

## Preparation of (*R*)-(+) -Lithium Lactate

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**Summary.** Optically pure (*R*)-(+) -lithium lactate (**7**) and its benzyl ether analogue (**6a**) were obtained from acetaldehyde using *Eliel's* 1,3-*trans*-oxathiane (**1**) as the chiral auxiliary for chromatographic separation.

**Keywords.** Lactic acid; Lithium lactate.

### Herstellung von (*R*)-(+) -Lithiumlactat

**Zusammenfassung.** Optisch reines (*R*)-(+) -Lithiumlactat (**7**) und sein Benzyletheranaloges (**6a**) wurden mittels *Eliel's* 1,3-*trans*-Oxathian (**1**) als chiralem Hilfsstoff zur chromatographischen Trennung aus Acetaldehyd hergestellt.

### Introduction

Although lactic acid is one of the simplest chiral building blocks, only racemic and (*S*)-(+) -lactic acid are found in nature. This situation is reflected by the enormous price difference between the two separate isomers or their derivatives. 1 kg of 85% *S*-lactic acid solution in water is available for US \$69.75, whereas only 500 mg of *R*-lactic acid lithium salt are traded for US \$94.55 (Aldrich, 1996–1997).

Both (*R*)-(–) - and (*S*)-(+) -lactic acid derivatives have been used for syntheses of biologically active molecules required for crop protection [1] and for human health [2,3] as well as for the preparation of other chiral compounds [4–8]. Each isomer can be obtained by fermentation processes [9,10] which are quite delicate to perform and require considerable amounts of energy to remove water. Other methods for the preparation of the valuable (*R*)-(–) -lactic acid are also complex and include treatment of pyruvic aldehyde with enzymes [11] and the use of *L*-alanine as a synthetic precursor [12]. In addition, the asymmetric reduction of ethyl pyruvate afforded the *R*-lactate with an enantiomeric excess of *ca.* 90% [13].

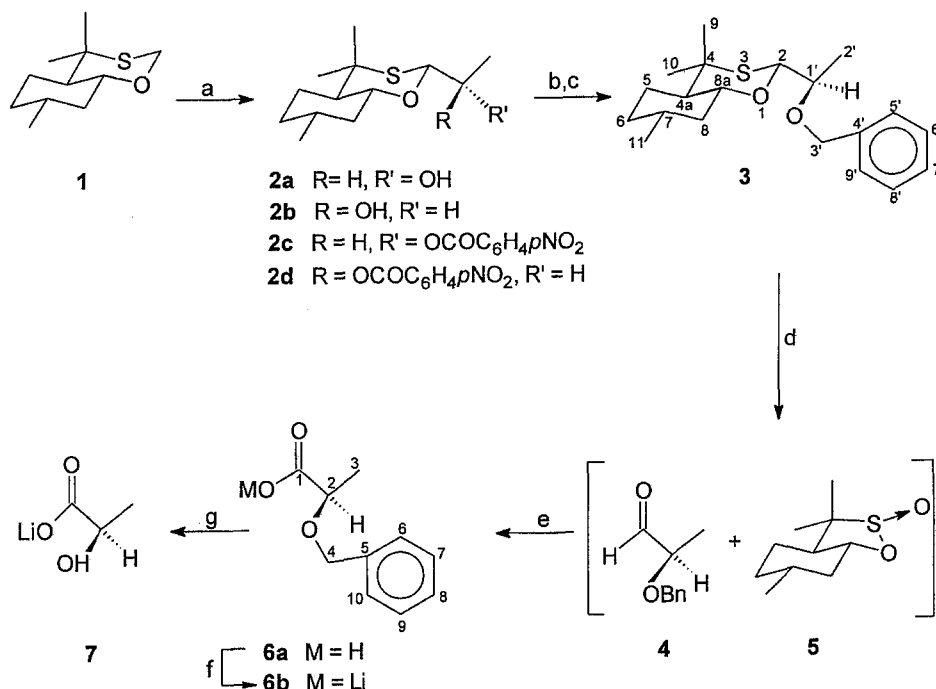
We describe herein the preparation of the desired (*R*)-(+) -lithium lactate using acetaldehyde and formaldehyde as the building blocks in a reaction sequence involving *Eliel's* 1,3-*trans*-oxathiane (**1**, [14]) which can be recycled in the reaction sequence [15].

