Stereoselective Access to γ-Nitro Carboxylates, Precursors for Highly Functionalized γ-Lactams

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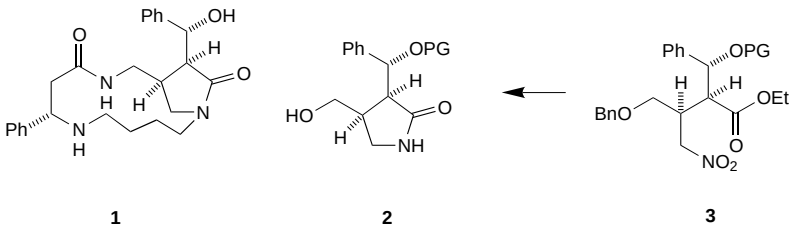
A straightforward synthesis of the enantiomerically pure nitro derivatives **31** and *epi*-**32**, which are particularly useful intermediates for the synthesis of highly functionalized γ-lactams, is presented. (+)-(*R*)-3-Hydroxy-3-phenylpropanoic acid (**20**) and its ethyl ester **25** were prepared from (+)-L-mandelic acid (**21**). Condensation of **20** with pivalaldehyde furnished the novel enantiomerically pure 1,3-dioxan-4-one **17**, the absolute configuration of which was established by X-ray crystal-structure analysis. Treating the lithium enolate of **17** with the nitro alkene **18** led, in a *Michael*-type addition, to a 1:1 mixture of two diastereoisomeric products. The stereocontrol of the addition was limited to the novel stereogenic center next to the lactone function. When the lithium enolate of **25** was treated with **18**, the same selectivity was observed but with a lower chemical yield. Very facile separation of the isomers was achieved later in the synthetic sequence, when one isomer cyclized selectively to the nitro lactone **31**, while the other one was isolated as hydroxy ester *epi*-**32**. The relative configuration of racemic *epi*-**32** could be established by X-ray crystal-structure analysis.

Introduction. – In the course of our investigations on the total synthesis of caesalpinine A (**1**; *Scheme 1*) [1], a cyclic spermidine alkaloid [2], we were interested in finding an easy access to the lactam **2**. The nitro ester **3** was assumed to be a useful precursor to **2**, as it should undergo lactamization as soon as the NO_2 group is reduced. In 1979, *Fráter* had found that β-hydroxybutyrate **4** can be alkylated with high diastereoselectivity, when its corresponding enolate is treated with alkyl bromides (*Scheme 2*) [3]. *Seebach* and co-workers applied this method for nitro alkenes **5** as alkylating agents [4]. Subsequent hydrogenation of the NO_2 groups afforded the corresponding γ-lactams through spontaneous cyclization of the *in situ* formed amino esters. The configuration of the novel stereogenic center in the α-position to the ester was in agreement with the findings of *Fráter*. The stereoselectivity can be explained by

Scheme 1

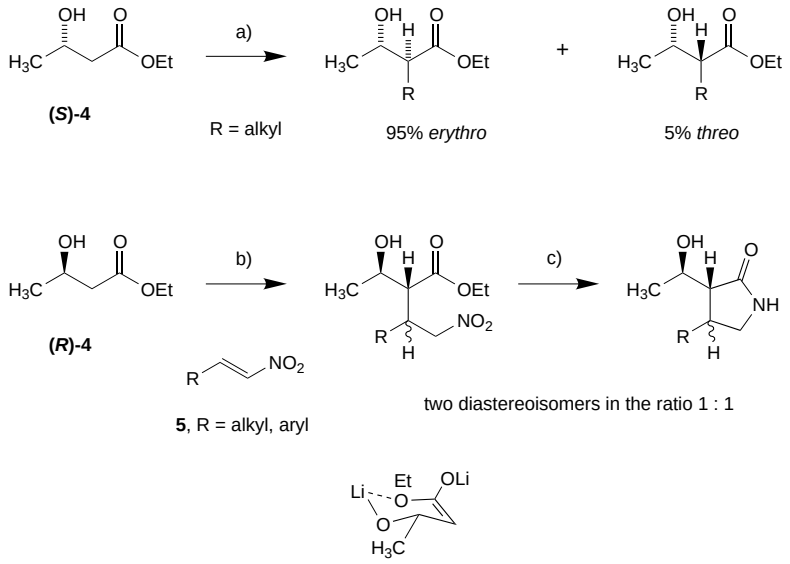


1 **2** **3**

PG = protecting group

[1]) Part of the Ph.D. thesis of *C. M.*, University of Zürich, 2002.

Scheme 2



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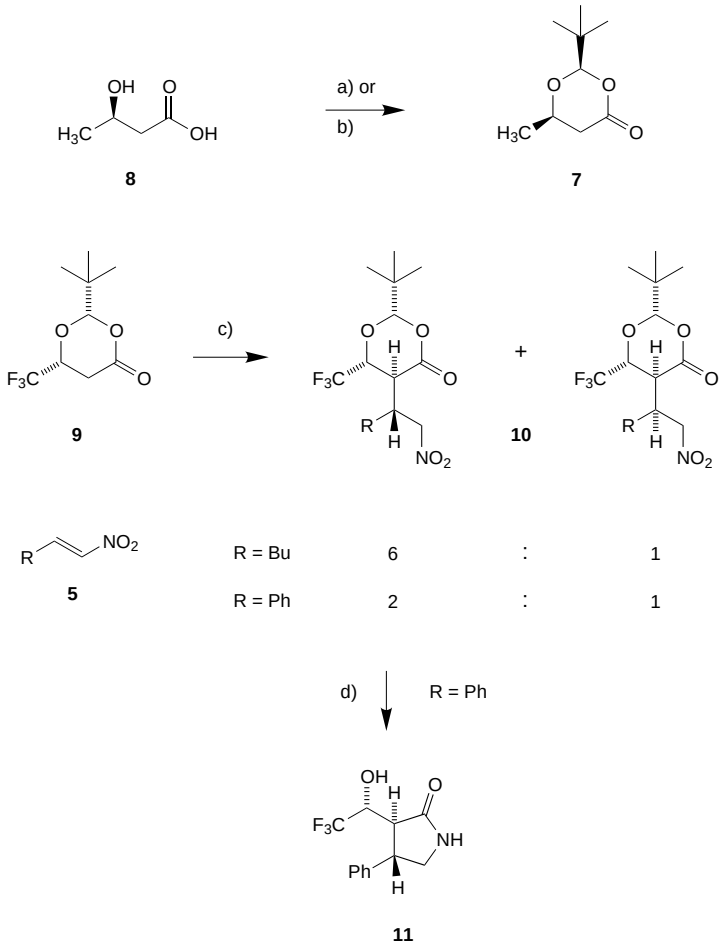
a) 1. 2.0 equiv. LiN(i-Pr)$_2$ (LDA), THF, hexamethylphosphoric triamide (HMPTA), $-20°$. 2. Alkyl bromide, -20 to $+25°$; 80%. b) 1. 2.0 equiv. LDA, THF, $-78°$; 2. **5**, $-78°$; 38 to 81%. c) H_2, *Raney*-Ni; 43 to 87%.

