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Synthesis of Optically Active 4-Hydroxypyrazolidin-3-ones as Precursors for β-Amino-α-hydroxycarboxylic Acid Derivatives

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Dedicated to Professor Dr. Hans-Georg Henning on the Occasion of his 70th Birthday

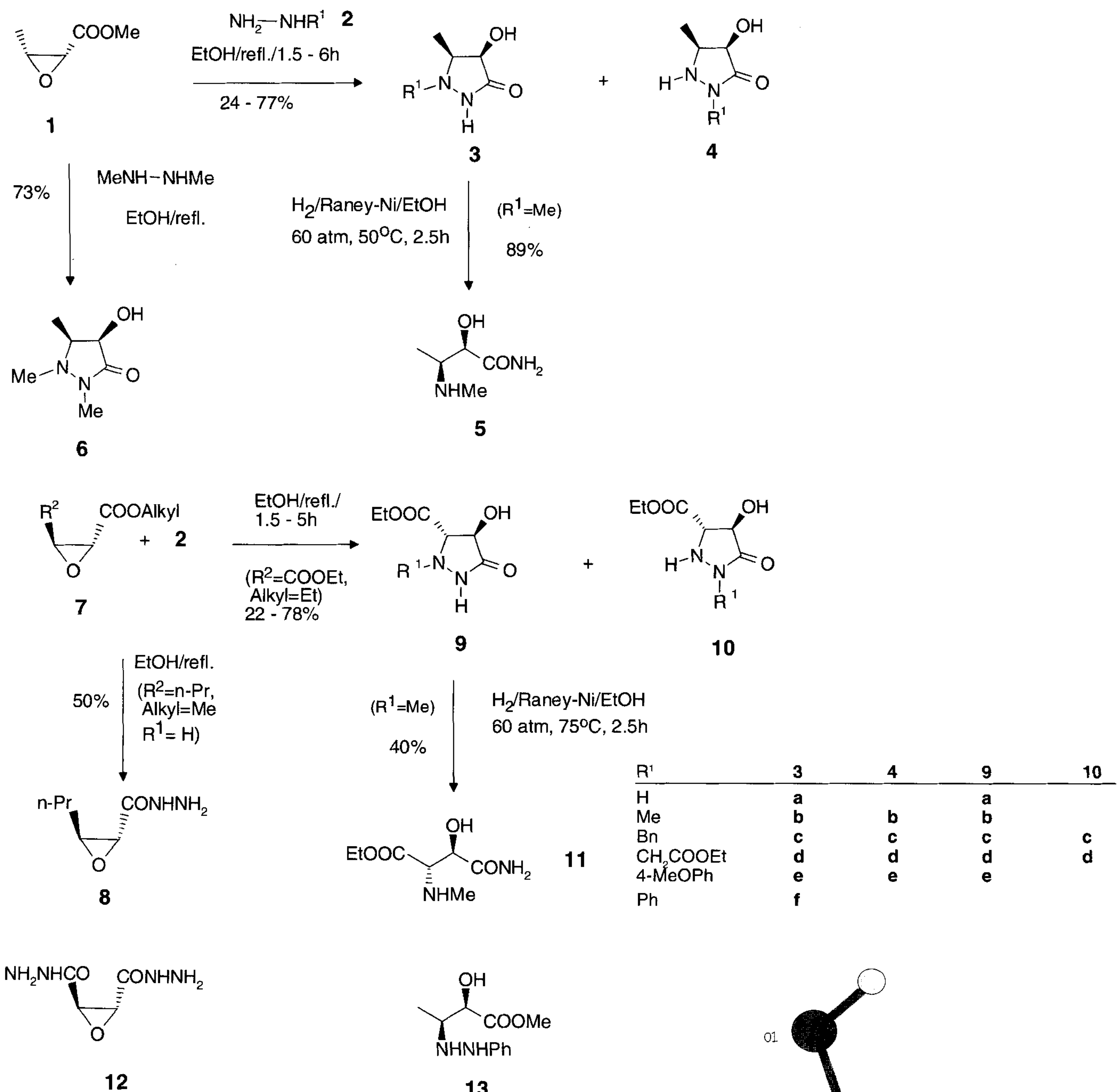
Abstract. The *cis* or *trans*-glycidic esters **1** or **7** give ring transformations with hydrazines affording optically active 4-hydroxypyrazolidin-3-ones **3** and **4** or **6** or **9** and **10**, respectively, in different regioselectivities. 4-Hydroxypyrazolidin-3-ones **3** and **9** can serve as precursors for enantiomerically pure β-amino-α-hydroxycarboxylic acid amides **5** and **11** by hydrogenation in the presence of Raney-Ni.