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## Results and Discussion

The synthesis of (*R*)-(+)-lithium lactate (**7**, Scheme) starts by reacting the lithium salt of *trans*-oxathiane (**1**, [14]) with acetaldehyde in *THF* at  $-78^{\circ}\text{C}$  to yield a mixture of diastereoisomers **2a** and **2b** (83%). Silica gel column separation [16] using hexane-AcOEt (96:4) allowed to obtain the less polar **2b** in 44% and the more polar **2a** in 39% yield. In order to determine the stereochemistry of the new chiral center, the *p*-nitrobenzoate esters (**2c** and **2d**) of **2a** and **2b** were subjected to X-ray analysis.

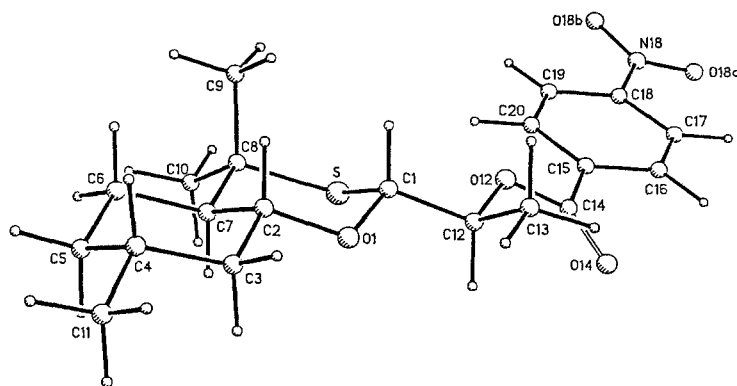
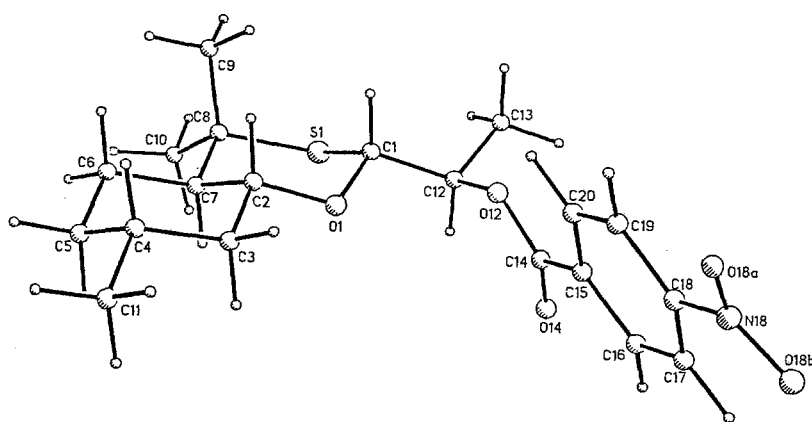
The single crystal X-ray diffraction analyses revealed the *S* absolute configuration at C1' for **2c** and *R* configuration for **2d**, as shown in Figs. 1 and 2, respectively, in



**Scheme 1** a: 1) *n*-BuLi/*THF*, 2) CH<sub>3</sub>CH=O,  $-78^{\circ}\text{C}$ ; b: chromatography, C<sub>6</sub>H<sub>14</sub>/AcOEt: 96/4; c: 1) NaH/*THF*, 2) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br; d: NCS, AgNO<sub>3</sub>, CH<sub>3</sub>CN/H<sub>2</sub>O=8/2,  $-5^{\circ}\text{C}$ ; e: NaClO<sub>2</sub>, Me<sub>2</sub>C=CHMe, NaH<sub>2</sub>PO<sub>4</sub>, *t*-BuOH; f: LiOH; g: H<sub>2</sub>Pd/C 10%

which the atom numbering differs from that in the text. Diastereoisomer **2b**, the most valuable one, showed a m.p. of  $61\text{--}62^{\circ}\text{C}$  and an optical rotation ( $[\alpha]_{365}$ ) of  $-19.7^{\circ}$  ( $c = 2.23$ , CHCl<sub>3</sub>).