the dianion **6**, which forms a lithium chelate and, thus, favors a *trans*-substitution relative to the Me group. A synthetic equivalent for β-hydroxy esters are dioxanones like **7**, which can be obtained by the condensation of the β-hydroxy acid **8** with pivalaldehyde (*Scheme 3*) [5–7]. These dioxanones and their enolates are conformationally stable due to their cyclic structure and, at the same time, give high chemical yields even with less reactive alkylating agents. In 1994, *Seebach* and co-workers investigated the addition of the enolate of **9** to nitro alkenes and observed the diastereoselectivities shown in *Scheme 3* [8]. The hydrogenation of **10** in the presence of *Raney*-Ni afforded the γ-lactam **11**. *Liebscher* and co-workers followed a slightly different route to the same class of products. They prepared the alkylidene or arylidene dioxanones **12** by a formal aldol condensation of **13** with aldehydes (*Scheme 4*) [5]. In the next step, the *Michael* addition of $MeNO_2$ afforded the nitro lactones **14** with the selectivities shown in *Scheme 4* [9]. Upon hydrogenation, the preferred products yielded the *cis*-configured γ-lactams **15**. We now wanted to apply the method of *Seebach* and co-workers [8] for the synthesis of **16**, and two new aspects had to be considered: first, we were interested to determine if the Ph-substituted dioxanone **17** would give the same selectivities for substitution in the α-position (*Scheme 5*), second, the nitro alkene **18** bears a BnO group, which needs to be converted to an amino group later in the synthesis, and it was unknown how such a function would influence the diastereoselectivity at the second novel stereogenic center of **19**.

Scheme 3

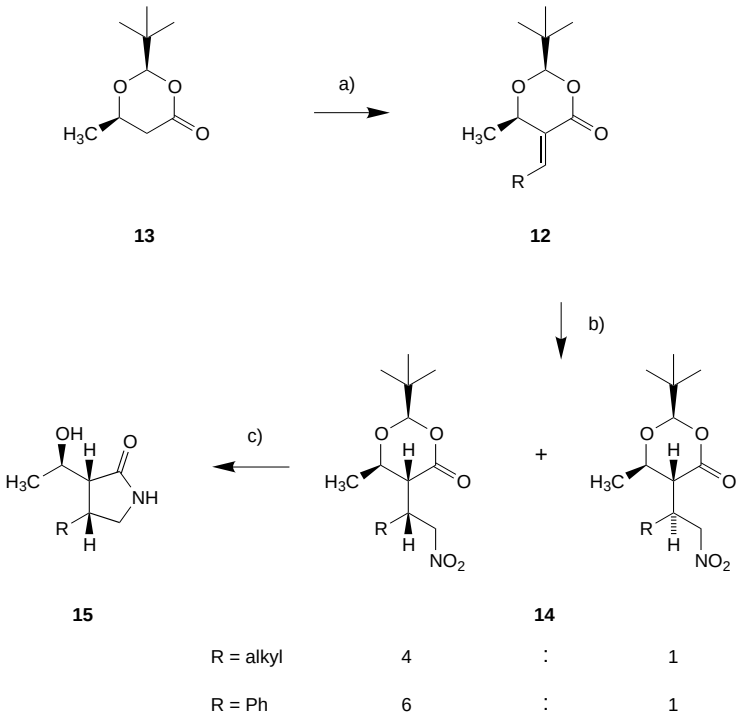


a) Pivalaldehyde, pyridinium toluene-4-sulfonate, benzene, 80°. b) 1. Me_3SiCl, Et_3N, CH_2Cl_2, r.t., 2. pivalaldehyde, Me_3Si-triflate, CH_2Cl_2, −78°. c) 1. *t*-BuLi, THF, −75°; 2. addition of **5**, −75°, 3 h; 97%. d) 1 bar H_2, EtOH, *Raney*-Ni, 12 h, r.t.; 41%.

Results and Discussion. – *Synthesis of the Hydroxy Acid* **20** *and the Hydroxy Ester* **25**. The preparation of (+)-(*R*)-3-hydroxy-3-phenylpropanoic acid (**20**) was achieved by a C_1-homologization of (+)-L-mandelic acid (**21**): according to [10], reduction of **21** followed by tosylation furnished **22** (*Scheme 6*). The nucleophilic substitution of the TsO group in **22** by CN produced the intermediate **23**, which was isolated in addition to the desired nitrile **24**, when the reaction was stopped prematurely. Base hydrolysis of **24** afforded the hydroxy acid **20**, and esterification according to [11] yielded the ethyl ester **25**.

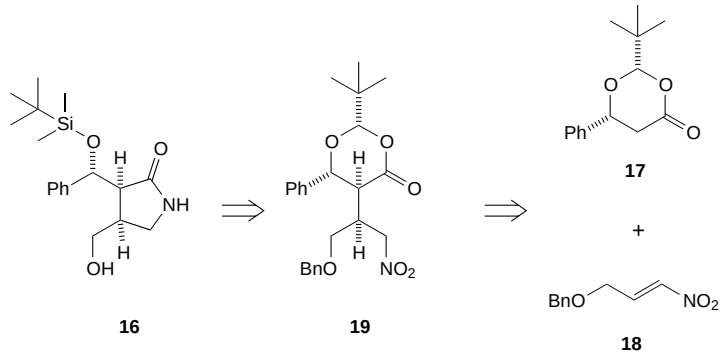
Synthesis and Structure of the Dioxanone **17**. Direct condensation of **20** with pivalaldehyde in benzene by azeotropic removal of H_2O [6] gave only mediocre yields

Scheme 4



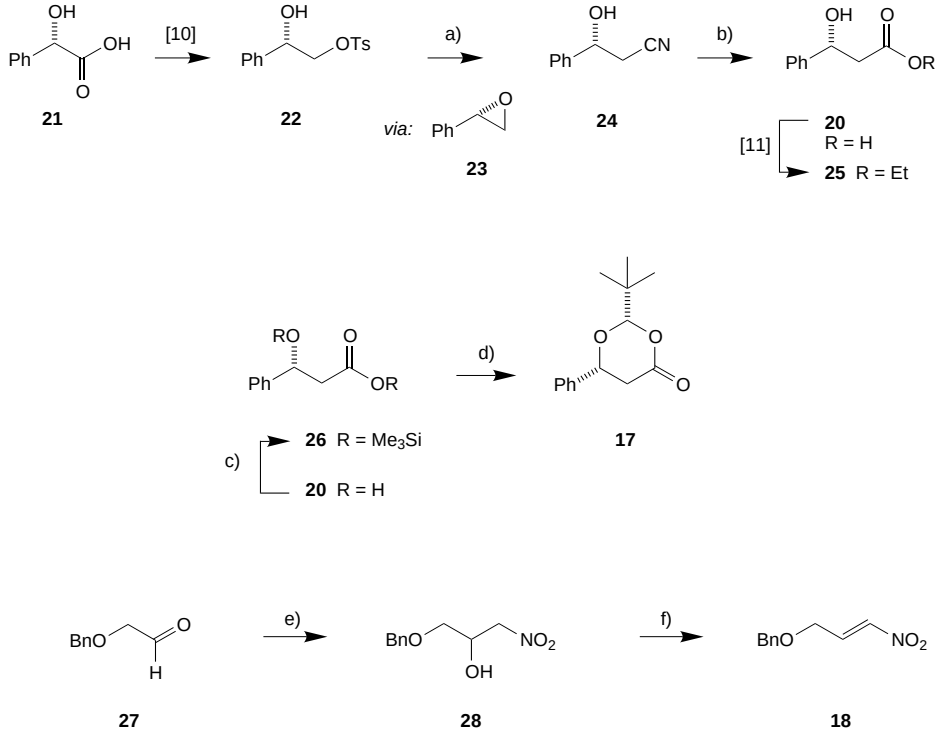
a) 1. LDA, THF, −78°; 2. RCHO, THF, −78°, 1 h; 3. MeCl, pyridine, 4-(dimethylamino)pyridine (DMAP), r.t., 30 min; 4. Et_3N, $CHCl_3$, 61°, 24 h; 42 to 54%. b) $MeNO_2$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), CH_2Cl_2, −30°, 4 h; r.t., 16 h. c) 1 bar H_2, MeOH, *Raney*-Ni, r.t., 20 h.

