1.34-1.19 (m, 4 H, 2'-H, 3'-H), 0.86 (t, ³J_{HH} = 7.2 Hz, 3 H, 4'-H).

¹³C-NMR (100 MHz, C₆D₆): δ = 170.0 (×, OC(O)CH₃), 131.2 (×, C-4), 129.7 (+, C-3), 74.0 (+, C-2), 67.9 (+, C-5), 65.4 (-, C-6), 34.4 (-, C-1'), 27.8 (-, C-2'), 23.0 (-, C-3'), 20.4 (+, 4-CH₃/OC(O)CH₃), 19.0 (+, 4-CH₃/OC(O)CH₃), 14.2 (+, C-4').

Trans-2-Butyl-5-methoxy-5,6-dihydro-2H-pyran (10d)

¹H-NMR (400 MHz, C₆D₆): δ = 5.29 (m, 1 H, 3-H), 4.25 (dd, ²J_{HH} = 10.7 Hz, ³J_{HH} = 4.9 Hz, 1 H, 6-H), 3.97 (m, 1 H, 2-H), 3.59 (m, 1 H, 5-H), 3.56 (dd, ²J_{HH} = 10.7 Hz, ³J_{HH} = 7.7 Hz, 1 H, 6-H), 3.07 (s, 3 H, OCH₃), 1.77 (s, 3 H, 4-CH₃), 1.63-1.28 (m, 6 H, 1'-H, 2'-H, 3'-H), 0.88 (t, ³J_{HH} = 7.3 Hz, 3 H, 4'-H).

¹³C-NMR (100 MHz, C₆D₆): δ = 134.2 (×, C-4), 127.9 (+, C-3), 74.8 (+, C-2/C-5), 74.4 (+, C-2/C-5), 66.4 (-, C-6), 57.0 (+, OCH₃), 35.2 (-, C-1'), 27.8 (-, C-2'), 23.1 (-, C-3'), 19.1 (+, 4-CH₃), 14.3 (+, C-4').

Trans-4-Methyl-6-phenyl-3,6-dihydro-2H-pyran-3-yl acetate (10e)

¹H-NMR (400 MHz, C₆D₆): δ = 7.40-7.38/7.27-7.25* (2m, 2 H, Aryl-H), 7.18/ 7.18-7.17* (2m, 2 H, Aryl-H), 7.12-7.11/7.10-7.09 (2m, 1 H, Aryl-H), 5.52*/5.45 (2m, 1 H, 3-H), 5.30-5.28*/5.02 (2m, 1 H, 5-H), 5.04*/4.74 (2m, 1 H, 2-H), 4.13/3.95* (2dd, ²J_{HH} = 11.9 Hz, ³J_{HH} = 4.2 Hz, 1 H, 6-H), 3.64*/3.53 (2dd, ²J_{HH} = 11.9 Hz, ³J_{HH} = 5.1 Hz, 1 H, 6-H), 1.67*/1.66 (2s, 3 H, OC(O)CH₃), 1.60*/1.56 (2s, 3 H, 4-CH₃).

¹³C-NMR (100 MHz, C₆D₆): δ = 170.5/170.1* (2×, OC(O)CH₃), 141.5/140.7* (2×, C-1'), 131.7* (×, C-4), 130.7*/129.7 (C-4'), 128.6*/128.5 (2+, C-3', C-5'), 128.0/ 127.9* (2+, C-2', C-6'), 127.4* (+, C-3), 76.8/75.4* (2+, C-5), 68.0/65.0* (2-, C-6), 67.9/67.5* (2+, C-2), 20.6/20.4* (2+, OC(O)CH₃), 20.2/19.3* (2+, 4-CH₃).

Trans-5-Methoxy-4-methyl-2-phenyl-5,6-dihydro-2H-pyran (10f)

¹H-NMR (400 MHz, C₆D₆): δ = 7.45-7.40/7.33-7.32* (2m, 2 H, Aryl-H), 7.23-7.08 (m, 3 H, Aryl-H), 5.71/5.47* (2m, 1 H, 3-H), 5.26/5.02* (2m, 1 H, 2-H), 4.11/3.95* (2dd, ²J_{HH} = 11.4 Hz,

$^3J_{\text{HH}} = 4.6 \text{ Hz}$, 1 H, 6-H), 3.49-3.47*/3.45-3.43 (2m, 1 H, 5-H), 3.11*/3.10 (2s, 3 H, OCH₃), 1.74*/1.68 (2s, 3 H, 4-CH₃).

^{13}C -NMR (100 MHz, C₆D₆): $\delta = 142.0/141.7^*$ ($\times$, C-1'), 137.4/134.1* (C-4), 131.1 ($\times$, C-4'), 128.6/128.5* (+, C-3', C-5'), 127.8/127.7* (+, C-2', C-6'), 127.2/127.1* (+, C-3), 77.0/76.0* (+, C-5), 74.2*/73.9 (+, C-2), 66.9/65.7* (-, C-6), 56.6*/55.4 (+, OCH₃), 20.5/19.3* (+, 4-CH₃).

