Palladium(0)-Catalyzed Cycloisomerization of Enallenes

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Experimental Section

**Compound 2b and 3b.** The reaction was carried out as in the general procedure above, to give 2b and 3b (ratio 6:1) as an inseparable mixture in 90% total yield. $^1$H NMR (400 MHz, CDCl$_3$) of the diastereoisomeric mixture of 2b: $\delta$ = 5.81 (m, 4H), 5.39 (dd, $J$ = 3.0, 1.5 Hz, 1H), 5.37 (dd, $J$ = 3.2, 1.4 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 3.68 (s, 1H), 3.67 (s, 3H), 3.41 (m, 2H), 3.11 (m, 2H), 2.24 (sextet, $J$ = 5.4 Hz, 1H), 2.10 (sextet, $J$ = 6.1 Hz, 1H), 1.98 (m, 4H), 1.62 (dqd, $J$ = 13.6, 7.5, 6.1 Hz, 1H), 1.50 (dqd, $J$ = 13.6, 7.5, 5.4 Hz, 1H), 1.38-1.20 (overlapping peaks, 6H), 1.07 (d, $J$ = 6.9 Hz, 3H), 0.99 (d, $J$ = 6.9 Hz, 3H), 0.88 (t, $J$ = 7.5 Hz, 3H), 0.76 (t, $J$ = 7.5 Hz, 3H). $^1$H NMR (400 MHz, CDCl$_3$) of 3b: significant peaks $\delta$ = 5.74 (m, 2H), 5.41 (t, $J$ = 1.7 Hz, 1H), 2.96 (m, 1H), 1.11 (d, $J$ = 7.2 Hz, 3H), 1.00 (d, $J$ = 7.2 Hz, 3H), 0.97 (t, $J$ = 7.4 Hz, 3H), 0.90 (d, $J$ = 7.4 Hz, 3H).

**Compound 2c and 3c.** The reaction was carried out as in the general procedure above, to give 2c and 3c (ratio 6:1) as an inseparable mixture in 90% total yield. $^1$H NMR (400 MHz, CDCl$_3$) of 2c: $\delta$ = 5.82 (m, 2H), 5.35 (dd, $J$ = 2.9, 1.5 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.45 (m, 1H), 3.11 (dqd, $J$ = 13.0, 6.2, 4.3 Hz, 1H), 1.98 (m, 3H), 1.85 (m, 2H), 1.68 (m, 4H), 1.27 (m, 5H), 0.99 (m, 1H). $^1$H NMR (400 MHz, CDCl$_3$) of 3c: significant peaks $\delta$ = 5.75 (m, 2H), 5.38 (t, $J$ = 1.7 Hz, 1H), 3.70 (s, 3H), 3.07 (s, 3H), 2.98 (m, 1H). Anal. Calcd. for (2c/3c) C$_{19}$H$_{26}$O$_4$: C, 71.67; H, 8.23. Found: C, 71.30; H, 8.13.
Compound 7 and 8. The reaction was carried out as in the general procedure above, to give 7 and 8 (ratio 3:1) in 92% total yield. $^1$H NMR (400 MHz, CDCl$_3$) of 7: $\delta$ = 5.71 (ddt, $J$ = 5.8, 1.4, 2.4 Hz, 1H), 5.36 (ddt, $J$ = 5.8, 1.4, 2.4 Hz, 1H), 5.30 (t, $J$ = 1.8 Hz, 1H), 4.16 (dddt, $J$ = 17.0, 9.1, 2.5, 2.5 Hz, 1H), 2.35 (m, 2H), 1.13 (d, $J$ = 6.7 Hz, 3H), 1.00 (d, $J$ = 6.7 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) of 7: $\delta$ = 171.7, 171.3, 158.2, 131.7, 129.4, 118.3, 69.1, 54.9, 52.8, 52.3, 48.4, 35.6, 27.6, 21.5, 20.8. Anal. Calcd. for (7) C$_{15}$H$_{20}$O$_4$: C, 68.16; H, 7.63. Found: C, 68.09; H, 7.63.