Scheme 5



of the dioxanone **17**, so it was prepared in two steps from **20** according to the method of *Tsunoda et al.* (*Scheme 6*) [7]. The hydroxy acid **20** could be transformed into the doubly silylated **26**. Then, **26** was condensed with pivalaldehyde at −78° to furnish **17**.

Scheme 6



a) KCN, MeOH, 6 d, r.t.; 76%. b) 5M aq. NaOH, H_2O_2, 23°; 57%. c) Me_3SiCl, Et_3N, CH_2Cl_2; 69%. d) pivalaldehyde, Me_3Si-triflate, CH_2Cl_2, −78°; 75%. e) $MeNO_2$, KOH in MeOH, r.t.; 88%. f) MsCl, Et_3N, DMAP, CH_2Cl_2, r.t.; 82%.

After recrystallization from THF, **17** was submitted to X-ray crystal-structure elucidation (*Fig. 1*). The configuration of the new stereogenic center at C(2) was established as (*S*) relative to the known (*R*)-configuration at C(6). This arrangement corresponds to our expectations that both substituents would be attached to the ring in an equatorial orientation. Moreover, *Fig. 1* clearly shows how the *Re*-face of the ring (with respect to the lactone) is sterically blocked by the Ph substituent. Therefore, it can be assumed that a substituent at C(5) would be introduced in *trans*-orientation to the Ph ring.

Synthesis of the Nitro Alkene **18**. The nitro alkene **18** was prepared by condensation of the corresponding aldehyde **27** with $MeNO_2$ (*Scheme 6*) analogously to [12]. Aldehyde **27** was synthesized as described in [13]. In basic methanolic solution, $MeNO_2$ and **27** formed the nitro alcohol **28**, which, upon treatment with MsCl and Et_3N, was converted to the desired nitro alkene **18**.

Addition of the Enolates of **17** *and* **25** *to* **18**. The dioxanone **17** was treated with LDA to generate its lithium enolate (*Scheme 7*). Addition of a THF solution of **18** at −75° furnished in 86% yield the diastereoisomers **19** and *epi*-**19** in the ratio 1:1. As found for the trifluoromethyl derivatives **10** by *Seebach* and co-workers [8], the dioxanone system properly induced the *trans*-configuration between the new substituent and the

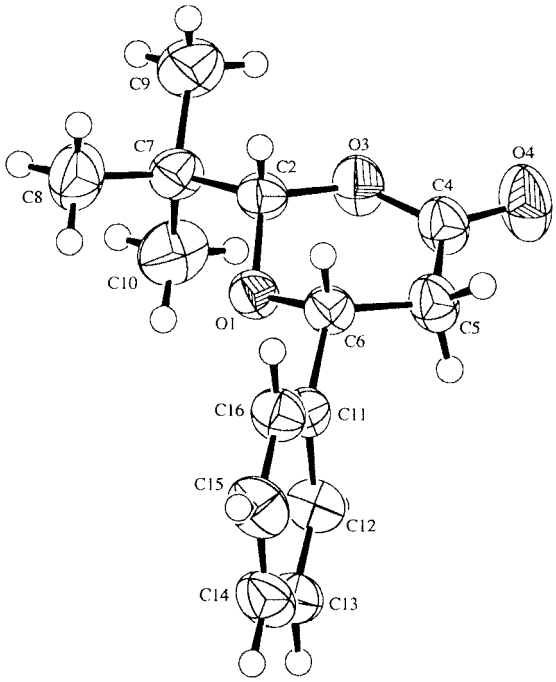
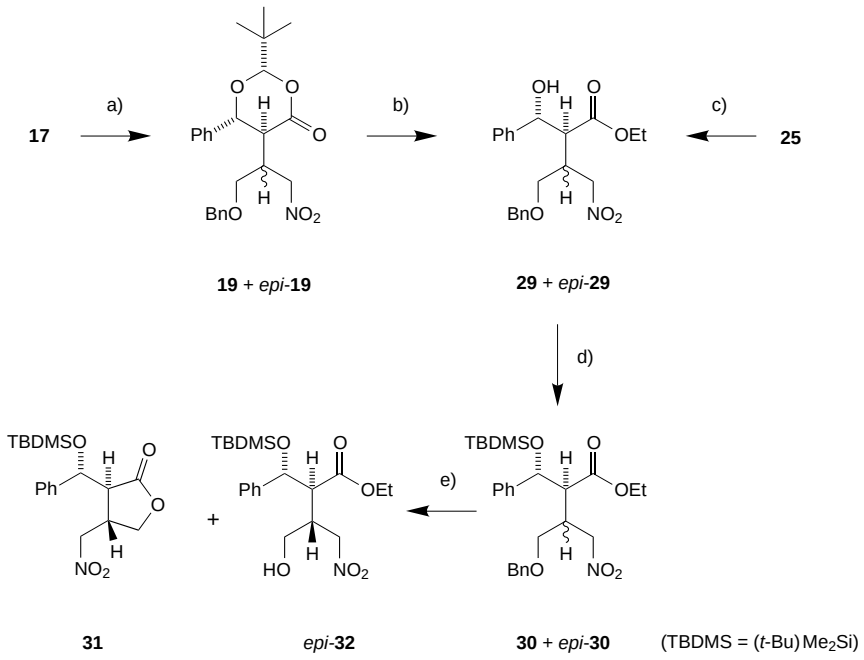


Fig. 1. *ORTEP Plot of the molecular structure of* **17** (with 50% probability ellipsoids)

Ph ring. On the other hand, no selectivity was observed for the formation of the second stereogenic center. This means that the two faces of **18** are not distinguished by the enolate; *Re* attack leads to **19** and *Si* attack to *epi*-**19**. Due to their apolar character, the diastereoisomers showed very similar chromatographic properties, so they were not separated before the next steps. The mixture **19**/*epi*-**19** was submitted to acid-catalyzed esterification in EtOH (*Scheme 7*), so, in one step, the pivaloyl group could be removed and the ethyl ester introduced to obtain **29** and *epi*-**29** in 69% yield. The quite low yield can be explained by partial elimination of H_2O, leading to a cinnamic acid derivative. In analogy to [3] and [4], direct alkylation of the β-hydroxy ester **25** was performed by treatment with 2 equiv. of LDA at -60 to $-10°$ in THF and adding 1.1 equiv. of **18** at $-7°$ (*Scheme 7*). A 1:1 mixture of the two diastereoisomers **29** and *epi*-**29** was isolated in 53% yield, as well as *ca.* 20% of starting material **25**. When 1.5 equiv. of **18** were added, the yield dropped to *ca.* 40%, probably due to *O*-alkylation of **25**. The secondary OH groups in **29** and *epi*-**29** had to be protected with a stable group for the rest of the synthesis, and we chose the (*t*-Bu)Me_2SiO group, as it can be introduced and removed specifically and under mild conditions. The protection was carried out with (*t*-Bu)Me_2Si-triflate, which is more reactive than the corresponding chloride. The very nonpolar silylated **30** and *epi*-**30** could be separated by repeated chromatography.

