

# **The mechanochemically initiated Achmatowicz rearrangement**

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# Supporting Information

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## Experimental

### General

Starting materials were purchased from commercial suppliers and used without any further purification. Solvents were used in p.a. quality and dried according to common procedures, if necessary. The mechanochemical reactions were performed on a Fritsch Pulverisette-6 (repulsion motor: 180 W, operating frequency: 200-425 rpm). The volume of the agate beaker was 500 cm<sup>3</sup> containing ten agate milling balls (8-10 mm). Thin-layer chromatography (TLC) for reaction monitoring was performed with alumina plates coated with Merck silica gel 60 F<sub>254</sub> (layer thickness: 0.2 mm) and analyzed under UV-light (254 nm). Flash column chromatography was performed with Sigma Aldrich MN silica gel 60M (0.040-0.063 mm, 230-400 mesh) as stationary phase. For lyophilization a Christ ALPHA 1-4 was used. NMR spectra were recorded using a Bruker Avance 300 (<sup>1</sup>H: 300 MHz, T = 295 K) or a Bruker Avance 400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 101 MHz, T = 300 K) instrument. The spectra are referenced against the NMR solvent and are reported as follows: <sup>1</sup>H: chemical shift  $\delta$  (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, qd = quartet of doublet), integration, coupling constant (*J* in Hz).

### Synthesis

**Ethyl 3-(furan-2-yl)-3-hydroxypropanoate (2c)**:<sup>[1]</sup> The agate beaker containing ten agate milling balls was filled with Zn (1.0 g), NH<sub>4</sub>Cl (0.40 g), **1a** (83  $\mu$ L, 1.0 mmol) and **4** (310  $\mu$ L, 3.0 mmol) and milling was performed for 45 min. The reaction mixture was diluted with Et<sub>2</sub>O (10 mL) and a saturated solution of NH<sub>4</sub>Cl (10 mL) and filtrated. The aqueous phase was extracted with Et<sub>2</sub>O (3x15 mL). The combined organic phases were washed with water (50 mL) and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and **2c** (70 mg, 38%) was obtained as brown oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.33 (d, 1H, *J* = 1.8 Hz), 6.29 (dd, 1H, *J* = 1.8, 3.2 Hz), 6.23 (d, 1H, *J* = 3.2 Hz), 5.10 (dd, 1H, *J* = 4.4, 8.4 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 2.86 (dd, 1H, *J* = 8.4, 16.3 Hz), 2.78 (dd, 1H, *J* = 4.4, 16.3 Hz), 1.22 (t, 3H, *J* = 7.1 Hz).

**1-(Benzofuran-2-yl)ethan-1-ol (2e)**:<sup>[2]</sup> The agate beaker containing ten agate milling balls was filled with **1c** (80 mg, 0.50 mmol), NaBH<sub>4</sub> (189 mg, 5.0 mmol) and choline chloride (200 mg) and milling was performed for 1 h. The reaction mixture was diluted with CHCl<sub>3</sub> (10 mL) and filtrated. The organic phase was washed with brine (10 mL), dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. **2e** (58 mg, 72%) was thus obtained as colourless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.56-7.52 (m, 1H), 7.46 (d, 1H, *J* = 7.2 Hz), 7.30-7.25 (m, 1H), 7.25-7.18 (m, 1H), 6.60 (s, 1H), 5.07-4.96 (m, 1H), 2.37 (bs, 1H), 1.64 (d, 3H, *J* = 6.6 Hz).

**6-Hydroxy-2-methyl-2H-pyran-3(6H)-one (3b)**:<sup>[3]</sup> Quartz sand (2.00 g), **2b** (210  $\mu$ L, 2.00 mmol) and *m*CPBA (694 mg, 4.00 mmol) were added together with ten agate milling balls in an agate beaker and milling was performed for 15 min. The reaction mixture was diluted with water (25 mL) and filtered. The water was removed by lyophilization and **3b** (182 mg, 71% [dr 2:1]) was thus obtained as yellow solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): *cis-isomer*:  $\delta$  = 6.89 (dd, 1H, *J* = 3.4, 10.3 Hz), 6.10 (d, 1H, *J* = 10.2 Hz), 5.63 (d, 1H, *J* = 3.4 Hz), 4.71 (q, 1H, *J* = 6.8 Hz), 1.39 (d, 3H, *J* = 6.8 Hz); *trans-isomer*:  $\delta$  = 6.94 (dd, 1H, *J* = 1.4, 10.3 Hz), 6.15 (dd, 1H,

