Experimental

General remarks

α-angelica lactone (98%), γ-valerolactone (99%), 2-pentenoic acid (98%), 3-pentenoic acid (≥ 95%), 4-pentenoic acid (≥ 98%), 2 4-pentadienoic acid (≥ 97%), 1-hexanol (99.5%), levulinic acid (≥ 98%), 2-methyltetrahydrofuran (99.5 %), 1,4-pentanediol (99%), 1-pentanol (≥ 99%), 2-pentanol (≥ 98%) and ruthenium (5 wt%) supported on carbon (Batch Nr°: MKBN8598V) were purchased from Sigma-Aldrich. Methanol (99.8%) and ethanol (99.9%) were purchased from Chemsolute. γ-Methylene-γ-butyrolactone (>98%) was purchased from TCI and valeric acid (99%) from Alfa Aesar. All chemicals were used without further purification or drying. GC analysis was performed on an Agilent HP6890.

General Procedure at high Pressure

A 50 mL Hastelloy high pressure autoclave (Schlesinger B18rb250-01) was charged with α-Angelica lactone (1.689 g, 17.22 mmol), Ru/C (5 wt%, 100 mg, 49 μmol Ru) and a magnetic stirring bar. The autoclave was flushed four times before applying the desired pressure and where necessary, heated using an aluminum block. A stirring speed of 500 RPM was used. After the reaction period, the autoclave was cooled down and depressurized. The reaction mixture was filtered using micro filters (Chromafil 45/25) and the liquid sample was diluted with ethanol and analyzed by GC (1-hexanol was used as internal standard).

General Procedure at Atmospheric Pressure

A 50 mL two-neck tubular glass reactor, fitted with a condenser was charged with α-angelica lactone (8.445 g, 86.10 mmol) and Ru/C (5 wt%, 500 mg, 0.245 mmol Ru). H_2 was sparged through the solution using a gas frit. The H_2 flow (130 mL/min or 500 mL/min) was calibrated with a digital flow meter. The reactor was heated using an oil bath and no additional agitation was provided. The exhaust gas was passed through a liquid N_2-cooled cold trap. Samples of the reaction mixture (≃ 75 mg) were collected by syringe and

centrifuged. The resulting clear samples were diluted with ethanol and analyzed by GC (1-hexanol was used as internal standard).

Sample Analysis

The identity of reaction products (e.g. β-angelica lactone, valeric acid, γ-methylene-γ-butyrolactone, 2,4-pentadienoic acid, pentenoic acid isomers and levulinic acid) was confirmed by GC-MS analysis and comparison with authentic samples. Quantitative analysis of samples of α-angelica lactone hydrogenation reactions was performed by GC-FID using a CP-Wax-52 column (60 m × 250 µm × 0.25 µm). Quantitative analysis of samples of 2-MTHF synthesis reactions was performed by GC-FID using a CP-Sil-Pona-CB column (50 m × 210 µm × 0.5 µm). Qualitative analysis was performed by GC-MS on a Trace GC chromatograph 1310 equipped with a Restek Rxi-1 MS column (60 m × 250 µm × 0.5 µm) and a Thermo Scientific ISQ mass spectrometer (EI+, 70 eV, 250 °C).

Isomerization of α-Angelica lactone

Experimental data

t (min)	α-AL	β-AL	γ-MBL
0	98,33%	0,51%	0,87%
15	94,6%	1,9%	3,5%
30	94,3%	2,4%	3,3%
45	92,2%	4,1%	3,7%
60	91,1%	5,1%	3,8%
75	89,7%	6,3%	4,0%
90	88,7%	7,3%	4,0%
180	85,1%	11,0%	4,0%
270	77,7%	17,5%	4,8%
360	80,5%	15,6%	3,9%

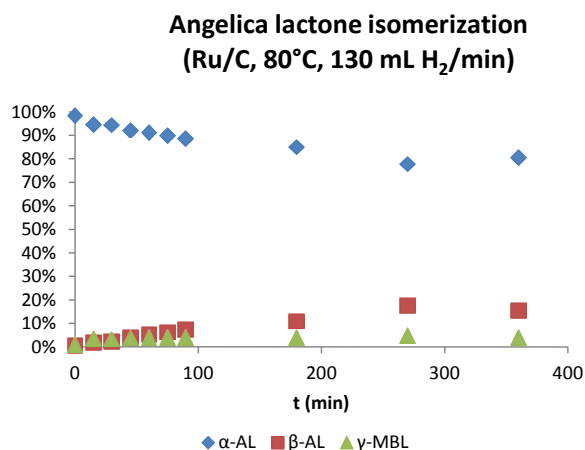*Figure 1 Relative lactone composition. (Conditions: α-AL (1.68 g, 17.13mmol), Ru/C (5 wt% Ru, 100 mg, 49 µmol Ru), 80 °C, 1 atm, 130 mL H₂/min)*

DFT Calculations

The computations in this work were carried out with the Gaussian09 program series (Revision D.01).[1] Geometry optimizations in ethylacetate phase were carried using the MN12-L12 density functional and the def2-TZVP basis set.[2] The automatic density fitting approximation was activated.[3] Solvent effects (ethylacetate) were considered implicitly by applying the IEF-PCM[4] formalism and the SMD radii model.[5] The structures were characterized by frequency calculations to be local minima (i = 0). Thermochemical corrections were computed for a temperature of 298.15 K. A pressure of 251 atm was specified to account for entropy corrections in the condensed phase as was described elsewhere.[6] The obtained energies and predicted equilibrium composition are listed in the tables below.

MN-12-L/def2-TZVP (Ethylacetat, 298.15 °K)

Compound	E	E_{zpe}	H	G
α-angelica lactone	-344.4090044	-344.306171	-344.299094	-344.330793
β-angelica lactone	-344.4090458	-344.305299	-344.298395	-344.329841
γ-methylenebutyrolactone	-344.403877	-344.300567	-344.293615	-344.325429

Boltzmann distribution

Compound	E_{rel} (KJ/mol)	EXP($-E_{rel}$/RT)	N_i/N_{tot} (%)
α-angelica lactone	0	1	73.09%
β-angelica lactone	2.499476	0.364827	26.66%
γ-methylenebutyrolactone	14.08318	0.003409	0.25%

References

1   Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T.

Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010

2   a) A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571; b) A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 1994, 100, 5829; c) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 1997, 97, 119 –124; d) F. Weigend, F. Furche, R. Ahlrichs, J. Chem. Phys. 2003, 119, 12753; e) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297 –3305.

3   a) B. I. Dunlap, *J. Chem. Phys.* 1983, **78**, 3140; b) B. Dunlap, *J. Mol. Struct.* 2000, **529**, 37–40.

4   a) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 2005, **105**, 2999–3093; b) E. Cances, B. Mennucci, J. Tomasi, *J. Chem. Phys.* 1997, 107, 3032

5   A. V. Marenich, C. J Cramer, D. G. Truhlar, *J. Phys. Chem. B.* 2009, **113**, 6378-6396.

6   a) R. L. Martin, P. J. Hay, L. R. Pratt, *J. Phys. Chem.* A 1998, **102**, 3565–3573; b) N. Sieffert, M. Bühl, *Inorg. Chem.* 2009, **48**, 4622 – 4624