

# Enantioselective Oxidative Coupling of the Titanium Enolate of 3-Phenylacetyl-2-oxazolidinone

Phu Q. Nguyen and Hans J. Schäfer\*

*Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse  
40, D 48125 Münster, Germany*

## Supporting Information

**General Procedures.** All reactions were performed under an argon atmosphere, using flame-dried glassware. All chemicals are either commercially available and used without further purification or have been prepared using reported procedures. THF was distilled from potassium metal-benzophenone ketyl before use. Dichloromethane was distilled from calcium hydride. Flash column chromatography was performed on Merck silica gel 60 (40 – 63  $\mu\text{m}$ ) using ethyl acetate/cyclohexane as eluting solvents. NMR spectra were recorded on a Bruker spectrometer WM 300 (300 MHz and 75.4 MHz, for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively;  $\text{CDCl}_3$  as solvent). The electrospray (ESI) spectra were measured on a Quattro LCZ (Micromass, Manchester, UK) with nanospray inlet. The measurement of GC/MS spectra was conducted on a Finnigan-MAT 8200 (70 eV) with a capillary column HP 5 (25 m, 0.20 mm i. d., 0.32  $\mu\text{m}$  film). Gas chromatography was carried out on a Hewlett-Packard HP 5890 Series II with the capillary column HP 1 (25 m, 0.20 mm i. d., 0.32  $\mu\text{m}$  film) and HP 5 (25 m, 0.20 mm i. d., 0.52  $\mu\text{m}$  film). The diastereoselectivities were determined by RP-HPLC (LiChrospher 100 RP 18-5, 250 mm, 2 mm i. d.) and the enantiomeric excess by chiral-HPLC (Grom Chiral OD-H Nr. 76, 250 mm, 2 mm i. d.).

**Typical procedure for the enantioselective oxidative coupling.** To a suspension of powdered molecular sieves 4Å (200 mg) and chiral ligand (1 mmol) in dry dichloromethane (3 ml) titanium tetrachloride (1 ml, 1M in dichloromethane) or ytterbium triflate (620 mg, 1 mmol) was added at 0 °C and stirred intensively for 1 h. If diols (**3-6**) were used as ligands triethylamine (276  $\mu\text{l}$ , 2 mmol) was added and stirred for one additional hour. To the resulting intensive red (with titanium tetrachloride) or yellow (with ytterbium triflate) suspension a solution of **1** (205 mg, 1 mmol) in dry dichloromethane (1ml) was introduced slowly at 0 °C. After stirring for 1 h at 0°C **10** (408 mg, 1.5 mmol) was added and the mixture was allowed to stir for 6 h at 0 °C and 12 h at RT. The reaction was hydrolyzed at 0 °C with 1 M HCl,

extracted with dichloromethane, washed with saturated NaCl and dried over MgSO<sub>4</sub>. The product was isolated by column chromatography on silica gel (ethyl acetate/cyclohexane = 1:1). The spectroscopic data of *dl*-**2** were in accordance with the literature values.<sup>1</sup>

***dl*-1,4-Bis-(2-oxo-oxazolidin-3-yl)-2,3-diphenylbutane-1,4-dione**

R<sub>f</sub> = 0.13 (ethyl acetate/cyclohexane = 1:1)

Melting point: 249 -250 °C Lit.<sup>1</sup>: 250 - 251 °C

**FT-IR** (neat):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3087, 3062, 3019, 3003 (w), 2958, 2924, 2852 (w), 1777 (s), 1684 (s), 1600, 1584 (w), 1478, 1455, 1384, 1335 (s), 1125 (s), 756, 717, 703.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>):

$\delta$  (ppm) = 3.86 (m, 2H), 4.02 (m, 2H), 4.21 (m, 2H), 4.34 (m, 2H), 5.59 (s, 2H), 7.03 - 7.11 (m, 10H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):

$\delta$  (ppm) = 42.67 (t), 53.53 (d), 61.74 (t), 127.47, 128.18, 129.36 (3d), 134.68 (s), 152.51 (s), 173.62 (s).

**ESI-MS** Pseudomolecular ions:

$m/z$  = 431 [M + Na]<sup>+</sup>, 409 [M + H]<sup>+</sup>.

***meso*-1,4-Bis-(2-oxo-oxazolidin-3-yl)-2,3-diphenylbutane-1,4-dione**

R<sub>f</sub> = 0.23 (ethyl acetate/cyclohexane = 1:1)

Melting point: 307 – 308 °C

**FT-IR** (neat):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3088, 3063, 3025 (w), 2993, 2958, 2921 (w), 1768 (s), 1687 (s), 1638, 1618, 1494 (w), 1479, 1455, 1386, 1362 (s), 1210, 1108 (s), 751, 723, 700, 688.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>):

$\delta$  (ppm) = 3.57 - 3.76 (m, 4H), 4.04 - 4.19 (m, 4H), 6.17 (s, 2H), 7.23 - 7.35 (m, 6H), 7.56 - 7.63 (m, 4H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):

$\delta$  (ppm) = 42.58 (t), 51.49 (d), 61.53 (t), 127.87, 128.59, 129.53 (3d), 136.11 (s), 152.78 (s), 173.40 (s).

**ESI-MS** Pseudomolecular ions:

$m/z$  = 431 [M + Na]<sup>+</sup>, 409 [M + H]<sup>+</sup>.

**Configuration assignment of the new formed stereogenic center.** *dl*- and *meso*-**2** were assigned to the diastereomers of **2** from their crystal structures. The absolute stereoconfiguration was determined by converting *dl*-**2** to the corresponding dimethyl 2,3-

<sup>1</sup> N. Kise, K. Kumada, Y. Terao, N. Ueda, *Tetrahedron* **1998**, 54, 2697 - 2708.

diphenylsuccinate by the reported method<sup>2</sup> followed by the measurement of the optical rotation.

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<sup>2</sup> D. A. Evans, T. C. Britton, J. A. Ellman *Tetrahedron Lett.* **1987**, 28, 6141-6144.