Supporting Information

“An Improved Protocol for the RuO₄-catalyzed Dihydroxylation of Olefins“

Bernd Plietker*, Meike Niggemann
Organic Chemistry II, Chemistry Faculty,
Dortmund University,
Otto-Hahn-Str. 6, D-44221 Dortmund.
e-mail: plietker@pop.uni-dortmund.de

General Remarks. All solvents were purified by distillation over CaCl₂ prior to use. RuCl₃ was obtained from Aldrich. A stock solution was prepared calculating with RuCl₃(H₂O)₂ and dissolving the catalyst (2.44 g, 10 mmol in 100 mL water (0.1 M). The deep brown solution can be stored on the bench for weeks without loss of activity. Flash-chromatography was done on silicagel 60 (230-400 mesh) using head pressure by means of compressed air. Infrared spectra (IR) were recorded as a thin film between KBr-plates. The instrument used was a Bruker IFS 66 FT-IR spectrophotometer. GC-MS spectra were recorded on a Finnigan Polaris GCQ spectrometer. Proton (¹H NMR, 400 MHz) and carbon (¹³C NMR, 100.6 MHz) nuclear magnetic resonance spectra were recorded in chloroform(d-1) and referenced to the solvent signal. The instrument used was a Bruker DRX 400.

General Procedure. A 50-mL round-bottomed flask equipped with magnetic stirring bar and overpressure valve NaIO₄ (642 mg, 3 mmol) was stirred in 1.5 mL H₂O. 2 N H₂SO₄ (400 µL, 0.4 mmol) was added. After all solids were dissolved the solution was cooled to 0 °C. A 0.1 M aqueous solution of RuCl₃ (100 µL, 0.01 mmol) was added and the mixture was stirred until the color turned bright yellow. Ethyl acetate (6 mL) was added and stirring was continued for 5 min. Acetonitrile (6 mL) was added and stirring was continued for further 5 min. The olefin (2 mmol) was added in one portion and the resulting slurry was stirred until all starting material was consumed. The mixture was poured onto 15 mL sat. NaHCO₃- and 20 mL sat. Na₂S₂O₃-solution. Phases were separated and the aqueous layer was extracted with ethyl acetate (3 x 30 mL). After drying the combined organic layer over Na₂SO₄ and evaporation of the solvent in vacuum the crude product was purified by flash-chromatography.

(2*S*^{*},3*R*^{*})-2,3-Dihydroxy-3-phenyl-propionic acid methyl ester (4).^[1] (329 mg, 1.68 mmol, 84 %). White solid. m.p. 79 °C. R_f 0.30 (4:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 3.49 (s, 2*H*), 3.70 (s, 3*H*), 4.28 (d, *J* = 3.3 Hz, 1*H*), 4.94 (d, *J* = 3.3 Hz, 1*H*), 7.22-7.38 (m, 5*H*) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 52.7, 74.5, 75.0, 126.3, 128.2, 128.4, 140.0, 173.2 ppm. IR (KBr): ν 3495 (s), 3378 (s), 3086 (m), 3062 (m), 3038 (m), 3007 (m), 2954 (s), 2931 (m), 1732 (s), 1493 (s), 1458 (s), 1324 (s), 1308 (s), 1104 (s), 1083 (s) cm⁻¹.

(1*R*^{*},2*R*^{*})-3-Azido-1-phenylpropan-1,2-diol (6). (251 mg, 1.30 mmol, 65 %). Yellow oil. R_f 0.31 (3:2 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 3.08 (s, 2*H*), 3.38 (ddd, *J* = 11.5, 5.7, 2.7 Hz, 1*H*), 3.55 (dt, *J* = 11.5, 3.5 Hz, 1*H*), 3.88 (m, 1*H*), 4.72 (dd, *J* = 6.7, 1.8 Hz, 1*H*), 7.18-7.43 (m, 5*H*) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 53.1, 75.20, 75.24, 126.7, 128.7, 128.9, 140.1 ppm. IR (film). ν 3394 (s), 3087 (w), 3064 (w), 3032 (w), 2924 (w), 2103 (s), 1083 (m), 1043 (m) cm⁻¹. MS (ESI, +ve, 100 eV). *m/z* (%). 193 (44), 177 (23), 147 (15), 106 (100). HRMS (FAB⁺LR, C₉H₁₁N₃O₂). Calc. 193.0851, found. 193.0832.

Acetic acid (2*S*^{*},3*S*^{*})-2,3-dihydroxy-3-phenyl-propyl ester (8).^[2] (331 mg, 1.56 mmol, 78 %). Colorless oil. R_f 0.38 (1:1 pentane / ethyl acetate). ¹H-NMR (400 MHz, CDCl₃). δ 2.02 (s, 3*H*), 2.86 (br. s., 2*H*), 3.91 (m, 2*H*), 4.04 (m, 1*H*), 4.58 (d, *J* = 6.4 Hz, 1*H*), 7.28-7.38 (m, 5*H*). ¹³C-NMR (100 MHz, CDCl₃). δ 20.9, 65.3, 74.1, 74.6, 126.7, 127.2, 128.5, 128.8, 140.1 ppm. IR (film). ν 3418 (s), 3032 (w), 2900 (w), 1723 (s), 1381 (m), 1244 (s), 704 (s) cm⁻¹.