Racemic 4-hydroxypyrazolidin-3-ones can be synthesized by ring transformation of glycidic esters with hydrazines [1–5]. Further hydrogenation afforded racemic β-amino-α-hydroxycarboxylic acid amides by reductive N,N-bond cleavage [5]. Optically active β-amino-α-hydroxycarboxylic acid derivatives have found wide interest in the synthesis of natural products [6, 7] and also in the preparation of biologically active peptides [8, 9]. Known synthesis of such acids give either incomplete stereoselectivity [10] or are limited to restricted substituent patterns [6, 8, 11]. We therefore developed the synthesis of enantiomerically pure 4-hydroxypyrazolidin-3-ones as precursors for β-amino-α-hydroxycarboxylic acid derivatives. A more direct synthesis of such β-amino-α-hydroxycarboxylic acid derivatives by reaction of glycidic acid derivatives with amines would not be possible as these reactions are known to give α-amino-β-hydroxycarboxylic acids [15, 16] unless arylglycidic acid derivatives are used [17].

Enantiopure glycidic esters such as **1** and **7** are easily accessible by Sharpless epoxidation followed by oxidation of the resulting hydroxymethyloxiranes [12] or by ring closure of (2*R*,3*R*)-(+) diethyltartrate [14] or L-threonine [13], respectively, therefore the ring transformation reaction with hydrazines mentioned above appeares as a promising route to the desired optically active 4-hydroxypyrazolidin-3-ones such as **3**, **4**, **6**, **9**, and **10**.

The *cis*-glycidic ester **1** reacted with hydrazine, monosubstituted hydrazines and *N,N'*-dimethylhydrazine in refluxing ethanol, forming directly 4-hydroxypyrazolidin-3-ones (see Scheme 1 and Table 1). Interestingly and unlike in previous reports in the racemic series [1–3], methylhydrazine and other monosubstituted hydrazines gave mixtures of regioisomeric products **3** and **4** rather than only 1-substituted products **3**. Possibly, the formation of regioisomers was overlooked before. The regioisomers can be separated by column chromatography. Remarkably, the *trans*-glycidic ester **7** (R^2= *n*-Pr) seemed reluctant to ring transformation with hydrazines and the only product obtained with hydrazine, was the hydrazide **8**. On the other hand *trans*-2,3-bis-(ethoxycarbonyl)-oxirane **7** ($R^2 = CO_2Et$) gave successful ring transformation reactions to 4-hydroxypyrazolidin-3-ones **9** and **10** (see Scheme 1 and Table 1). Obviously, the electrophilicity of the oxirane carbon atom is enhanced by the second ethoxycarbonyl group in this *trans*-diester **7** ($R^2 = CO_2Et$) thus enabling a successful ring transformation. Mixtures of regioisomers **9** and **10** were only observed with benzylhydrazine and ethyl hydrazinoacetate (**2** with R^1 = Bn or CO_2Et, respectively).

The structural elucidation of the 4-hydroxypyrazolidin-3-ones **3**, **4**, **6**, **9**, and **10** was possible by X-ray crystal analysis (see Figure 1) of compound **3b** and by spectroscopic methods, particularly NMR-spectroscopy (see Table 1). Regioisomers such as **3** and **4** or **9** and **10** can be distinguished by the ^1H NMR shift of the NH-proton which is shifted downfield in products