Cleavage of the BnO groups of **30** *and* epi-**30** *by Catalytic Hydrogenation.* It was originally planned to convert the NO_2 groups of **30** and *epi*-**30** to NH_2 groups, and to remove the BnO groups at once by catalytic hydrogenation. During the search for

Scheme 7

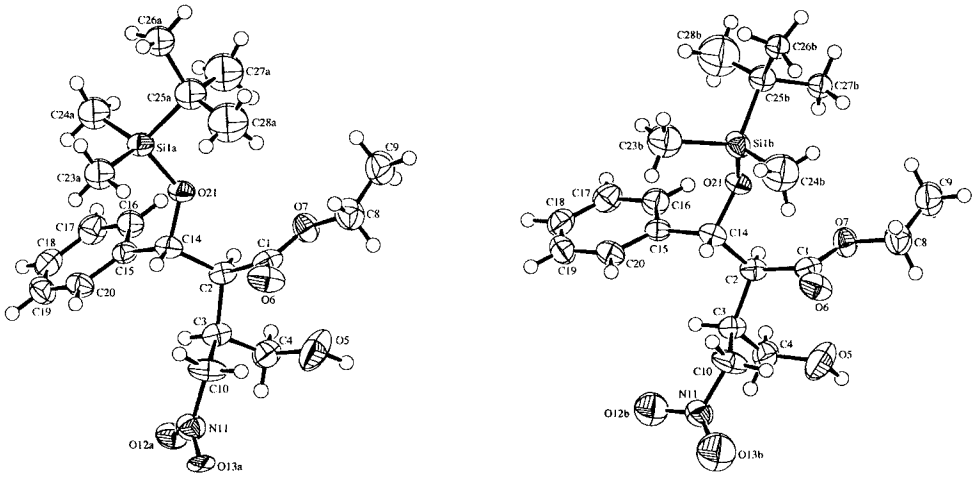


a) 1. LDA, THF, −75°; 2. **18**, THF, −75°, 86%. b) EtOH, conc. H_2SO_4, 78°, 17 h; 69%. c) 1. 2 equiv. LDA, THF, −60 to −10°; 2. 1.1 equiv. **18**, THF, −7 to +14°, 2 h; 53%. d) (*t*-Bu)Me_2Si-triflate, DMF/CH_2Cl_2, 0°, 7 h; 93%. e) 3.5 bar H_2, AcOH/CH_2Cl_2/$CHCl_3$ 70:5:0.5, 10% Pd/C, 24 h; 94%.

suitable conditions, we discovered that the hydrogenation of **30** and *epi*-**30** in the presence of 10% Pd/C in AcOH with *ca.* 10% chlorinated solvents (CH_2Cl_2 and traces of $CHCl_3$) at 3.5 bar H_2 pressure cleaved the BnO groups selectively (*Scheme 7*). The NO_2 groups were not affected at all, while, under different conditions, at least partial reduction to the hydroxylamines was observed. The chemical yield of *ca.* 90% was reached only with a special lot of catalyst, different lots seem to vary in their activity. Unexpectedly, one of the formed hydroxy esters spontaneously cyclized to the lactone **31**, whereas the product emerging from *epi*-**30** did not show any tendency to cyclize and could be isolated as hydroxy ester *epi*-**32**. Based on the dramatic differences in polarity, **31** (R_f 0.70) and *epi*-**32** (R_f 0.42) could be very easily separated by column chromatography (CH_2Cl_2/AcOEt 20:1).

Configurations of epi-**32** *and* **31**. The relative configuration of *epi*-**32** could be elucidated by X-ray crystal-structure analysis of racemic *epi*-**32** crystallized from EtOH. In the crystal, (±)-*epi*-**32** is present in two conformations A and B in the ratio 63:37, but they differ only in the orientation of the (*t*-Bu)Me_2Si and NO_2 groups (*Fig. 2*). The two halves of the molecule linked by the C(2)–C(3) bond show a staggered conformation. For the torsion angle C(1)–C(2)–C(3)–C(4), the value −71.4(4)° was found, which corresponds almost with −60°, the theoretical value for perfect staggering. Knowing that the (*R*)-configuration at C(1′) originated from (+)-L-

mandelic acid, the absolute configuration of the enantiomerically pure *epi*-**32** could be assigned as (1′*R*,2*S*,3*R*). This enabled us to determine the configuration of *epi*-**30**, the precursor of *epi*-**32**, and the configurations of **30** and **31**. The reason for different cyclization behaviors of the two hydroxy esters **32** and *epi*-**32** may be explained by their different relative configurations.



conformation A conformation B

Fig. 2. *ORTEP Plot of the two disordered conformations in the molecular structure of (±)*-epi-**32** (with 50% probability ellipsoids)

Conclusions. – The enantiomerically pure nitro derivatives **31** and *epi*-**32**, which are particularly useful intermediates for the synthesis of highly functionalized γ-lactams, are readily accessible by a straightforward synthesis. In the key step, the enolate of the β-hydroxy ester **25** or its dioxanone derivative **17** are added in a *Michael*-type addition to the nitro alkene **18** to form a 1:1 mixture of two diastereoisomers. The stereoselectivity with respect to the novel stereogenic centre in the α-position to the ester group is controlled by the cyclic structures of both the ester and the dioxanone enolate. Furthermore, later in the synthesis, one of the two isomers underwent lactonization, while its epimer could be isolated as a hydroxy ester. This chemoselectivity allows a very facile separation by simple column chromatography.

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Experimental Part

General. All commercially available reagents were used without further purification. Solvents were either *puriss. p.a.* grade (*Fluka*) or distilled prior to use. THF for the reaction with LDA was dried over Na-benzophenone and freshly distilled before use. Reactions were normally *not* carried out under N_2, unless stated otherwise; they were monitored by TLC on *Merck* precoated plates *Kieselgel 60* F_{254}. All extracts were dried

before evaporation over $MgSO_4$, unless stated otherwise. Column chromatography (CC): *Kieselgel 60* (230–400 mesh ASTM) from *Merck*. M.p.: *Mettler Fp 5*. IR [cm^{-1}]: in $CHCl_3$ (*Fluka* for IR spectroscopy); *Perkin-Elmer 781*. Optical rotations ($[\alpha]_D^{21}$): in $CHCl_3$ (filtrated over Alox I), except stated otherwise; *Perkin-Elmer 241* polarimeter. NMR Spectra: in $CDCl_3$, except stated otherwise; ^{1}H-NMR: *Bruker ARX-300* (300 MHz) or *Bruker DRX-600* (600 MHz); ^{13}C-NMR: *Bruker ARX-300* (75 MHz) or *Bruker DRX-600* (150 MHz); chemical shifts δ in ppm rel. to Me_4Si as internal standard; coupling constants J in Hz. MS: *Finnigan SSQ-700* for chemical ionization (CI) with NH_3, *Finnigan MAT-90* for electron impact (EI, 70 eV), and *Finnigan TSQ-700* for electrospray ionization (ESI); *m/z* (rel. intensity in %). Hydrogenation: *Parr-Instruments Company Inc.* (3.5 bar H_2).