Reaction of **2b** with NaH in *THF* at room temperature afforded the sodium alcoholate which reacted with benzyl bromide in *THF* to give the benzyl ether **3** in 95% yield after chromatographic purification (b.p. =  $130^{\circ}\text{C}/0.25\text{ mm}$ , Kugelrohr;  $[\alpha]_{365} = +72.2^{\circ}$  ( $c = 2.52$ , CHCl<sub>3</sub>)). Treatment of **3** with NCS and AgNO<sub>3</sub> [17] in CH<sub>3</sub>CN-H<sub>2</sub>O (8:2) resulted in a non-separable mixture of aldehyde **4** and the sultine **5**. This mixture was oxidized with NaClO<sub>2</sub>, 2-methyl-2-butene [18] in *t*-BuOH, and a NaH<sub>2</sub>PO<sub>4</sub> buffer solution to produce the acid **6a** (56%) after separation. Neutralization with LiOH in H<sub>2</sub>O yielded the lithium salt **6b** in 89% (m.p. =  $210\text{--}215^{\circ}\text{C}$ ,  $[\alpha]_{365} = +210.8^{\circ}$  ( $c = 2.04$ , H<sub>2</sub>O)). Finally, hydrogenolysis of the benzyl ether **6b**

Fig. 1. X-ray structure of **2c**Fig. 2. X-ray structure of **2d**

with 10% Pd/C in ethanol at room temperature and under normal pressure gave (*R*)-(+)-lithium lactate (**7**) in 90% yield ( $[\alpha]_{\text{D}} = +13.7^{\circ}$  ( $c = 2.11$ ,  $\text{H}_2\text{O}$ ), Ref. [19];  $[\alpha]_{\text{D}} = +13.5^{\circ}$  ( $c = 3.84$ ,  $\text{H}_2\text{O}$ )). The NMR assignments given in the experimental section were performed based on literature analogues [20].

## Experimental

$^1\text{H}$ ,  $^{13}\text{C}$ , COSY and HETCOR NMR spectra: Varian XL-300GS ( $^1\text{H}$ : 300 MHz,  $^{13}\text{C}$ : 75 MHz, TMS,  $\text{CDCl}_3$  unless otherwise stated); IR spectra: Perkin Elmer 16F PC FT-IR spectrophotometer (KBr unless otherwise stated); specific rotations; Perkin Elmer 241 polarimeter; flash column chromatography: Merck silica gel, particle size: 0.040–0.063 mm (230–400 mesh ASTM). The melting points were measured using a Fisher-Johns apparatus and are uncorrected, as is the boiling point.

### Hexahydro-2(*l*-hydroxyethyl)-4,4,7-trimethyl-4*H*-1,3-benzoxathiin (**2b**)

A solution of **1** (12.0 g, 60 mmol) in dry THF (70 ml) under  $\text{N}_2$  was cooled ( $-78^{\circ}\text{C}$ ) and stirred for 10 min. *n*-Buli (65 mmol) was added slowly; after stirring for 15 min, the mixture was warmed to  $0^{\circ}\text{C}$  and

recooled to  $-78^{\circ}\text{C}$ . Acetaldehyde (8.0 g, 160 mmol) in *THF* (10 ml) was added; after stirring for 4 h at  $-78^{\circ}\text{C}$ , the mixture was allowed to warm to room temperature overnight. A saturated solution of  $\text{NH}_4\text{Cl}$  (50 ml) was added. Extraction with ether ( $2 \times 60$  ml), washing with brine and water, drying over  $\text{Na}_2\text{SO}_4$ , and evaporation of ether afforded a yellow liquid (16.5 g). Separation by flash chromatography with hexane-AcOEt (96:4) allowed to obtain-after successive chromatographies-the less polar diastereoisomer **2b** (6.4 g, 44%). M.p. =  $61\text{--}62^{\circ}\text{C}$ ;  $[\alpha]_{\text{D}} = +2.7^{\circ}$ ,  $[\alpha]_{578} = +2.2^{\circ}$ ,  $[\alpha]_{546} = +1.8^{\circ}$ ,  $[\alpha]_{436} = -2.7^{\circ}$ ,  $[\alpha]_{365} = -19.7^{\circ}$  ( $c = 2.23$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$ :  $\delta = 4.68$  (d,  $J = 7$  Hz, H2), 1.46 (m, H4a, H7), 1.85 (m, H5 $\alpha$ ), 0.86–0.96 (m, H5 $\beta$ , H6 $\alpha$ ), 1.72 (m, H6 $\beta$ ), 1.12 (td,  $J = 11.0/12.0$  Hz, H8 $\alpha$ ), 1.97 (m, H8 $\beta$ ), 3.41 (td,  $J = 4.0/10.0$  Hz, H8a), 1.43 (s, Me9), 1.27 (s, Me10), 0.93 (d,  $J = 7.0$  Hz, Me11), 3.79 (quintet,  $J = 6.0$  Hz, H1'), 1.20 (d,  $J = 6.0$  Hz, Me2') ppm;  $^{13}\text{C NMR}$ :  $\delta = 83.2$  (C2), 43.0 (C4), 50.7 (C4a), 24.3 (C5), 34.6 (C6), 31.3 (C7), 41.6 (C8), 77.0 (C8a), 22.9 (C9), 29.5 (C10), 22.0 (C11), 69.5 (C1'), 18.4 (C2') ppm; IR:  $\nu_{\text{max}} = 3576, 3440, 1614, 1418, 1062$   $\text{cm}^{-1}$ . The more polar diastereoisomer **2a** was obtained as a nearly colorless liquid (5.7 g, 39%).