R^1	3	4	9	10
H	a		a	
Me	b	b	b	
Bn	c	c	c	c
CH_2COOEt	d	d	d	d
4-MeOPh	e	e	e	
Ph	f			

Scheme 1

3 and **9** (CONH >8 ppm) as compared to the NH-proton (4–6 ppm) of isomers **4** and **10**. The mechanism of the ring transformation of glycidic esters **1** and **7** to 4-hydroxypyrazolidin-3-ones **3**, **4**, **6**, **9**, and **10** is presumably the same as reported in the racemic series, *i.e.* primary formation of glycidic carboxylic acid hydrazides (similar to **8**) followed by nucleophilic S_N2-like reaction (inversion of configuration) resulting in the opening of the oxirane ring at the β-position by the other amino group of the hydrazine **2**. Interestingly, an alternative primary attack at the oxirane ring was indi-

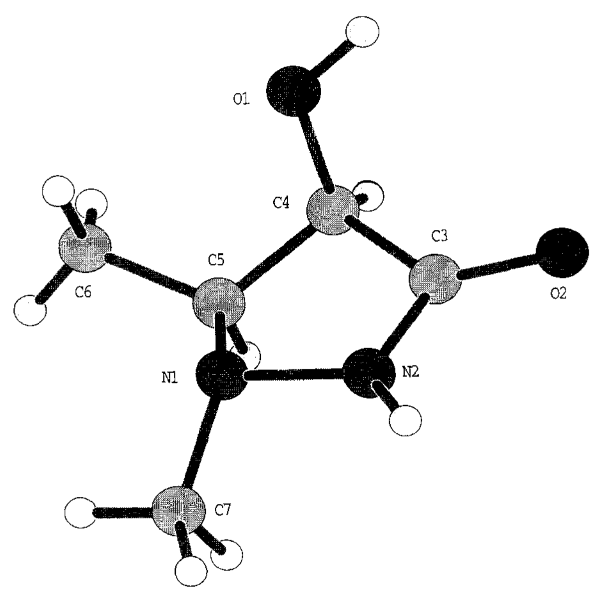


Fig. 1 X-Ray crystal analysis of compound **3b**

Table 1 4-Hydroxypyrazolidin-3-ones **3**, **4**, **6**, **9**, **10**, *β*-Amino-*α*-hydroxycarboxylic Acid Amides **5** and **11**, Dihydrazide **12**, and 3-Hydrazino-2-hydroxyester **13**

