

Supporting Information

Rearrangement of Allyl Homoallyl Ethers to γ,δ -Unsaturated Carbonyl Compounds Catalyzed by Iridium Complexes

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Experimental Procedure and Compound Characterization Data

General

The starting allyl homoallyl ethers **1**, **4**, **6**, **8**, **10**, and **12**, were synthesized by the following reaction; The reaction of the corresponding carbonyl compounds with allylmagnesium bromide in THF gave homoallylic alcohols. Subsequently, etherification of the corresponding potassium alkoxides with allyl bromide in refluxing THF furnished the allyl homoallyl ethers.¹ The starting diallyl ethers **14**, **16** and **18** were synthesized by the reaction of the corresponding allylic alcohols with allyl bromide in refluxing THF under the influence of potassium hydride.

GC analysis was performed with a flame ionization detector using a 0.2 mm x 25 m capillary column (OV-1). ¹H and ¹³C NMR spectra were measured at 270 and 67.5 MHz, respectively, in CDCl₃ with Me₄Si as the internal standard. The yields of all products were estimated from the peak areas based on the internal standard technique. The compounds **15**, **17** and **19** were reported previously (see ref 6 in text).

Compound Characterization Data

4-Cyclohexyliden-2,3-dimethylbutanal (2): **2** was obtained in a ca. 1 : 1 diastereomeric mixture. ¹H NMR δ 9.64 (s, 1H), 4.95 (d, *J* = 9.6 Hz, 1H), 2.84-2.75 (m, 1H), 2.22-2.13 (m, 1H), 2.13-2.06 (m, 4H), 1.58-1.42 (6H), 1.05 (d, *J* = 7.2 Hz, 6H); ¹³C NMR δ 205.6, 140.4, 124.2, 51.9, 37.2, 32.7, 29.1, 28.6, 27.8, 26.8, 18.5, 10.9. And ¹H NMR δ 9.62 (s, 1H), 4.86 (d, *J* = 9.9 Hz, 1H), 2.84-2.75 (m, 1H), 2.22-2.13 (m, 1H), 2.13-2.06 (m, 4H), 1.58-1.42 (6H), 1.00 (d, *J* = 7.2 Hz, 6H); ¹³C NMR δ 205.6, 140.4, 123.4, 52.3, 37.3, 32.2, 29.2, 28.7, 27.9, 26.8, 19.6, 11.0.

1-Allyl-1-propenylloxycyclohexane (3): **3** was obtained in a ca. 1:1 geometric

mixture : ^1H NMR δ 6.12 (d, J = 11.9 Hz, 1H), 5.72 (s, 1H), 5.01-4.90 (3H), 2.18 (d, 2H), 1.67 (d, 2H) 1.48 (d, 6H), 1.36 (d, 2H), 1.29-1.19 (3H); ^{13}C NMR δ 139.4, 133.4, 117.5, 103.9, 77.5, 42.9, 34.6, 25.7, 21.6, 12.6. And ^1H NMR δ 6.12 (d, J = 11.8 Hz, 1H), 5.72 (s, 1H), 5.01-4.90 (3H), 2.18 (d, 2H), 1.67 (d, 2H) 1.48 (d, 6H), 1.36 (d, 2H), 1.29-1.19 (3H); ^{13}C NMR δ 139.4, 133.4, 117.5, 103.9, 77.4, 42.8, 34.4, 25.5, 21.5, 12.6.

2,3,5-Trimethyl-4-hexenal (5): **5** was obtained in a ca.1:1 diastereomeric mixture : ^1H NMR δ 9.56 (s, 1H), 4.86 (d, J = 9.8 Hz, 1H), 2.72-2.64 (m, 1H), 2.18-2.12 (m, 1H), 1.62 (s, 3H), 1.56 (s, 3H), 0.99-0.90 (6H); ^{13}C NMR δ 205.6, 132.2, 126.7, 52.3, 33.3, 25.8, 19.1, 18.0, 10.8. And ^1H NMR δ 9.55 (s, 1H), 4.94 (d, J = 9.9 Hz, 1H), 2.72-2.64 (m, 1H), 2.18-2.12 (m, 1H), 1.62 (s, 3H), 1.56 (s, 3H), 0.99-0.90 (6H); ^{13}C NMR δ 205.5, 132.0, 127.5, 51.8, 33.7, 25.7, 19.1, 18.0, 10.7.

(E)-2,3-Dimethyl-4-hexenal (7): **7** was obtained in a ca.1:1 diastereomeric mixture : ^1H NMR δ 9.58 (s, 1H), 5.44-5.32 (m, 1H), 5.21 (d, J = 7.2 Hz, 1H), 2.52-2.42 (m, 1H), 2.28-2.15 (m, 1H), 1.59 (d, J = 3.0 Hz, 3H), 0.97-0.92 (6H); ^{13}C NMR δ 205.6, 133.7, 125.9, 51.5, 37.5, 17.8, 16.9, 10.5. And ^1H NMR δ 9.56 (s, 1H), 5.44-5.32 (m, 1H), 5.17 (d, J = 7.9 Hz, 1H), 2.52-2.42 (m, 1H), 2.28-2.15 (m, 1H), 1.59 (d, J = 3.0 Hz, 3H), 0.97-0.92 (6H); ^{13}C NMR δ 205.6, 132.7, 125.4, 51.2, 37.5, 18.4, 16.9, 10.2.

