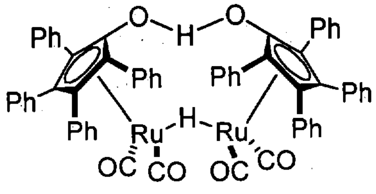
Supplementary Information

Shvo Catalyst Preparation[1]



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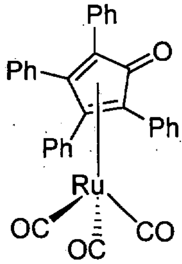
Step 1

$Ru_3(CO)_{12}$ (0.5 mmol, 0.320 g) and tetraphenylcyclopentadienone (2 mmol, 0.769 g) were placed in a Schlenk tube. Mesitylene[2] (5 ml) was added and the mixture was flushed with argon during *ca.* 1 min before the system was closed. The reaction was stirred at 150°C (bath temperature[3]) during 24 h, then cooled down and the reaction mixture bubbled with argon to remove the carbon monoxide in solution (WARNING; when the reaction vessel is opened, CO is released). The system was closed and stirred at the same temperature for an additional 5 h. The reaction was cooled down again, the solvent distilled off under reduce pressure and the product was purified by flash chromatography using a short column (hight; 4 cm, diameter; 3 cm) using hexane, hexane / CH_2Cl_2 and finally CH_2Cl_2 as eluent (hexane and hexane / CH_2Cl_2 until the red fraction in the column was out) yielding 0.83 g of pure compound **8**, as a pale yellow solid (on TLC one single spot, Rf 0.2 in CH_2Cl_2) (97% yield).



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Step 2

The product from the first step was dissolved in acetone[4] (60 ml). Sat[1]. Na_2CO_3 (aq.) (30 ml) was added and the mixture was stirred under argon at ambient temperature for 1.5 h. The light yellow color of the reaction mixture changed to bright orange during the course of the reaction. Saturated NH_4Cl (aq) (150 ml) was added till neutralization and the acetone was removed *in vacuo*. The aqueous solution was extracted with CH_2Cl_2 (3×50 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the orange residue was purified on a short silica column (5-6 cm). Hexane was used until the red fraction had moved about 2-3 cm on the column and then hexane/CH_2Cl_2 (gradient 50:50 to 0:100) was employed to yield compound **3** (0.491 g, 62%). Rf 0.60 in hexane / CH_2Cl_2, 1/1.

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[1] A slight modification of the previously reported preparation (Bäckvall *et al.*, *J. Am. Chem. Soc.* **1999**, *121*, 1645.) has been proved to give better yield.

[2] Alternatively the reaction can be carried out in toluene at 150 °C, using a 35 ml Ace pressure tube (Aldrich), giving slightly better results.

[3] The temperature is crucial for the stability of the intermediate.

*Typical procedure for the racemization of methyl mandelate (L)-***1a**

The ruthenium catalyst (2 mol%) was placed in a Schlenk tube which was evacuated and filled with argon. In a conical flask argon was bubbled through a solution of (*S*)-methyl mandelate (83mg, 0.5 mmol) and methyl 2-oxo-2-phenylacetate (appropriate quantity) in 1.25 ml of the appropriate solvent and transferred via a canula to the Schlenk tube containing the catalyst. The reaction mixture was heated at 60°C. The reaction was followed by chiral GC, worked up by filtration through a bed of celite.

Typical procedure for the kinetic resolution of α-hydroxy esters **1**

To a solution of the α-hydroxy ester **1** (0.5 mmol), p-chlorophenyl acetate (1 mmol) in the appropriate solvent (2.5 ml) was added 30 mg of the corresponding enzyme and the mixture was heated at the desired temperature under stirring. The reaction was followed by ^{1}H-NMR and stopped after nearly 50% of conversion. The crude reaction mixture was washed with dilute NaOH solution and water, dried over sodium sulfate. The solvent was evaporated and the crude was purified by column chromatography (9:1, hexane/ethyl acetate). The ee of the products **2** was measured by chiral HPLC.

Typical procedure for the dynamic kinetic resolution of α-hydroxy ester **1c**

The ruthenium catalyst **3** (11 mg, 2 mol%) and the enzyme PS-C from Amano (30 mg) were placed in a Schlenk tube which was evacuated and filled with argon. In a conical flask, argon was bubbled through a solution of α-hydroxy ester **1c** (0.098 g, 0.5 mmol), *p*-chlorophenyl acetate (0.171 g, 1mmol) in 2.5 ml of the cyclohexane and transferred via a canula to the Schlenk tube containing the catalyst and the enzyme. The reaction mixture was heated at 60°C for 48 h. The reaction was worked up by filtration through a bed of celite and purified by column chromatography (9:1, hexane/ethyl acetate) to give 0.087 g (73% yield) of **2c** which was of 94% ee according to HPLC.

HPLC and GC Datas

O-Acetyl methyl mandelate **2a**
OD-H Chiracel column
Flow rate : 0.5ml/ min
Eluent: 99.5 Hexane:0.5 *iso*-propanol; λ_{max} = 210 nm
Retention times: (*S*)-**2a**, 19.067min; (*R*)- **2a**, 20.500 min

O-Acetyl ethyl mandelate **2b**
OD-H Chiracel column
Flow rate : 0.5ml/ min
Eluent: 99.5 Hexane:0.5 *iso*-propanol; λ_{max} = 210 nm
Retention times: (*S*)-**2b**, 22.077 min; (*R*)-**2b**, 24.467 min

O-Acetyl methyl p-*methoxymandelate* **2c**
OK-H Chiracel column
Flow rate : 1.0 ml/ min
Eluent: 98.0 Hexane:2.0 *iso*-propanol; λ_{max} = 220 nm
Retention times: (*S*)-**2c**, 45.634 min; (*R*)-**2c**, 54.848 min

O-Acetyl methyl p-*Bromomandelate* **2d**
OK-H Chiracel column
Flow rate : 1.0 ml/ min
Eluent: 99.0 Hexane:1.0 *iso*-propanol; λ_{max} = 220 nm

Retention times: (*S*)-**2d**, 36.609 min; (*R*)-**2d**, 41.946 min

O-Acetyl methyl- α-hydroxy naphthyl -2-acetate **2i**

OK-H Chiracel column

Flow rate : 0.75 ml/ min

Eluent: 92.0 Hexane:8.0 *iso*-propanol; λ_{max} = 220 nm

Retention times: (*S*)-**2i**, 46.884 min; (*R*)-**2i**, 53.611 min

O-Acetyl methyl-2-hydroxy-4-phenyl-butyrate **2f**

Chiralcel OK-H,

1 ml flow rate / min,

Eluent: 99.5 Hexane: :0.5 *iso*-propanol; λ_{max} = 210nm.

Retention times: (*S*)-**2f**, 43.431 min, (*R*)-**2f**, 49.092 min

O-Acetyl methyl 2-cyclohexyl-2-hydroxyacetate **2e**

OD-H chiracel column

Flow rate : 0.5ml/min

Eluent : 99 Hexane:1 *iso*-propanol; λ_{max} = 214nm.

Retention times: (*S*)-**2e**, 13.228 min; (*R*)-**2e**, 15.769 min

O-Acetyl-methyl-2-hydroxy caproate **2g**

GC with Cyclodex-B 30m X 0.32mm

Flow rate :1.8 ml/min

Temperature program: 90°C cte. for 25min.

Retention times

(*R*)-**2g**, 22.965 min; (*S*)-**2g**, 23.400 min