Product [a]	Yield/ Time	*m.p.* (°C) Solvent	$[\alpha]_D^{20}$ (c = 1)	^{1}H NMR δ, *J* (Hz)	^{13}C NMR δ/ppm
3a	65/4 h	162–163 (AcOEt)	+31.8 (MeOH)	(DMSO-d_6) 1.12 (d, *J*=6.66, 3H), 3.55 (m, 1H), 4.13 (d, *J*=5.14, 1H), 5.59 (s, 1H), 9.21 (s, 1H)	12.7 (CH_3), 57.8, 71.9 (CH), 176.3 (C)
3b	54/6 h	192–193 (EtOH)	+219 (H_2O)	(DMSO-d_6) 1.01 (d, *J*=6.69, 3H), 2.45 (s, 3H), 2.94 (m, 1H), 4.17 (dd, *J*=5.14, 10.87, 1H), 5.53 (d, *J*=5.77, 1H), 9.45 (s, 1H)	12.5, 45.6 (CH_3), 64.8, 70.5 (CH), 172.7 (C)
3c	44/6 h	130–131 (hexane/AcOEt)	+167.5 (MeOH)	($CDCl_3$) 1.11 (d, *J*=6.79, 3H), 3.47 (m, 1H), 3.78 (d, *J*=12.72, 1H), 3.95 (d, *J*=12.72, 1H), 4.48 (d, 7.05, 1H), 7.19–7.30 (m, 5H), 7.7–8.0 (s, 1H)	13.2 (CH_3), 63.0 (CH_2), 62.6, 69.7, 128.4, 129.0, 129.7 (CH), 136.5, 175.0 (C)
3d	24/6 h	101–102 (hexane/AcOEt)	+135.4 ($CHCl_3$)	($CDCl_3$) 1.16 (d, *J*=6.88, 3H), 1.19 (t, *J*=7.12, 3H), 3.43 (m, 1H), 3.53 (d, *J*=16.4, 1H), 3.67 (d, *J*=16.49, 1H), 4.14 (q, *J*=7.12, 2H), 4.15–4.4 (s, 1H), 4.51 (d, *J*=6.76, 1H), 8.25–8.45 (s, 1H)	12.5, 14.5 (CH_3), 59.0, 61.8, (CH_2), 63.5, 69.8 (CH), 170.0, 174.8 (C)
3e	21/5 h	150–51 (hexane/AcOEt)	+249.7 (MeOH)	(DMSO-d_6) 1.31 (d, *J*=6.81, 3H), 3.76 (s, 3H), 3.92 (m, 1H), 4.61 (d, *J*=7.11, 1H), 6.81 (d, *J*=8.95, 2H), 6.97 (d, *J*=8.95, 2H), 8.7–9.1 (S, 1H)	15.5, 57.5 (CH_3), 69.9, 70.6 (CH), 116.4, 120.7 (CH), 145.9, 158.0, 177.7 (C)
3f	24/6 h	165 (hexane/AcOEt)	+321.3 (MeOH)	(DMSO-d_6) 1.22 (d, *J*=6.51, 3H), 4.15 (m, 1H), 4.38 (d, *J*=7.17, 1H), 6.90–7.29 (m, 5H), 10.02 (S, 1H)	14.2 (CH_3), 66.1, 68.3, 115.9, 121.7, 129.5 (CH), 151.5, 174.2 (C)
4b	11/6 h	124–125 (hexane/AcOEt)	+6.2 (H_2O)	(DMSO-d_6) 0.75 (d, 6.72, 3H), 2.61 (s, 3H), 3.15 (d, *J*=6.54, 1H), 3.80 (m, 1H), 5.28 (s, 1H), 5.32 (d, *J*=5.78, 1H),	11.5, 30.6 (CH_3), 53.9, 70.7 (CH), 170.7 (C)
4c	34/6 h	122–123 (hexane/AcOEt)	+10.8 (MeOH)	($CDCl_3$) 0.92 (d, *J*=6.70, 3H), 1H), 4.17 (d, *J*=5.91, 3.40 (m, 1H), 4.43 (d, *J*=15.20, 1H), 4.47 (d, *J*=15.20, 1H), 5.2–5.9 (s, 1H), 7.23–7.36 (m, 5H)	12.6 (CH_3), 48.3 (CH_2), 55.7, 72.1, 128.1, 128.5, 129.2 (CH), 137.7, 172.6 (C)