$^1$H NMR (400 MHz, CDCl$_3$) of 7-$d_1$: $\delta$ = 5.71 (ddt, $J$ = 5.8, 1.4, 2.4 Hz, 1H), 5.36 (ddt, $J$ = 5.8, 1.4, 2.4 Hz, 1H), 5.30 (d, $J$ = 1.7 Hz, 1H), 4.15 (ddtt, $J$ = 17.0, 9.1, 2.5, 2.5 Hz, 1H), 2.34 (m, 1H), 1.12 (s, 3H), 0.98 (s, 3H).

$^1$H NMR (400 MHz, CDCl$_3$) of 8: $\delta$ = 5.78 (dtd, $J$ = 5.8, 2.8, 1.7 Hz, 1H), 5.65 (ddt, $J$ = 5.8, 2.6, 1.8 Hz, 1H), 5.35 (t, $J$ = 1.8 Hz, 1H), 3.87 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.65 (dt, $J$ = 9.9, 7.3 Hz, 1H), 2.49 (ddd, $J$ = 16.8, 9.8, 2.8, 1.7 Hz, 1H), 1.98 (dddt, $J$ = 16.8, 7.6, 2.7, 1.9 Hz, 1H), 1.10 (d, $J$ = 6.7 Hz, 3H), 1.03 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) of 8: $\delta$ = 171.9, 171.6, 157.2, 130.9, 130.3, 118.2, 68.4, 57.9, 52.8, 52.3, 46.3, 35.6, 28.4, 21.6, 20.9. $^1$H NMR (400 MHz, CDCl$_3$) of 8-$d_1$: $\delta$ = 5.78 (ddt, $J$ = 5.8, 2.8, 1.7 Hz, 1H), 5.64 (ddt, $J$ = 5.8, 2.6, 1.8 Hz, 1H), 5.35 (d, $J$ = 1.9 Hz, 1H), 3.87 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.65 (dt, $J$ = 9.9, 7.3 Hz, 1H), 2.49 (ddd, $J$ = 16.8, 9.8, 2.8, 1.7 Hz, 1H), 1.98 (dddt, $J$ = 16.8, 7.6, 2.7, 1.9 Hz, 1H), 1.09 (s, 3H), 1.02 (s, 3H).