$J = 1.6, 10.3$  Hz), 5.68 (d, 1H,  $J = 1.4$  Hz), 4.22 (qd, 1H,  $J = 1.2, 6.7$  Hz), 1.45 (d, 3H,  $J = 6.7$  Hz).

**Ethyl 2-(6-hydroxy-3-oxo-3,6-dihydro-2H-pyran-2-yl)acetate (3c):**<sup>[4, 5]</sup> A solution of **2c** (257 mg, 1.40 mmol) in Et<sub>2</sub>O (3 mL) was mixed with quartz sand (2.00 g) and the solvent was removed under reduced pressure. The mixture was filled to an agate beaker equipped with ten agate milling balls, *m*CPBA (552 mg, 3.20 mmol) was added and milling was performed for 30 min. The mixture was diluted with water (20 mL), filtered and the water was removed by lyophilization. The crude product was purified by flash column chromatography (PE/EtOAc:1/1) and **3c** (238 mg, 84% [dr 3:1]) was thus obtained as yellow-brown oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): *major diastereomer*:  $\delta = 6.92$  (dd, 1H,  $J = 3.5, 10.3$  Hz), 6.14 (d, 1H,  $J = 10.3$  Hz), 5.63 (d, 1H,  $J = 3.5$  Hz), 5.02 (dd, 1H,  $J = 3.9, 7.6$  Hz), 4.15 (q, 2H,  $J = 7.1$  Hz), 2.99 (dd, 1H,  $J = 4.0, 16.8$  Hz), 2.74 (dd, 1H,  $J = 7.6, 16.7$  Hz), 1.25 (t, 3H,  $J = 7.2$  Hz); *minor diastereomer*:  $\delta = 6.96$  (dd, 1H,  $J = 1.6, 10.3$  Hz), 6.18 (dd, 1H,  $J = 1.6, 10.3$  Hz), 5.73-5.70 (m, 1H), 4.60-4.55 (m, 1H), 4.16 (q, 2H,  $J = 7.1$  Hz), 3.02 (d, 1H,  $J = 16.7$  Hz), 2.82 (d, 1H,  $J = 7.9$  Hz), 1.26 (t, 3H,  $J = 7.1$  Hz).

**6-Hydroxy-6-(hydroxymethyl)-2H-pyran-3(6H)-one (3d):**<sup>[6]</sup> The agate beaker was equipped with ten agate milling balls, **2d** (41 mg, 0.32 mmol), choline chloride (40 mg) and *m*CPBA (111 mg, 0.64 mmol) and milling was performed for 60 min. The reaction mixture was diluted with EtOAc (20 mL), filtered and the solvent was removed under reduced pressure. The crude product was dissolved in water (20 mL), filtered and the water was removed by lyophilization to obtain a 5:1 mixture of **3d** (29 mg, 63%) and the corresponding hemiacetal **5** as red brown oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): **3d**:  $\delta = 6.84$  (d, 1H,  $J = 10.4$  Hz), 6.19 (d, 1H,  $J = 10.4$  Hz), 4.61 (d, 1H,  $J = 16.9$  Hz), 4.16 (d, 1H,  $J = 16.9$  Hz), 3.81 (d, 1H,  $J = 11.4$  Hz), 3.64 (d, 1H,  $J = 11.5$  Hz); **5**: 6.90 (d, 1H,  $J = 10.4$  Hz), 6.18 (d, 1H,  $J = 10.4$  Hz), 4.60 (d, 1H,  $J = 16.9$  Hz), 4.46 (d, 1H,  $J = 11.7$  Hz), 4.19 (d, 1H,  $J = 16.9$  Hz), 4.08 (d, 1H,  $J = 11.8$  Hz).

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