4d	24/6 h	46–50	+25.8 ($CDCl_3$)	($CDCl_3$) 1.31 (d, *J*=6.76, 3H), 1.93 (t, *J*=7.15, 3H), 3.79 (m, 1H), 4.31 (q, *J*=7.15, 2H), 4.29 (d, *J*=7.15,1H), 4.33 (d, *J*=7.15, 1H), 4.48 (d, *J*=5.05, 1H), 4.5–5.0 (s, 1H)	12.0, 14.5 (CH_3), 46.5, 62.1 (CH_2), 56.2, 72.2 (CH), 168.6, 173.7 (C)
4e	18/5 h	157–158 (hexane/AcOEt)	+15.7 (MeOH)	($CDCl_3$) 1.03 (d, *J*=6.71, 3H), 3.56 (m, 1H), 3.72 (s, 3H), 4.34 (d, *J*=6.25, 1H), 6.71 (d, *J*=9.16, 2H), 6.89 (d, *J*=9.16, 2H)	12.8, 56.0 (CH_3), 55.0, 73.6, 114.5, 120.2 (CH), 133.6, 156.3, 171.7 (C)
5	89/2.5 h	107–109 (AcOEt)	+49.4 (MeOH)	(DMSO-d_6) 0.95 (d, *J*=6.53, 3H), 2.25 (s, 3H), 2.70 (m, 1H), 3.67 (d, *J*=4.32, 1H), 3.1–4.0 (s, 2H), 7.14, 7.27 (2s, 2H)	16.1, 33.8 (CH_3), 57.3, 73.4 (CH), 175.8 (C)
6	73/5 h	91 (hexane/AcOEt)	+153.3 ($CHCl_3$)	($CDCl_3$) 1.15 (d, *J*=6.78, 3H), 2.63 (s, 3H), 2.97 (s, 3H), 3.29 (m, 1H), 4.65 (s, 1H), 4.73 (d, *J*=7.20, 1H)	12.9, 30.2, 42.6 (CH_3), 63.1, 70.1 (CH), 171.7 (C)
9a	22/2 h	109 (hexane/AcOEt)	+55 ($CHCl_3$)	($CDCl_3$) 1.23 (t, *J*=7.10, 3H), 4.10 (d, *J*=8.48, 1H), 4.1–4.25 (m, 2H), 4.51 (t, *J*=8.53, 1H), 9.5–9.8 (s, 1H)	14.4 (CH_3), 62.6 (CH_2), 66.2, 72.7 (CH), 170.5, 174.7 (C)
9b	78/1.5 h	95 (hexane/AcOEt)	–58.4 ($CHCl_3$)	($CDCl_3$) 1.24 (t, *J*=7.10, 3H), 2.69 (s, 3H), 3.43 (d, *J*=7.25, 1H), 4.19 (q, *J*=7.10, 2H), 6.59 (d, *J*=7.52, 1H), 5.3–5.7 (s, 1H), 9.3–9.7 (S, 1H)	14.5, 47.7 (CH_3), 62.4 (CH_2), 72.8, 73.7 (CH), 169.3, 171.2 (C)
9c	36/1.5 h	114 (hexane/AcOEt)	–78.8 ($CHCl_3$)	($CDCl_3$) 1.23 (t, *J*=7.07, 3H), 3.72 (d, *J*=6.27, 1H), 4.13 (dd, *J*=4.98, 19.1, 2H), 4.1–4.2 (m, 2H), 5.35–5.6 (s, 1H), 7.28–7.34 (m, 5H), 8.95–9.2 (s, 1H)	14.4 (CH_3), 62.6, 64.6 (CH_2), 72.7, 73.4, 128.5, 128.6, 128.7, 129.0, 130.2 (CH), 134.9, 169.5, 171.6 (C)
9d	20/1.5 h	95–96 (hexane/AcOEt)	–90.6 ($CHCl_3$)	($CDCl_3$) 1.15–1.3 (2t, 6H), 3.67 (d, *J*=6.41, 1H), 3.56 (d, *J*=16.77, 1H), 3.88 (d, *J*=16.77, 1H), 4.05–4.25 (m, 4H), 4.54 (d, *J*=6.41, 1H), 5.1–5.4 (s, 1H), 8.6–8.9 (s, 1H)	14.4 (CH_3), 60.2, 61.9, 62.4 (CH_2), 71.1, 71.9 (CH), 168.8, 169.7, 171.8 (C)