*(+)-(*R*)-3-Hydroxy-3-phenylpropanenitrile* (**24**). A soln. of 40.44 g (138 mmol) of *(+)-(*S*)-2-hydroxy-2-phenylethyl 4-methylbenzenesulfonate* (**22**, prepared according to [10], m.p. 70.0–72.4° (*t*-BuOMe), $[\alpha]_D = +51.5$ ($c = 2.365$, $CHCl_3$)), in 500 ml of MeOH was treated with 8.99 g (138 mmol) of KCN dissolved in ca. 50 ml of MeOH and stirred at r.t. for 8.5 h and, later, another 8.09 g (124 mmol) of KCN was added. After 6 d, the dark blue mixture was evaporated, the residue was poured into H_2O and extracted with CH_2Cl_2. High-vacuum distillation afforded 15.40 g (76%) of **24** as a colorless oil. Upon storage at r.t., the product acquired a deep blue color, so it was kept under Ar at −18°. $[\alpha]_D = +50.4$ ($c = 4.945$, MeOH). IR ($CHCl_3$): 3590*m*, 3400*m* (br.), 3000*m*, 2890*m*, 2250*m*, 1950*w*, 1875*w*, 1810*w*, 1700*w*, 1600*m*, 1490*m*, 1450*m*, 1410*m*, 1310*m*, 1280*m*, 1170*m*, 1080*m*, 1050*s*, 1025*m*, 935*m*, 910*m*, 865*m*, 690*m*, 630*m*. ^{1}H-NMR (300 MHz): 7.40–7.31 (*m*, 5 H); 4.99 (*dt*, $J =$ 6.2, 3.8, 1 H); 2.84 (*d*, $J = 3.8$, 1 H); 2.72 (*d*, $J = 6.0$, 2 H). ^{13}C-NMR (75 MHz): 141.0 (*s*); 128.8 (*d*); 128.7 (*d*); 125.5 (*d*); 117.2 (*s*); 70.0 (*d*); 27.9 (*t*). CI-MS: 165 ($[M+18]^+$).

*(*S*)-2-Phenyloxirane* (**23**). A sample of 21.1 g (72 mmol) of **22** was dissolved in 300 ml of MeOH, then 8.93 g (137 mmol) of KCN and a few grains of 4-(dimethylamino)pyridine (DMAP) were added, and the mixture was stirred at r.t. for 23 h. The mixture was evaporated and poured into H_2O, extracted with CH_2Cl_2, and purified by CC (CH_2Cl_2/AcOEt 20:1) to give 3.74 g (43%) of **23** and 4.19 g (39.5%) of **24**. ^{1}H-NMR (300 MHz) of **23**: 7.37–7.24 (*m*, 5 H); 3.84 (*dd*, $J = 4.2, 2.7$, 1 H); 3.13 (*dd*, $J = 5.4, 4.0$, 1 H); 2.79 (*dd*, $J = 5.7, 2.7$, 1 H). ^{13}C-NMR (75 MHz): 137.6 (*s*); 128.4 (*d*); 128.1 (*d*); 125.5 (*d*); 52.3 (*d*); 51.1 (*t*).

*(+)-(*R*)-3-Hydroxy-3-phenylpropanoic Acid* (**20**). A soln. of 4.15 g (28.2 mmol) of **24** in 100 ml of aq. 5M NaOH was treated with 40 ml of 32% H_2O_2, whereby the temp. rose to 35°. After stirring at r.t. for 6.5 h, the mixture was poured into 100 ml of 40% aq. H_3PO_4 and extracted with CH_2Cl_2. Recrystallization from 80 ml of *t*-BuOMe/hexane 1:1 at −18° afforded 2.69 g (57.4%) of **20**. Colorless needles. M.p. 115.5–117.0°. $[\alpha]_D = +22.4$ ($c = 4.135$, MeOH). IR (KBr): 3293*m*, 2921*m*, 2654*m*, 1699*s*, 1496*w*, 1456*m*, 1417*m*, 1353*w*, 1273*m*, 1211*m*, 1177*m*, 1084*m*, 1054*m*, 1017*m*, 925*w*, 886*w*, 837*w*, 766*m*, 703*s*, 611*m*, 532*w*. ^{1}H-NMR (300 MHz; DMSO; $\delta =$ 2.54 ppm): 7.47–7.30 (*m*, 5 H); 5.04 (*t*, $J = 6.9$, 1 H); 2.63 (*d*, $J = 6.9$, 2 H). ^{13}C-NMR (75 MHz; DMSO; $\delta =$ 39.7 ppm): 172.4 (*s*); 145.2 (*s*); 128.2 (*d*); 127.1 (*d*); 126.0 (*d*); 69.7 (*d*); 44.7 (*t*). EI-MS: 166 (40, $M^{+\bullet}$), 107 (100), 106 (30), 105 (28), 79 (89), 77 (64). CI-MS: 218 (8), 184 (100, $[M+18]^+$), 166 (17).

*Trimethylsilyl (*R*)-3-Phenyl-3-[(trimethylsilyl)oxy]propanoate* (**26**). A suspension of 2.62 g (15.8 mmol) of **20** in 20 ml of CH_2Cl_2 was chilled with an ice-bath, then 4.83 ml (37.7 mmol) of Et_3N and 4.39 ml (34.7 mmol) of Me_3SiCl were added slowly. Stirring at r.t. was maintained for 5 d, and the thick suspension was liquefied from time to time by adding CH_2Cl_2. The mixture was diluted with 20 ml of pentane, filtered, and the cake was washed with pentane and *t*-BuOMe, followed by washing the filtrate with aq. 1M HCl and H_2O. High-vacuum distillation yielded 3.384 g (69%) of **26** as a colorless oil, which was stored under Ar at −18°. ^{1}H-NMR (300 MHz): 7.35–7.22 (*m*, 5 H); 5.11 (*dd*, $J = 9.0, 4.4$, 1 H); 2.72 (*dd*, $J = 15.1, 9.0$, 1 H); 2.57 (*dd*, $J = 15.1, 4.4$, 1 H); 0.26 (*s*, 18 H). ^{13}C-NMR (75 MHz): 172.6 (*s*); 143.9 (*s*); 128.2 (*d*); 127.4 (*d*); 125.9 (*d*); 72.0 (*d*); 47.6 (*t*); 0.0 (*q*).

*(+)-(2*S*,6*R*)-2-*(tert-*Butyl)-6-phenyl-1,3-dioxan-4-one* (**17**). In a flame dried-vessel under Ar, 7.59 g (24.4 mmol) of **26** was dissolved in 50 ml of CH_2Cl_2. At −70°, 2.96 ml (26.9 mmol) of pivalaldehyde and, 80 min later at −60°, 220 µl (1.23 mmol) of Me_3Si-triflate were added. The mixture was stirred for 7 h at −70°, then the reaction was stopped by addition of 200 µl of pyridine and slow warming to r.t. Another 50 ml CH_2Cl_2 was poured into the mixture, before it was washed twice with sat. aq. $NaHCO_3$ soln. The product was purified by crystallization (*t*-BuOMe/hexane 1:1) to give 4.307 g (75%) of **17**. Colorless needles. M.p.: 135.4–139.8°. $[\alpha]_D = +93.7$ ($c = 1.965$, $CHCl_3$). IR ($CHCl_3$): 2980*m*, 2960*m*, 2910*w*, 2880*w*, 1740*s*, 1600*w*, 1485*m*, 1450*w*, 1410*w*, 1370*m*, 1345*m*, 1315*w*, 1280*m*, 1110*m*, 1070*w*, 990*s*, 700*w*. ^{1}H-NMR (300 MHz): 7.41–7.32 (*m*, 5 H); 5.11 (*s*, 1 H); 4.93 (*dd*, $J = 10.8, 4.5$, 1 H); 2.95 (*dd*, $J = 17.6, 4.5$, 1 H); 2.69 (*dd*, $J = 17.6, 10.8$, 1 H); 1.06 (*s*, 9 H). ^{13}C-NMR (75 MHz): 167.6 (*s*); 139.4 (*s*); 128.8 (*d*); 128.5 (*d*); 125.3 (*d*); 108.4 (*d*); 75.4 (*d*); 38.1 (*t*); 35.5 (*s*); 24.0 (*q*). EI-MS: 234 (6, $M^{+\bullet}$), 205 (4), 177 (25), 131 (100), 107 (30), 104 (90), 79 (15), 78 (20), 77 (25), 57 (60). CI-MS:

252 (100, $[M+18]^+$), 235 (14, $[M+1]^+$), 166 (59), 148 (5), 131 (7), 104 (9). Crystals suitable for X-ray crystal-structure analysis were obtained from THF.