#### Hexahydro-2(*l*-benzyloxyethyl)-4,4,7-trimethyl-4H-1,3-benzoxathiin (**3**)

Into a suspension of NaH (0.5 g, 20.8 mmol) and  $\text{NBu}_4\text{SO}_4\text{H}$  (0.05 g) in dry *THF* (50 ml) under  $\text{N}_2$ , a solution of **2b** (2.7 g, 11.06 mmol) in *THF* (10 ml) was added dropwise and stirred over 15 min. A solution of benzyl bromide (1.96 g, 11.5 mmol) and *THF* (5 ml) was added and refluxed over 40 min and then left at room temperature overnight. The reaction was quenched by addition of a saturated solution of  $\text{NH}_4\text{Cl}$  (10 ml), then filtered over celite through a *Büchner* funnel. The organic layer was washed with brine and water, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated under vacuum to give a yellow liquid. Flash chromatography with hexane-AcOEt (96:4) afforded pure **3** (3.5 g, 95%). B.p. =  $130^{\circ}\text{C}/0.25$  mm (Kugelrohr);  $[\alpha]_{\text{D}} = +25.3^{\circ}$ ,  $[\alpha]_{578} = +29.4^{\circ}$ ,  $[\alpha]_{546} = +32.9^{\circ}$ ,  $[\alpha]_{436} = +53.2^{\circ}$ ,  $[\alpha]_{365} = +72.2^{\circ}$  ( $c = 2.52$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$ :  $\delta = 4.49$  (d,  $J = 6.0$  Hz, H2), 1.46 (m, H4a, H7), 1.81 (m, H5 $\alpha$ ), 0.83–0.98 (m, H5 $\beta$ , H6 $\alpha$ ), 1.69 (m, H6 $\beta$ ), 1.14 (td,  $J = 11.0/12.0$  Hz, H8 $\alpha$ ), 1.96 (m, H8 $\beta$ ), 3.39 (td,  $J = 4.0/10.0$  Hz, H8a), 1.40 (s, Me9), 1.26 (Me10), 0.91 (d,  $J = 7.0$  Hz, Me11), 3.68 (quintet,  $J = 6.0$  Hz, Me2'), 1.21 (d,  $J = 6.0$  Hz, H2'), 4.68 (dd,  $J = 12.0/17.0$  Hz, H3'), 7.30 (m, HAr) ppm;  $^{13}\text{C NMR}$ :  $\delta = 83.0$  (C2), 42.7 (C4), 50.6 (C4a), 24.2 (C5), 34.6 (C6), 31.3 (C7), 41.6 (C8), 77.0 (C8a), 22.8 (C9), 29.6 (C10), 22.0 (C11), 76.4 (C1'), 16.6 (C2'), 72.1 (C3'), 138.7 (C4'), 127.6 (C5', C9'), 128.0 (C6', C8'), 127.2 (C7') ppm; IR (film):  $\nu_{\text{max}} = 2926, 1454, 1150, 1094, 1070$   $\text{cm}^{-1}$ .