(1*R*^{*},2*S*^{*})-1-Phenyl-3-(phenylsulfonyl)propan-1,2-diol (10). (0.55 g, 1.88 mmol, 94 %). Yellow solid. m.p. 133 °C. R_f 0.48 (3:2 pentane / ethyl acetate). ¹H-NMR (400 MHz, CDCl₃). δ 2.60 (s, 2*H*), 3.21 (dd *J* = 14.6, 0.2 Hz, 1*H*), 3.25 (dd, *J* = 14.6, 9.4 Hz, 1*H*), 4.24 (ddd, *J* = 9.4, 6.0, 2.0 Hz, 1*H*), 4.56 (d, *J* = 6.0 Hz, 1*H*), 7.20-7.30 (m, 5*H*), 7.49-7.65 (m, 3*H*), 7.80-7.84 (m, 2*H*) ppm. ¹³C-NMR (100 MHz, CDCl₃). δ 37.1, 58.8, 70.5, 126.9, 128.0, 128.7, 128.9, 129.5, 134.2, 139.0, 139.2 ppm. IR (KBr). ν 3521 (s), 3064 (w), 3028 (w), 2976 (w), 2942 (w), 2925 (w), 1168 (s), 1147 (m), 1084 (m) cm⁻¹. MS (ESI, -10 eV). *m/z* (%) 310 (42), 275 (100), 132 (27). HRMS (FAB⁺LR, C₁₅H₁₇O₄S). Calc. 293.0848, found. 293.0829.

(5*S*^{*},6*S*^{*})-5,6-Dihydroxydecane (12).^[3] (317 mg, 1.82 mmol, 91 %). Colourless solid. m.p. 50 °C. R_f 0.56 (5:1 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 0.90 (t, *J* = 7.2 Hz, 6*H*), 1.26 – 1.50 (m, 12*H*), 2.12 (s, 2*H*), 3.36 – 3.40 (m, 2*H*) ppm. ¹³C NMR

(100 MHz, CDCl₃). δ 14.1, 22.7, 27.9, 33.3, 74.5 ppm. IR (KBr). ν 3380 (s), 2930 (m), 2858 (s), 1457 (m), 1132 (m), 1071 (m), 740 (m) cm⁻¹.

(2*S*^{*},3*S*^{*})-2,3-Dihydroxycyclohexanone (14).^[2] (179 mg, 1.38 mmol, 69 %). Colorless solid. m.p. 52 °C. R_f. 0.25 (3:2 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 1.75-1.82 (m, 2*H*), 2.03-2.14 (m, 2*H*), 2.32 (dt, *J* = 13.6, 1.2 Hz, 1*H*), 2.49 (dq, *J* = 13.6, 2.3 Hz, 1*H*), 3.49 (s, 2*H*), 4.13 (dd, *J* = 3.3, 1.2 Hz, 1*H*), 4.35-4.39 (m, 1*H*) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 21.2, 29.0, 39.1, 72.8, 77.5, 210.2 ppm. IR (KBr). ν 3405 (s), 2949 (m), 1718 (s), 1140 (m), 1107 (m), 1075 (m) cm⁻¹.

(1*S*^{*},2*S*^{*},3*S*^{*})-2,3-Dihydroxycyclohexylacetate (16).^[2] (210 mg, 1.50 mmol (mixture of diastereoisomers), 75 %). Colorless Oil. R_f. 0.19 (3:2 pentane / ethyl acetate). ¹H NMR (400 MHz, CDCl₃). δ 1.26-1.36 (m, 1*H*), 1.38-1.44 (m, 1*H*), 1.45-1.51 (m, 1*H*), 1.62-1.71 (m, 1*H*), 1.78-1.85 (m, 1*H*), 1.88-1.94 (m, 1*H*), 2.01 (s, 3*H*), 3.30 (s, 2*H*), 3.52 (dd, *J* = 8.5, 3.0 Hz, 1*H*), 4.03 (ddd, *J* = 4.3, 2.8 Hz, 1*H*), 4.95 (ddd, *J* = 9.7, 4.3 Hz, 1*H*) ppm. ¹³C NMR (100 MHz, CDCl₃). δ 18.3, 21.5, 29.2, 30.1, 70.1, 74.4, 77.1, 172.0 ppm. IR (film). ν 3442 (s), 2942 (w), 2870 (w), 1732 (s), 1066 (m), 1042 (m) cm⁻¹.

Refernces

- [1] M. Fujita, D. Laine, S. V. Ley, J. Chem. Soc., Perkin Trans. 1 1999, 1647.
- [2] T. K. M. Shing, E. K. W. Tam, V. W. F. Tai, I. H. F. Chung, Q. Jiang, *Chem. Eur. J.* **1996**, 2, 50.
- [3] C. Döbler, G. M. Mehlretter, U. Sundermeier, M. Beller, *J. Am. Chem. Soc.* **2000**, 122, 10289.

6.1

2.8

1.1

1.0

1.2

5.0

2.6

2.5

1.8

0.8

0.8

6.7

3.3

2.4

1.0

1.0

1.0