2-Butyl-2-methyl-1,2,5,6-tetrahydropyridin (13)

^1H -NMR (400 MHz, C₆D₆): $\delta = 5.59\text{-}5.56$ (m, 1 H, 4-H), 5.43-5.40 (m, 1 H, 3-H), 2.84-2.82 (m, 2 H, 6-H), 1.91-1.86 (m, 1 H, 5-H), 1.78-1.72 (m, 1 H, 5-H), 1.50-1.21 (m, 6 H, 1'-H, 2'-H, 3'-H), 1.11 (s, 3 H, 2-CH₃), 0.90 (t, $^3J_{\text{HH}} = 7.0 \text{ Hz}$, 3 H, 4'-H).

^{13}C -NMR (100 MHz, C₆D₆): $\delta = 135.3$ (+, C-3), 124.3 (+, C-4), 53.4 ($\times$, C-2), 41.7 (-, C-6), 38.6 (-, C-1'), 26.3 (-, C-5), 26.2 (+, 2-CH₃), 25.3 (-, C-2'/C-3'), 23.7 (-, C-2'/C-3'), 14.4 (+, C-4').

2-Butyl-2-methyl-5,6-dihydro-2H-pyran (5)

2-Butyl-2-methyl-5,6-dihydro-2H-pyran

2-Butyl-2-methyl-5,6-dihydro-2H-pyran

2-*t*-Butyl-2-methyl-5,6-dihydro-2H-pyran (8a)

2-*t*-Butyl-2-methyl-5,6-dihydro-2H-pyran

2-*t*-Butyl-2-methyl-5,6-dihydro-2H-pyran

2-*t*-Butyl-2-butyl-5,6-dihydro-2*H*-pyran (8b)

2-*tert*-Butyl-2-butyl-5,6-dihydro-2*H*-pyran

2-*tert*-Butyl-2-butyl-5,6-dihydro-2*H*-pyran

6-Butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran (8c)

6-Butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran

6-Butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran

Ethyl 6-butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran-3-carboxylate (8d)

6-Butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran-3-carbonsäureethylester

6-Butyl-2,2,6-trimethyl-3,6-dihydro-2H-pyran-3-carbonsäureethylester

1-Hydroxy-3,6,6-trimethylhepta-3,4-dien-2-yl acetate (9a)

1-Hydroxy-3,6,6-trimethylhepta-3,4-dien-2-yl acetate

1-Hydroxy-3,6,6-trimethylhepta-3,4-dien-2-yl acetate

Cis-6-*t*-Butyl-4-methyl-3,6-dihydro-2*H*-pyran-3-yl acetate (**10a**)

6-*tert*-Butyl-4-methyl-3,6-dihydro-2*H*-pyran-3-ylacetat

6-*tert*-Butyl-4-methyl-3,6-dihydro-2*H*-pyran-3-ylacetat

Trans-2-Acetoxymethyl-5-*t*-butyl-3,5-dimethyl-2,5-dihydrofuran (11a)

5-*tert*-Butyl-2-acetoxymethyl-3,5-dimethyl-2,5-dihydrofuran

5-*tert*-Butyl-2-acetoxymethyl-3,5-dimethyl-2,5-dihydrofuran

Trans-6-*t*-Butyl-4-methyl-3,6-dihydro-2H-pyran-3-yl acetate (10b)

6-*tert*-Butyl-4-methyl-3,6-dihydro-2H-pyran-3-ylacetat

6-*tert*-Butyl-4-methyl-3,6-dihydro-2H-pyran-3-ylacetat

Cis-2-Acetoxymethyl-5-*t*-butyl-3,5-dimethyl-2,5-dihydrofuran (11b)

5-*tert*-Butyl-2-acetoxymethyl-3,5-dimethyl-2,5-dihydrofuran

5-*tert*-Butyl-2-acetoxymethyl-3,5-dimethyl-2,5-dihydrofuran

Trans-6-Butyl-4-methyl-3,6-dihydro-2H-pyran-3-yl acetate (10c)

6-Butyl-4-methyl-3,6-dihydro-2H-pyran-3-ylacetat

6-Butyl-4-methyl-3,6-dihydro-2H-pyran-3-ylacetat

Trans-2-Butyl-5-methoxy-5,6-dihydro-2H-pyran (10d)

2-Butyl-5-methoxy-5,6-dihydro-2H-pyran

2-Butyl-5-methoxy-5,6-dihydro-2H-pyran

Trans-4-Methyl-6-phenyl-3,6-dihydro-2H-pyran-3-yl acetate (10e)

4-Methyl-6-phenyl-3,6-dihydro-2H-pyran-3-ylacetat

4-Methyl-6-phenyl-3,6-dihydro-2H-pyran-3-ylacetat

Trans-5-Methoxy-4-methyl-2-phenyl-5,6-dihydro-2H-pyran (10f)

5-Methoxy-4-methyl-2-phenyl-5,6-dihydro-2H-pyran

5-Methoxy-4-methyl-2-phenyl-5,6-dihydro-2H-pyran

2-Butyl-2-methyl-1,2,5,6-tetrahydropyridin (13)

2-Butyl-2-methyl-1,2,5,6-tetrahydropyridin

2-Butyl-2-methyl-1,2,5,6-tetrahydropyridin