#### (*R*)-*O*-Benzyl lactic acid (**6a**)

A solution of **3** (1.5 g, 4.5 mmol) in  $\text{CH}_3\text{CN}$  (5 ml) was added at once to a solution of NCS (1.2 g, 9 mmol) and  $\text{AgNO}_3$  (1.53 g, 9 mmol) in 30 ml of a mixture of  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  (80:20) at  $-4^{\circ}\text{C}$  and stirred over 10 min. Saturated solutions of  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and NaCl (6.0 ml each) were added at intervals of 1 min. The resulting mixture was stirred at  $0^{\circ}\text{C}$  for 10 min, ether (60 ml) was added, and the mixture was filtered through a *Büchner* funnel with celite and rinsed with ether. The organic layer was washed with brine and water, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated under vacuum below  $40^{\circ}\text{C}$  to give aldehyde **4** and sultine **5** (non-separable). To the crude mixture, *tert*-butanol (25 ml) and 2-methyl-2-butene (5 ml) were added. Then, a solution of  $\text{NaClO}_2$  (1.4 g, 12.3 mmol) in  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (1.6 M, 1.6 ml) was added dropwise at room temperature, and the mixture was stirred for 20 h. The *pH* was adjusted to 10.2 with 3 N NaOH. The mixture was evaporated in a rotatory evaporator, and  $\text{H}_2\text{O}$  (60 ml) was added. The suspension was extracted three times with hexane-AcOEt (70:30). The organic layer was evaporated to yield **5** as a waxy solid. The aqueous layer was acidified to *pH* = 2.9 with 3 N HCl and extracted three times with 50 ml portions of ether. The ethereal layer was dried over  $\text{Na}_2\text{SO}_4$  and evaporated to yield **6** as a colorless liquid (0.45 g, 56%).  $^1\text{H NMR}$ :  $\delta = 4.11$  (q,  $J = 7.0$  Hz, H2), 1.49 (d,  $J = 7.0$  Hz, Me3), 4.51 and 4.72 (2d,  $J = 12.0$  Hz,  $\text{OCH}_2$ ), 7.30–7.37 (m, HAr) ppm;  $^{13}\text{C NMR}$ :  $\delta = 178.1$  (C1), 73.5 (C2), 18.3 (C3), 72.1 (C4), 137.1 (C5), 127.9 (C6, C10), 128.5 (C7, C9), 128.0 (C8) ppm.

**Lithium salt 6b**

A solution of **6a** (0.45 g, 2.5 mmol) in CH<sub>3</sub>OH (4 ml) containing 10 drops of water was potentiometrically neutralized with 0.6 *M* aqueous LiOH solution (4.2 ml, 2.52 mmol). The aqueous layer was washed with three 10 ml portions of hexane-AcOEt (90:10), and the organic layer was discarded. To the aqueous solution, 15 ml of benzene were added and evaporated under vacuum; this operation was repeated twice until no more water was present in the white solid (0.415 g, 89%). M.p. = 210–25°C;  $[\alpha]_{\text{D}} = +67.2^\circ$ ,  $[\alpha]_{578} = +69.6^\circ$ ,  $[\alpha]_{546} = +77.9^\circ$ ,  $[\alpha]_{436} = +135.3^\circ$ ,  $[\alpha]_{365} = +210.8^\circ$  ( $c = 2.04$ , H<sub>2</sub>O); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta = 3.84$  (q,  $J = 7.0$  Hz, H2), 1.22 (d,  $J = 7.0$  Hz, Me3), 4.37 and 4.64 (2d,  $J = 12.0$  Hz, OCH<sub>2</sub>), 7.24–7.35 (m, HAr) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta = 176.4$  (C1), 76.3 (C2), 18.9 (C3), 69.7 (C4), 139.2 (C5), 127.4 (C6, C10), 127.9 (C7, C9), 126.9 (C8) ppm; IR:  $\nu_{\text{max}} = 3414, 3197, 1585, 1427, 1124$  cm<sup>-1</sup>.

**(*R*)-(+)-Lithium lactate (7)**

A solution of **6b** (0.1804 g, 0.97 mmol) in 95% ethanol (15 ml) containing 10% Pd/C (0.150 g) was hydrogenated with stirring at room temperature under normal pressure for 48 h and then filtered off. The solvent was vacuum evaporated to give **7** (0.089 g, 90%).  $[\alpha]_{\text{D}} = +13.7^\circ$ ,  $[\alpha]_{578} = +14.7^\circ$ ,  $[\alpha]_{546} = +18.0^\circ$ ,  $[\alpha]_{436} = +28.9^\circ$  ( $c = 2.11$ , H<sub>2</sub>O); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta = 3.75$  (q,  $J = 7.0$  Hz, H2), 1.17 (d,  $J = 7.0$  Hz, Me3) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta = 178.6$  (C1), 67.5 (C2), 21.3 (C3) ppm; IR:  $\nu_{\text{max}} = 3421, 1618, 1427, 1117, 703$  cm<sup>-1</sup>.