(±)-3-(Benzyloxy)-1-nitropropan-2-ol (**28**). A soln. of 6.034 g (40 mmol) of **27** [13] in 21.5 ml (400 mmol) of $MeNO_2$ was treated dropwise with 3 ml of a 3M methanolic KOH soln., which induced a remarkable warming. After 1.5-h stirring at r.t., 70 drops conc. H_2SO_4 were added. The mixture was poured into H_2O, extracted twice with *t*-BuOMe, the org. phase was washed with aq. sat. $NaHCO_3$ soln. and brine: 7.40 g (88%) **28**. An anal. sample was obtained by CC (CH_2Cl_2/AcOEt 20:1). ^{1}H-NMR (300 MHz): 7.40–7.29 (*m*, 5 H); 4.60–4.44 (*m*, 5 H); 3.56–3.55 (*m*, 2 H); 2.91 (br. *s*, 1 H). ^{13}C-NMR (75 MHz): 137.1 (*s*); 128.5 (*d*); 128.1 (*d*); 127.8 (*d*); 78.0 (*t*); 73.6 (*t*); 70.4 (*t*); 67.7 (*d*).

3-(Benzyloxy)-1-nitroprop-1-ene (**18**). At r.t., 4.66 ml (60 mmol) of MsCl and a few grains of DMAP were added to a soln. of 7.40 g (35 mmol) of crude **28** in 75 ml of CH_2Cl_2. Upon dropwise addition of 11.2 ml (80 mmol) of Et_3N, the soln. warmed up until boiling. After stirring for 1 h at r.t., the mixture was poured into H_2O and extracted with CH_2Cl_2. The product was purified by CC (CH_2Cl_2): 5.55 g (82%) of **18**. Yellow oil. Storage under Ar at −18°. IR ($CHCl_3$): 3120*w*, 3000*w*, 2860*m*, 1660*m*, 1635*w*, 1525*s*, 1495*m*, 1450*m*, 1355*s*, 1275*w*, 1120*s*, 1020*m*, 930*s*, 825*w*, 690*w*. ^{1}H-NMR (300 MHz): 7.41–7.20 (*m*, 7 H); 4.60 (*s*, 2 H); 4.27–4.25 (*m*, 2 H). ^{13}C-NMR (75 MHz): 139.7 (*d*); 138.3 (*d*); 137.0 (*s*); 128.6 (*d*); 128.1 (*d*); 127.7 (*d*); 73.3 (*t*); 65.5 (*t*). CI-MS: 211 (100, $[M+18]^+$), 177 (51), 147 (27), 108 (38).

*(2*S*,5*S*,6*R*)-5-[(*S*)-2-(Benzyloxy)-1-(nitromethyl)ethyl]-2-(*tert*-butyl)-6-phenyl-1,3-dioxan-4-one* (**19**) *and (2*S*,5*S*,6*R*)-5-[(*R*)-2-(Benzyloxy)-1-(nitromethyl)ethyl]-2-(*tert*-butyl)-6-phenyl-1,3-dioxan-4-one* (*epi*-**19**). In a flame-dried bottle under Ar, a soln. of 310 µl (2.2 mmol) of (i-Pr)$_2$NH in 2 ml of THF was treated at −70° with 1.4 ml (2.2 mmol) of a 1.6M BuLi soln. in hexane. The cooling was removed for 5 min, and, after the temp. of the soln. had reached −70° again, a soln. of 468 mg (2.0 mmol) of (+)-**17** in 4 ml of THF was added during 3 min. The temp. rose to −60° during stirring, and, after 45 min, it was cooled to −95°, and a soln. of 510 µl (3.0 mmol) of **18** in 2 ml of THF was added dropwise over 3 min. Stirring was maintained at −75° for another 45 min, then the mixture was poured into 20 ml of aq. sat. NH_4Cl soln. and extracted with *t*-BuOMe. CC (pentane/*t*-BuOMe 3:1) of the crude product afforded 739 mg (86%) of **19**/*epi*-**19** in a 1:1 ratio according to the ^{1}H-NMR spectra. IR ($CHCl_3$): 2960*m*, 2900*w*, 2870*m*, 1730*s*, 1550*s*, 1480*m*, 1450*m*, 1405*m*, 1375*m*, 1365*m*, 1345*m*, 1315*m*, 1280*m*, 1100*s*, 1025*w*, 990*s*, 950*w*, 935*w*, 910*w*, 845*w*, 690*w*. ^{1}H-NMR (600 MHz): 7.42–7.20 (*m*, 20 H); 5.01 (*s*, 1 H); 4.90 (*d*, *J* = 10.5, 1 H); 4.81 (*s*, 1 H); 4.69 (*d*, *J* = 11.0, 1 H); 4.64 (*dd*, *J* = 13.5, 7.0, 1 H); 4.56 (*dd*, *J* = 13.5, 7.0, 1 H); 4.52 (*d*, *J* = 11.2, 1 H); 4.46 (*d*, *J* = 11.2, 1 H); 4.37 (*AB*, 2 H); 4.25–4.23 (*m*, 2 H); 3.70–3.68 (*m*, 1 H); 3.66–3.62 (*m*, 3 H); 3.55–3.52 (*m*, 1 H); 3.12–3.09 (*m*, 1 H); 3.00 (*dd*, *J* = 11.0, 1.8, 1 H); 2.76 (*dd*, *J* = 10.5, 1.4, 1 H); 2.72–2.69 (*m*, 1 H); 0.97 (*s*, 9 H); 0.91 (*s*, 9 H). ^{13}C-NMR (150 MHz): 168.8 (*s*); 168.7 (*s*); 137.8 (*s*); 137.7 (*s*); 137.2 (*s*); 137.1 (*s*); 129.5 (*d*); 129.2 (*d*); 129.0 (*d*); 128.9 (*d*); 128.6 (*d*); 128.5 (*d*); 128.2 (*d*); 128.1 (*d*); 127.9 (*d*); 127.7 (*d*); 127.4 (*d*); 127.1 (*d*); 108.5 (*d*); 108.1 (*d*); 80.0 (*d*); 79.1 (*d*); 76.8 (*t*); 74.7 (*t*); 73.9 (*t*); 73.1 (*t*); 69.5 (*t*); 68.0 (*t*); 48.2 (*d*); 47.9 (*d*); 36.3 (*d*); 35.4 (*s*); 35.3 (*d*); 35.2 (*s*); 23.9 (*q*). CI-MS: 445 (94, $[M+18]^+$), 359 (100), 315 (38), 206 (87).