Table 1 (continued)

9e	34/4 h	oil	−86.6 ($CHCl_3$)	($CDCl_3$) 1.19 (t, J=7.12, 3H), 3.64 (s, 3H), 3.96 (d, J=4.56, 1H), 4.14 (q, J=7.12, 2H), 4.51 (d, J=4.56, 1H), 5.1–5.2 (s, 1H), 6.70, 6.97 (d, J=8.95, 4H), 9.35–9.55 (s, 1H)	14.4, 55.8 (CH_3), 62.5 (CH_2), 72.9, 75.1, 114.9, 120.7 (CH), 143.9, 157.3, 169.7, 171.7 (C)
10c [b]	14/1.5 h	116–117 (hexane/AcOEt)	+52.3 ($CHCl_3$)	($CDCl_3$) 1.22 (t, J=7.14, 3H), 3.98 (dd, J=9.49, 9.57, 1H), 4.13–4.29 (m, 2H), 4.41 (d, J=14.7, 1H), 4.65 (d, J=14.7, 1H), 4.55 (d, J=8.44, 1H), 4.78 (d, J=10.26,1H), 4.6–5.2 (s, 1H), 7.17–7.13 (m, 5H)	14.5 (CH_3), 49.2, 62.7 (CH_2), 64.5, 73.5, 128.6, 128.8, 129.3 (CH), 135.1, 170.5, 170.6 (C)
10d	22/1.5 h	oil	+77.7 ($CHCl_3$)	($CDCl_3$) 1.19–1.28 (2t. 6H), 3.99 (d, J=17.42, 1H), 4.08 (m, 4H), 4.36 (d, J=17.42, 1H), 4.59 (d, J=9.26, 1H), 5.38 (d, J=10.6, 1H), 4.85–5.05 (s, 1H)	16.8 (2 CH_3), 49.1, 64.5, 64.9 (CH_2), 67.0, 75.2 (CH), 170.6, 172.4, 174.2 (C)
11	40/2.5 h			(DMSO-d_6) 1.18 (t, J=7.12, 3H), 2.27 (s, 3H), 3.38 (d, J=4.81, 1H), 4.02 (d, J=4.81, 1H), 4.05–4.11 (m, 2H), 5.6–5.75 (s, 1H), 7.15–7.25 (s, 2H)	15.0, 35.2 (CH_3), 60.7 (CH_2), 66.4, 73.3 (CH), 172.1, 174.5 (C)
12	62/2 h	110 (dec.)	+20.9 (H_2O)	(DMSO-d_6) 3.49 (s, 2H), 4.40 (s, 4H), 9.66 (s, 2H)	52.5 (CH), 165.6 (C)
13	39/6 h	oil	− 65.4 ($CHCl_3$)	($CDCl_3$) 10.85 (d, J=6.69, 3H), 3.50 (m, 1H), 3.68 (s, 3H), 3.1– 3.9 (s, 2H), 3.80 (s, 1H), 4.15 (d, J=2.37, 1H), 6.76–7.23 (m,5H)	16.2, 52.7 (CH_3), 57.3, 73.1, 112.9, 119.7, 129.5 (CH), 149.2, 175.4 (C)

[a]) With the exception of compounds **5**, **9e** and **11** (for HRMS see footnote c) satisfactory microanalyses were obtained: C ± 0.39, H ± 0.37, N ± 0.36. [b]) MS *m/z* (%) 280 (5), 134 (100), 107 (23), 92 (24), 77 (37). [c]) HR-MS: **5** $C_5H_{13}N_2O_2$ + 1H, calc.: 133.0977, found: 133.0972; **9e** $C_{13}H_{16}N_2O_5$, calc.: 280.1059, found: 280.1064; **11** $C_7H_{15}N_2O_4$ + 1H, calc.: 191.1032, found: 191.1033

cated by the formation of the 3-phenylhydrazinoester **13** as a by-product of the reaction of the glycidic ester **1** with phenylhydrazine leading to the pyrazolidin-3-one **3f**. However a corresponding cyclization product **4** was not formed obviously due to the low nucleophilicity of the anilino group. Since glycidic esters in general are polyfunctional electrophiles, other competing reactions such as interaction with two equivalents of hydrazine **2** have to be taken into consideration as they could probably be responsible for the modest yields achieved in some cases. Thus, in the case of the synthesis of the 4-hydroxypyrazolidin-3-one **9a** the oxiranedicarboxylic acid hydrazide **12** was obtained as the major product. In other cases, highly polar by-products were observed which could not be purified and hence were not further investigated.

As indicated in the introduction and as shown before in the racemic series, 4-hydroxypyrazolidin-3-ones can be considered for hydrogenolytic ring opening reactions as precursors to β-amino-α-hydroxy carboxylic acid derivatives. In order to prove the effect of the hydrogenation conditions on the configurations at the stereogenic centers of the 4-hydroxypyrazolidin-3-ones, **3b** and **9b** were subjected to Raney-Ni catalyzed hydrogenation at 60 atm at elevated temperatures affording the corresponding isothreonine amide **5** and the hydroxyasparagine ester **11**, respectively. While no epimerization was observed in the former case, compound **11** was formed in a 90:10 diastereomeric ratio probably due to partial epimerization at CH–N.