(E)-2,3-Dimethyl-5-phenyl-4-pentenal (9): **9** was obtained in a ca.1:1 diastereomeric mixture : ^1H NMR δ 9.69 (s, 1H), 7.36-7.18 (5H), 6.42 (d, J = 15.8 Hz, 1H) 6.21-6.01 (dd, J = 7.6, 8.3 Hz, 1H), 2.82-2.72 (m, 1H), 2.48-2.34 (m, 1H), 1.18-1.08 (6H); ^{13}C NMR δ 204.8, 137.1, 132.8, 130.2, 128.5, 127.3, 126.1, 51.2, 37.7, 16.6, 10.1. And ^1H NMR δ 9.71 (s, 1H), 7.36-7.18 (5H), 6.42 (d, J = 15.8 Hz, 1H) 6.21-6.01 (dd, J = 7.6, 8.3 Hz, 1H), 2.82-2.72 (m, 1H), 2.48-2.34 (m, 1H), 1.18-1.08 (6H); ^{13}C NMR δ 204.8, 137.1, 131.8, 130.6, 128.5, 127.3, 126.1, 51.6, 37.9, 18.3, 10.9.

(E)-2,3-Dimethyl-4-decanal (11): **11** was obtained in a ca.1:1 diastereomeric mixture : ^1H NMR δ 9.65 (s, 1H), 5.52-5.36 (m, 1H), 5.31-5.02 (m, 1H), 2.59-2.50 (m, 2H), 1.99 (q, 2H), 1.40-1.26 (6H), 1.08-0.96 (6H), 0.85 (t, 3H); ^{13}C NMR δ 205.4, 132.5, 131.6, 51.6, 37.5, 32.4, 31.3, 29.1, 22.5, 18.5, 14.0, 10.5. And ^1H NMR δ 9.65 (s, 1H), 5.52-5.36 (m, 1H), 5.31-5.02 (m, 1H), 2.59-2.50 (m, 1H), 2.34-2.23 (m, 1H), 1.99 (q, 2H), 1.40-1.26 (6H), 1.08-0.96 (6H), 0.85 (t, 3H); ^{13}C NMR δ 205.4, 131.4, 131.2, 51.2, 37.5, 32.4, 31.3, 29.1, 22.5, 16.9, 14.0, 10.2.

(E)-2,3-Dimethyl-5-phenyl-4-hexenal (13): **E-13** was obtained in a ca.1:1 diastereomeric mixture : ^1H NMR δ 9.44 (s, 1H), 7.37-7.10 (5H), 5.30 (d, J = 10.6 Hz, 1H), 2.64-2.48 (m, 1H), 2.21-2.14 (m, 1H), 2.01 (s, 3H), 1.03-0.96 (6H); ^{13}C NMR δ 205.4, 142.1, 137.5, 128.9, 128.3, 127.6, 126.7, 51.8, 34.2, 26.1, 18.2, 10.8. And ^1H NMR δ 9.43 (s, 1H), 7.37-7.10 (5H), 5.28 (d, J = 10.2 Hz, 1H), 2.64-2.48 (m, 1H),

2.21-2.14 (m, 1H), 2.01 (s, 3H), 1.03-0.96 (6H); ^{13}C NMR δ 205.3, 142.0, 138.0, 129.9, 128.2, 127.6, 126.7, 52.1, 33.8, 26.0, 19.4, 10.7.

(Z)-2,3-Dimethyl-5-phenyl-4-hexenal (13): **Z-13** was obtained in a ca.1:1 diastereomeric mixture : ^1H NMR δ 9.70 (s, 1H), 7.38-7.23 (5H), 5.66-5.54 (d, J = 11.6 Hz, 1H), 2.99-2.90 (m, 1H), 2.41-2.32 (m, 1H), 2.07 (s, 3H), 1.14-1.09 (6H); ^{13}C NMR δ 205.1, 143.6, 135.5, 130.3, 128.2, 126.9, 125.8, 52.3, 34.0, 18.9, 16.3, 11.3. And ^1H NMR δ 9.69 (s, 1H), 7.38-7.23 (5H), 5.64 (d, J = 9.9 Hz, 1H), 2.99-2.90 (m, 1H), 2.41-2.32 (m, 1H), 2.07 (s, 3H), 1.14-1.09 (6H); ^{13}C NMR δ 205.0, 143.6, 135.3, 131.0, 128.2, 126.9, 125.8, 51.7, 34.2, 17.7, 16.2, 10.7.

Reference

1. Maier, M. E.; Bugl, M. *Synlett* **1999**, 1390.