***p*-Nitrobenzoate (2c)**

To a solution of **2a** (0.25 g, 1.02 mmol) in dry pyridine (3 ml), *p*-nitrobenzoyl chloride (0.375 g, 2.0 mmol) and 4-dimethylaminopyridine (0.03 g) were added. The reaction mixture was heated on a steam bath for two hours. H<sub>2</sub>O (10 ml) was added and stirred for 15 min; then, solid NaHCO<sub>3</sub> was added until neutralization and extracted twice with 30 ml portions of AcOEt. The organic layer was washed four times with 20 ml portions of 5% HCl, brine, and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. AcOEt was vacuum evaporated to give a solid which was recrystallized from hexane/AcOEt to give a white solid (0.29 g, 72%). M.p. = 106–107°C;  $[\alpha]_{\text{D}} = +5.6^\circ$ ,  $[\alpha]_{578} = +4.3^\circ$ ,  $[\alpha]_{546} = +6.1^\circ$ ,  $[\alpha]_{436} = +16.4$  ( $c = 2.31$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR:  $\delta = 5.14$  (d,  $J = 4.0$  Hz, H2), 1.38–1.54 (m, H4a, H7), 1.85 (m, H5 $\alpha$ ), 0.81–1.00 (m, H5 $\beta$ , H6 $\alpha$ ), 1.71 (m, H6 $\beta$ ), 1.12 (td,  $J = 11.0/12.0$  Hz, H8 $\alpha$ ), 1.97 (m, H8 $\beta$ ), 3.44 (td,  $J = 4.2/10.5$  Hz, H8a), 1.44 (s, Me9), 1.29 (s, Me10), 0.92 (d,  $J = 6.6$  Hz, Me11), 5.24 (m, H1'), 1.46 (d,  $J = 6.5$  Hz, Me2'), 8.23 (m, H5', H9'), 8.29 (m, H6', H8') ppm; <sup>13</sup>C NMR:  $\delta = 80.6$  (C2), 43.3 (C4), 50.7 (C4a), 24.3 (C5), 34.6 (C6), 31.4 (C7), 41.7 (C8), 77.3 (C8a), 22.8 (C9), 29.6 (C10), 22.0 (C11), 73.4 (C1'), 15.8 (C2'), 163.9 (C3'), 135.9 (C4'), 130.9 (C5', C9'), 123.4 (C6', C8'), 150.5 (C7') ppm.

***p*-Nitrobenzoate (2d)**

As in the previous case, **2d** was obtained as a colorless solid (79% yield). M.p. = 122–123°C;  $[\alpha]_{\text{D}} = -24.2^\circ$ ,  $[\alpha]_{578} = -25.0^\circ$ ,  $[\alpha]_{546} = -29.2^\circ$ ,  $[\alpha]_{436} = -58.3^\circ$  ( $c = 2.4$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR:  $\delta = 5.14$  (d,  $J = 5.5$  Hz, H2), 1.49 (m, H4a), 1.86 (m, H5 $\alpha$ , H8 $\beta$ ), 0.81–1.05 (m, H5 $\beta$ , H6 $\alpha$ ), 1.70 (m, H6 $\beta$ ), 1.62 (m, H7), 1.11 (td,  $J = 11.0/12.5$  Hz, H8 $\alpha$ ), 3.41 (td,  $J = 4.3/10.5$  Hz, H8a), 1.43 (s, Me9), 1.28 (s, Me10), 0.90 (d,  $J = 6.5$  Hz, Me11), 5.33 (quintet,  $J = 6.0$  Hz, H1'), 1.43 (d,  $J = 6.5$  Hz, Me2'), 8.22 (m, H5', H9'), 8.28 (m, H6', H8') ppm; <sup>13</sup>C NMR:  $\delta = 80.6$  (C2), 43.2 (C4), 50.7 (C4a), 24.4 (C5), 34.7 (C6), 31.4 (C7), 41.6 (C8), 77.4 (C8a), 22.9 (C9), 29.7 (C10), 22.0 (C11), 72.9 (C1'), 16.0 (C2'), 164.0 (C3'), 135.9 (C4'), 130.9 (C5', C9'), 123.5 (C6', C8'), 150.5 (C7') ppm.