The aforementioned results showed that 4-hydroxypyrazolidin-3-ones can be obtained in enantiomerically pure form by ring transformation of glycidic esters **1** and **7** with hydrazines. However, the ring transformations turned out to be less smooth than reported before in the racemic series, where possibly regioisomers were overlooked. Often separable mixtures of regioisomeric 1- and 2-substituted 4-hydroxypyrazolidin-3-ones were obtained rather than pure 1-substituted compounds. The 4-hydroxypyrazol-3-ones **3** and **9** can serve as precursors for optically active β-amino-α-hydroxycarboxylic acid derivatives **5** and **11**.

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Experimental

^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz respectively on a BRUKER AC-300 with TMS as internal standard. Optical rotation was determined with a PERKIN ELMER polarimeter 241. Mass spectra (HP 5995

A) and high-resolution mass spectra (MAT 711, Varian) were measured at 70 eV. Some of the highly polar products did not give satisfactory microanalyses but showed clear NMR spectra and satisfactory high resolution mass spectra. For preparative column chromatography Silicagel (0.04 – 0.063 mm, MERCK) was used. Starting materials **1** [13] and **7** (R^2 = *n*-Pr [12], COOEt [14] were obtained according to literature procedures.

4-Hydroxypyrazolidin-3-ones 3, 4, 6, 9, 10 and Dihydrazide 12 and 3-Hydrazino-2-hydroxyester 13 (General Procedure)

The hydrazine **2** (1.1 mmol) or 1,2-dimethylhydrazine (1 mmol) was added to a solution of the glycidic ester **1** or **7** (1 mmol) in EtOH (2 ml). $NaHCO_3$ or triethylamine was added to generate the free hydrazine **2** if hydrazine hydrochlorides were used. After 2 – 6 h of refluxing, the solvent was evaporated *in vacuo*, and the remaining material was submitted to column chromatography ($CHCl_3$/MeOH 9 : 1 for compounds **9a**, **9b**, **6**; CH_2Cl_2/Me_2CO 95 : 5 for compounds **3c**–**3f**, **4b**–**4e**; hexane/EtOAc 9 : 1 for compounds **9c** and **10c**). Compounds **3a** and **3b** were precipiated from the reaction mixture by dilution with diethyl ether.

β-Amino-α-hydroxycarboxylic Acid Amides 5 and 11 by Hydrogenolytic Ring Cleavage of 4-Hydroxypyrazolidin-3-ones (General Procedure)

Raney-Ni (50 – 100 mg in 2 ml EtOH) was added to a solution of the 4-hydroxypyrazolidin-3-one **3** (200 mg, 1.54 mmol) or **9** (200 mg, 1.06 mmol) in dry EtOH (2 ml). The mixture was stirred under hydrogen at 60 atm at 50 °C or 75 °C for 2.5 h respectively. Raney-Ni was filtered off and the solvent was stripped from the filtrate. The remaining material was purified by column chromatography at silica ($CHCl_3$/MeOH 7 : 3)

Crystal Structure Determination for Compound 3b

Crystals were obtained by crystallization from hot ethanol. A colorless crystal of **3b** with dimensions 0.65 × 0.34 × 0.11 mm^3 was measured on a STOE Stadi4 diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Crystal data: $C_5H_{10}N_2O_2$, M = 130.17 g/mol, orthorhombic space group P 2_1 2_1 2_1, a = 7.270 (2) Å, b = 7.887 (3) Å, c = 11.527 (5) Å, V = 660.9 (4) $Å^3$, Z = 4, D_c = 1.308 g/cm^3, $F(000)$ = 280, μ (Mo-K_α) = 0.064 cm^{-1}. At 293(2) K in the range of 3.13° <=Θ <= 23.98° 1286 reflections were measured ($R_{(\sigma)}$ = 0.0220) of witch 627 were unique ($R_{(int)}$ = 0.0561) and 538, flagged as observed, had intensities larger than 2σ(I). The structure was elucidated by direct methods and refined by least squares procedure within the SHELX program system. All hydrogen atoms were located in a difference Fourier map. The final residuals were $wR_{2(all)}$ = 0.0709, $R_{1(all)}$ = 0.0366 and $R_{1(obs)}$ = 0.0268. The maximum and minimum peaks in the final difmap were 0.09 and –0.10 e/$Å^3$, respectively.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. A full literature citation and the reference number CSD 407155 should be quoted for any request of the material.

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