Compound 10 and 11. The reaction was carried out as in the general procedure above, except that Pd(dba)$_2$ was used in 10 mol% of 9 and the mixture was microwave-heated to 120 °C for 40 minutes to give 10 and 11 (ratio 2:1) as an inseparable mixture in 73% total yield. $^1$H NMR (400 MHz, CDCl$_3$) of 10: $\delta$ = 5.75 (s, 1H), 5.44 (qt, $J$ = 7.0, 2.5 Hz, 1H), 3.73 (s, 6H), 3.11 (bs, 2H), 2.50 (heptet, $J$ = 6.9 Hz, 1H), 1.71 (bd, $J$ = 7.5 Hz, 3H), 1.11 (d, $J$ = 6.7 Hz, 6H). $^1$H NMR (400 MHz, CDCl$_3$) of 11: $\delta$ = 5.61 (dt, $J$ = 16.9, 10.0 Hz, 1H), 5.48 (t, $J$ = 1.8 Hz, 1H), 5.09 (dd, $J$ = 16.9, 1.6 Hz, 1H), 5.02 (dd, $J$ = 10.0, 1.6 Hz, 1H), 3.71 (s, 6H), 3.45 (dt, $J$ = 15.0, 7.8 Hz, 1H), 2.76 (dd, $J$ = 13.8, 8.5 Hz, 1H), 2.27 (heptet, $J$ = 6.9 Hz, 1H), 2.16 (dd, $J$ = 13.6, 6.3 Hz, 1H), 1.10 (d, $J$ = 6.7 Hz, 3H), 0.98 (d, $J$ = 6.7 Hz, 3H).
Compound 13 and 14. The reaction was carried out as in the general procedure above, except that Pd(dba)$_2$ was used in 10 mol% of 12 and the mixture was microwave-heated to 120 °C for 40 minutes to give 13 and 14 (ratio 2:1) as an inseparable mixture in 74% total yield. $^1$H NMR (400 MHz, CDCl$_3$) for 13: $\delta = 7.35$ (brd, $J = 7.0$ Hz, 2H), 7.30 (t, $J = 7.0$ Hz, 2H), 7.21 (t, $J = 7.0$ Hz, 1H), 6.49 (d, $J = 16.6$ Hz, 1H), 6.01 (dd, $J = 16.6$, 9.6 Hz, 1H), 5.53 (t, $J = 1.8$ Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.62 (q, $J = 7.7$ Hz, 1H), 2.83 (dd, $J = 14.0$, 8.4 Hz, 1H), 2.22 (dd, $J = 14.0$, 6.3 Hz, 1H), 2.31 (heptet, $J = 6.9$ Hz, 1H), 1.10 (d, $J = 6.7$ Hz, 3H), 1.01 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) of 13: $\delta =$ 172.4, 172.0, 158.3, 137.3, 132.3, 131.2, 128.7, 127.4, 126.3, 120.8, 65.2, 52.8, 50.0, 39.2, 28.2, 21.3, 21.0. Anal. Calcd. for (13) C$_{20}$H$_{24}$O$_4$: C, 73.15; H, 7.36. Found: C, 73.58; H, 7.36. $^1$H NMR (400 MHz, CDCl$_3$) for 14: $\delta = 7.35$ (brd, $J = 7.0$ Hz, 2H), 7.30 (t, $J = 7.0$ Hz, 2H), 7.21 (t, $J = 7.0$ Hz, 1H), 5.83 (s, 1H), 5.56 (tt, $J = 7.2$, 2.4 Hz, 1H), 3.75 (s, 6H), 3.46 (d, $J = 7.8$ Hz, 2H), 3.22 (s, 1H), 2.52 (heptet, $J = 6.9$ Hz, 1H), 1.12 (d, $J = 6.7$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) of 14: $\delta =$ 171.6, 154.9, 142.5, 140.8, 128.6, 128.5, 126.2, 118.8, 63.4, 53.0, 36.2, 35.7, 25.9, 22.0.

Compound 16 and 17. The reaction was carried out as in the general procedure above, except that Pd(dba)$_2$ was used in 10 mol% of 15 and the mixture was heated to 80 °C for 10 h (in an oil-bath) to give 16 and 17 (ratio 13:3) as an inseparable mixture in 52% total yield. $^1$H NMR (300 MHz, CDCl$_3$) for 16: $\delta = 5.88$ (s, 1H), 4.93 (m, 2H), 3.71 (s, 6H), 3.15 (t, $J = 1.9$ Hz, 2H), 2.52 (heptet, $J = 6.7$ Hz, 1H), 1.12 (d, $J = 6.4$ Hz, 6H). $^1$H NMR (300 MHz, CDCl$_3$) of 17: $\delta = 5.69$ (s, 1H), 5.05 (s, 1H), 5.01 (s, 1H), 3.71 (s, 6H), 3.08 (m, 1H), 2.69 (dd, $J = 13.7$, 8.7 Hz, 1H), 2.23 (dd, $J = 13.7$, 2.8 Hz, 1H), 1.91 (s, 3H).

Analysis of deuterium content in products 2a, 7, and 8. The analysis was made on the methyl signals of the isopropyl group. Due to the isotope effect the shift of the methyl groups in the deuterated and nondeuterated compounds differs slightly (ca. 0.01 ppm).
$^1$H and $^{13}$C NMR spectra