**Crystal structure determinations**

Single crystal X-ray diffraction analyses were performed using a Nicolet R3m four circle diffractometer equipped with Cu-K $\alpha$  monochromated radiation ( $\lambda = 1.54178$  Å) operating in the  $\theta - 2\theta$  scan mode

and using the software provided by the diffractometer manufacturer. Crystal data for **2c**:  $C_{20}H_{27}NO_5S$ , MW = 393.5, orthorhombic, space group  $P2_12_12_1$ ,  $a = 7.755(3)$ ,  $b = 8.670(3)$ ,  $c = 30.85(2)$  Å,  $V = 2074.29$  Å<sup>3</sup>,  $D_c = 1.21$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F_{000} = 840$ , scan speed 4.0–29.3, scan limits  $3^\circ \geq 2\theta \geq 110^\circ$ . Of the 1572 collected reflections, 1434 [ $I = 3\sigma(I)$ ] were considered as observed. The structure was refined to  $R = 4.56\%$  using 1426 independent reflections. Crystal data for **2d**:  $C_{20}H_{27}NO_5S$ , MW = 393.5, orthorhombic, space group  $P2_12_12_1$ ,  $a = 6.860(2)$ ,  $b = 14.715(4)$ ,  $c = 20.991(8)$  Å,  $V = 2119.08$  Å<sup>3</sup>,  $D_c = 1.23$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F_{000} = 840$ , scan speed 4.0–29.3, scan limits  $3^\circ \geq 2\theta \geq 110^\circ$ . Of the 1595 collected reflections, 1491 [ $I = 3\sigma(I)$ ] were considered as observed. The structure was refined to  $R = 3.56\%$  using 1485 independent reflections. Tables containing atomic coordinates, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and their temperature factors, torsion angles, and comparison of the calculated with the observed structure factors have been deposited and may be ordered from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. Federal Republic of Germany, referring to the deposition number CSD-59396, the names of the authors, and the citation of the present paper.

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## References

- [1] Crosby J (1992) Chirality in Industry. An Overview. In: Collins AN, Sheldrake GN, Crosby J (eds) Chirality in Industry. Wiley, New York, pp 10–11
- [2] Pham VC, Charlton JL (1995) *J Org Chem* **60**: 8051
- [3] (a) Hintzer K, Weber R, Schurig V (1981) *Tetrahedron Lett* **22**: 55; (b) Dirlam NL, Moore BS, Urban FJ (1987) *J Org Chem* **52**: 3587
- [4] (a) Greiner A, Ortholand J-Y (1990) *Tetrahedron Lett* **31**: 2135; (b) Ortholand J-Y, Greiner A (1993) *Bull Soc Chim Fr* **130**: 133
- [5] Seebach D, Naef R, Calderari G (1984) *Tetrahedron* **40**: 1313
- [6] Tottie L, Baeckström P, Moberg Ch, Tegenfeldt J, Heumann A (1992) *J Org Chem* **57**: 6579
- [7] Tottie L, Moberg Ch, Heumann A (1993) *Acta Chem Scand* **47**: 492
- [8] Heumann, A, Faure R (1993) *J Org Chem* **58**: 1276
- [9] Voelskow H, Sukatsch D (1984) US Pat No 4,467,034
- [10] Cooper B, Kuesters W (1988) US Pat No 4,769,329
- [11] Patterson MAK, Szajewski RP, Whitesides GM (1981) *J Org Chem* **46**: 4682
- [12] Kunz H, Lerchen H-G (1987) *Tetrahedron Lett* **28**: 1873
- [13] Noyori R (1994) *Asymmetric Catalysis in Organic Synthesis*. Wiley, New York, pp 359–361 and references therein
- [14] Eliel EL, Lynch JE, Kume F, Frye SV (1987) *Org Synth* **65**: 215
- [15] Linch JE, Eliel EL (1984) *J Am Chem Soc* **106**: 2943
- [16] Ko K-Y, Frazee WJ, Eliel EL (1984) *Tetrahedron* **40**, 1333
- [17] Corey EJ, Erickson BW (1971) *J Org Chem* **36**: 3553
- [18] Kraus GA, Roth B (1980) *J Org Chem* **45**: 4825
- [19] Purdie T, Walker JW (1895) *J Chem Soc* **67**: 616
- [20] Cervantes-Cuevas H, Joseph-Nathan P (1988) *Tetrahedron Lett* **29**: 5535

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