*Ethyl (2*S*,3*S*)- and (2*S*,3*R*)-4-(Benzyloxy)-2-[(*R*)-hydroxy(phenyl)methyl]-3-(nitromethyl)butanoate* (**29** and *epi*-**29**, resp.). a) *By Transesterification of* **19** *and* epi-**19**. Ten drops of conc. H_2SO_4 were added to a soln. of **19**/*epi*-**19** (ratio 1:1) in 15 ml of EtOH. The mixture was heated to reflux during 17 h, the solvent was evaporated, and the residue was poured into H_2O and extracted with CH_2Cl_2. Purification by CC (CH_2Cl_2/AcOEt 20:1) yielded 449 mg (69%) of a 1:1 mixture **29**/*epi*-**29**.

b) *By Addition of the Enolate of* **25** *to* **18**. In a flame-dried bottle under Ar, a soln. of 1.23 ml (8.7 mmol) of (i-Pr)$_2$NH in 2 ml of THF was treated at 0° with 5.45 ml (8.7 mmol) of a 1.6M BuLi soln. in hexane, and the mixture was cooled to −60°. After the dropwise addition of a soln. of 847 mg (4.36 mmol) of *ethyl (+)-(*R*)-3-hydroxy-3-phenylpropanoate* (**25**, prepared according to [11], $[\alpha]_D = +51.6$ ($c = 1.105$, $CHCl_3$)) in 2 ml of THF, the mixture was allowed to warm slowly. When the temp. had reached −7° (after 2 h), a soln. of 820 µl (4.8 mmol) of **18** in 2 ml of THF was added, whereby the temp. rose to 0°. Another 2 h later, the temp. reached +14°, and the mixture was poured into sat. aq. NH_4Cl soln. and extracted with CH_2Cl_2. CC (CH_2Cl_2/AcOEt 20:1) yielded 900 mg (53%) of a 1:1 mixture **29**/*epi*-**29**. IR ($CHCl_3$): 3600*w*, 3500*w* (br.), 3090*w*, 3060*w*, 2980*w*, 2900*w*, 2870*m*, 1720*s*, 1555*s*, 1495*m*, 1455*m*, 1430*m*, 1395*m*, 1375*s*, 1330*m*, 1180*s*, 1115*m*, 1095*s*, 1060*m*, 1020*m*, 910*w*, 870*w*, 830*w*, 695*m*. ^{1}H-NMR (300 MHz): 7.38–7.25 (*m*, 20 H); 5.04 (br. *t*, *J* = 6.8, 1 H); 4.95 (br. *t*, *J* = 6.4, 1 H); 4.69 (*d*, *J* = 6.2, 2 H); 4.64–4.42 (*m*, 6 H); 4.04–3.90 (*m*, 4 H); 3.69 (*dd*, *J* = 10.0, 4.4, 1 H); 3.58–3.51 (*m*, 3 H); 3.38 (br. *d*, *J* = 7.8, 1 H); 3.21 (br. *d*, *J* = 7.5, 1 H); 3.07–3.00 (*m*, 2 H); 2.90–2.78 (*m*, 2 H); 1.03 (*t*, *J* = 7.1, 3 H); 1.03 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (75 MHz): 173.0 (*s*); 141.2 (*s*); 140.8 (*s*); 137.4 (*s*); 128.6 (*d*); 128.5 (*d*); 128.1 (*d*); 127.9 (*d*); 127.8 (*d*); 127.7 (*d*); 125.9 (*d*); 125.7 (*d*); 75.0 (*t*); 74.8 (*t*); 73.4 (*t*); 72.4 (*d*); 72.3 (*d*) 68.2 (*t*);

67.8 (*t*); 61.1 (*t*) 51.7 (*d*); 51.1 (*d*); 37.9 (*d*); 37.7 (*d*); 13.8 (*q*). CI-MS: 405 (100, $[M+18]^+$), 387 (90), 370 (19), 358 (15), 318 (16), 299 (30), 294 (22), 278 (52).

*Ethyl (−)-(2*S*,3*S*)- and (+)-(2*S*,3*R*)-4-(Benzyloxy)-2-[(*R*)-{[(*tert*-butyl)dimethylsilyl]oxy}(phenyl)methyl]-3-(nitromethyl)butanoate* (**30** and *epi*-**30**, resp.). To a 1:1 mixture of 724 mg (1.87 mmol) of **29**/*epi*-**29**, dissolved in 3.5 ml of DMF and 3.5 ml of CH_2Cl_2, 330 µl (2.83 mmol) of 2,6-lutidine, and 515 µl of (*t*-Bu)Me_2Si-triflate were added at 0°. The mixture was stirred during 7.5 h, poured into H_2O, and extracted with CH_2Cl_2. The org. phase was washed twice with aq. $CuSO_4$ soln. and with aq. NH_4Cl soln., and evaporated. After CC (pentane/*t*-BuOMe 9:1), 872 mg (93%) of **30**/*epi*-**30** were obtained. The two diastereoisomeric products could be separated without loss by repeated CC.

Data of **30**: $[\alpha]_D = -4.6$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2950*m*, 2930*m*, 2890*w*, 2860*m*, 1725*s*, 1555*s*, 1495*w*, 1470*w*, 1460*w*, 1455*m*, 1430*w*, 1380*m*, 1360*m*, 1295*w*, 1255*m*, 1180*m*, 1080*s*, 1025*w*, 1005*w*, 940*w*, 915*w*, 895*w*, 885*w*, 870*w*, 840*s*, 695*w*. ^{1}H-NMR (600 MHz): 7.36–7.25 (*m*, 10 H); 4.95 (*d*, $J = 9.4$, 1 H); 4.45 (*dd*, $J = 13.6$, 6.2, 1 H); 4.40–4.38 (*m*, 2 H); 4.27 (*dd*, $J = 13.6$, 7.6, 1 H); 4.14 (*q*, $J = 7.2$, 2 H); 3.56 (*dd*, $J = 10.0$, 4.4, 1 H); 3.40 (*dd*, $J = 10.0$, 7.7, 1 H); 2.93 (*dd*, $J = 9.4$, 4.1, 1 H); 2.42–2.39 (*m*, 1 H); 1.26 (*t*, $J = 7.2$, 3 H); 0.78 (*s*, 9 H); −0.01 (*s*, 3 H); −0.34 (*s*, 3 H). ^{13}C-NMR (150 MHz): 171.8 (*s*); 140.9 (*s*); 137.6 (*s*); 128.6 (*d*); 128.5 (*d*); 128.4 (*d*); 127.8 (*d*); 127.6 (*d*); 127.2 (*d*); 75.6 (*t*); 74.9 (*d*); 73.1 (*t*); 67.0 (*t*); 60.8 (*t*) 53.7 (*d*); 36.6 (*d*); 25.5 (*q*); 17.9 (*s*); 14.2 (*q*); −4.6 (*q*); −5.4 (*q*). CI-MS: 519 (27, $[M+18]^+$), 387 (81), 370 (26), 295 (8), 278 (100).

*Data of epi-***30**: $[\alpha]_D = +42.2$ ($c = 0.925$, $CHCl_3$). IR ($CHCl_3$): 2950*m*, 2930*m*, 2890*w*, 2860*m*, 1725*s*, 1555*s*, 1495*w*, 1470*w*, 1460*w*, 1455*m*, 1430*w*, 1395*w*, 1380*m*, 1360*m*, 1330*w*, 1255*m*, 1180*m*, 1090*s*, 1025*w*, 1005*w*, 940*w*, 915*w*, 840*s*, 695*w*. ^{1}H-NMR (600 MHz): 7.38–7.23 (*m*, 10 H); 4.85 (*d*, $J = 9.6$, 1 H); 4.68 (*dd*, $J = 13.5$, 3.2, 1 H); 4.62 (*dd*, $J = 13.5$, 9.7, 1 H); 4.38–4.36 (*m*, 2 H); 4.11–3.99 (*m*, 2 H); 3.39 (*dd*, $J = 9.8$, 4.9, 1 H); 3.32 (*dd*, $J = 9.8$, 4.6, 1 H); 3.01 (*dd*, $J = 9.5$, 3.4, 1 H); 2.35–2.28 (*m*, 1 H); 1.21 (*t*, $J = 7.2$, 3 H); 0.80 (*s*, 9 H); −0.02 (*s*, 3 H); −0.32 (*s*, 3 H). ^{13}C-NMR (150 MHz): 172.5 (*s*); 141.2 (*s*); 137.6 (*s*); 128.7 (*d*); 128.5 (*d*); 128.3 (*d*); 127.7 (*d*); 127.5 (*d*); 127.0 (*d*); 75.3 (*d*); 74.0 (*t*); 73.2 (*t*); 70.0 (*t*); 60.8 (*t*) 55.3 (*d*); 36.7 (*d*); 25.5 (*q*); 17.9 (*s*); 14.0 (*q*); −4.7 (*q*); −5.5 (*q*). CI-MS: 519 (37, $[M+18]^+$), 387 (100), 370 (12), 278 (14), 219 (7).

*Ethyl (+)-(2*S*,3*R*)-2-[(*R*)-{[(*tert*-Butyl)dimethylsilyl]oxy}(phenyl)methyl]-4-hydroxy-3-(nitromethyl)butanoate* (*epi*-**32**). In a 500-ml flask for the *Parr* apparatus, 215 mg (0.43 mmol) of *epi*-**30** were dissolved in 70 ml of AcOH, 5 ml of CH_2Cl_2 and 0.5 ml of $CDCl_3$. After addition of 95 mg of 10% Pd/C, the mixture was hydrogenated during 24 h under 3.5 bar H_2 pressure. Filtration, evaporation, and CC (CH_2Cl_2/AcOEt 50:1) afforded 152 mg (86%) oily *epi*-**32**. $[\alpha]_D = +56.0$ ($c = 1.15$, $CHCl_3$). IR ($CHCl_3$): 2960*m*, 2930*m*, 2890*w*, 2860*m*, 1725*s*, 1555*s*, 1470*w*, 1460*w*, 1455*w*, 1395*m*, 1380*m*, 1360*m*, 1330*w*, 1255*m*, 1085*s*, 1020*w*, 1005*w*, 970*w*, 940*w*, 915*w*, 870*w*, 840*s*, 700*w*. ^{1}H-NMR (600 MHz): 7.38–7.30 (*m*, 5 H); 4.87 (*d*, $J = 9.6$, 1 H); 4.65 (*dd*, $J = 13.5$, 3.2, 1 H); 4.52 (*dd*, $J = 13.5$, 9.8, 1 H); 4.18 (*q*, $J = 7.2$, 2 H); 3.53 (*d*, $J = 5.3$, 2 H); 3.02 (*dd*, $J = 9.6$, 3.4, 1 H); 2.20–2.17 (*m*, 1 H); 1.85 (br. *s*, 1 H); 1.30 (*t*, $J = 7.2$, 3 H); 0.80 (*s*, 9 H); −0.02 (*s*, 3 H); −0.33 (*s*, 3 H). ^{13}C-NMR (150 MHz): 172.6 (*s*); 141.0 (*s*); 128.7 (*d*); 128.6 (*d*); 126.9 (*d*); 75.0 (*d*); 73.7 (*t*); 62.9 (*t*); 61.0 (*t*) 54.9 (*d*); 38.3 (*d*); 25.5 (*q*); 17.8 (*s*); 14.1 (*q*); −4.7 (*q*); −5.5 (*q*). CI-MS: 429 (6, $[M+18]^+$), 383 (6), 297 (100), 251 (13). From racemic *epi*-**32**, which was prepared from (±)-**17**, crystals suitable for X-ray crystal-structure analysis could be obtained from EtOH (m.p. 83.5–86.5°).

*(+)-(3*S*,4*S*)-3-[(*R*)-{[(*tert*-Butyl)dimethylsilyl]oxy}(phenyl)methyl]-2,3,4,5-tetrahydro-4-(nitromethyl)furan-2-one* (**31**). Analogously to the preparation of *epi*-**32**, reaction of **30** (165 mg, 0.33 mmol) and 10% Pd/C (71 mg) in 80 ml of AcOH, 5 ml of CH_2Cl_2, and 0.5 ml of $CDCl_3$ in a *Parr* apparatus (3.5 bar H_2 pressure) yielded, after CC (CH_2Cl_2/AcOEt 50:1), colorless crystals of **31** (96 mg, 80%). M.p. 69.5–71.6° (AcOEt). $[\alpha]_D = +41.0$ ($c = 1.01$, $CHCl_3$). IR ($CHCl_3$): 2950*m*, 2930*m*, 2880*w*, 2860*m*, 1775*s*, 1720*w*, 1610*w*, 1555*s*, 1460*w*, 1450*w*, 1430*w*, 1375*m*, 1255*m*, 1160*m*, 1090*m*, 1060*m*, 1025*m*, 1005*w*, 940*w*, 900*w*, 835*s*. ^{1}H-NMR (600 MHz): 7.37–7.32 (*m*, 5 H); 5.44 (*d*, $J = 3.9$, 1 H); 4.83 (*dd*, $J = 13.6$, 4.7, 1 H); 4.47 (*dd*, $J = 13.6$, 9.7, 1 H); 4.03 (*dd*, $J = 9.6$, 8.1, 1 H); 3.95 (*dd*, $J = 9.6$, 7.5, 1 H); 3.17–3.09 (*m*, 1 H); 2.90 (*dd*, $J = 8.7$, 3.8, 1 H); 0.93 (*s*, 9 H); 0.10 (*s*, 3 H); −0.03 (*s*, 3 H). ^{13}C-NMR (150 MHz): 173.8 (*s*); 139.1 (*s*); 128.6 (*d*); 128.4 (*d*); 126.3 (*d*); 76.6 (*t*); 72.9 (*d*); 69.4 (*t*); 51.3 (*d*) 34.5 (*d*); 25.7 (*q*); 18.1 (*s*); −4.9 (*q*); −5.3 (*q*). CI-MS: 748 (46, $[2M+18]^+$), 616 (6), 471 (10), 383 (100, $[M+18]^+$), 308 (13), 251 (6).

Hydrogenation of a Mixture **30**/epi-**30**. In a 500-ml flask of a *Parr* apparatus, 300 mg (0.60 mmol) of a mixture *epi*-**30**/**30** 27:73 was dissolved in 70 ml of AcOH, 5 ml of CH_2Cl_2, and 0.5 ml of $CDCl_3$. After addition of 130 mg of 10% Pd/C, the mixture was hydrogenated during 27 h under 3.5 bar H_2 pressure. Filtration, evaporation, and CC (CH_2Cl_2/AcOEt 50:1) afforded 146 mg (0.40 mmol, 67%) of **31** and 66 mg (0.16 mmol, 27%) of *epi*-**32**. The total yield of the two very easily separable products was 94%.

Crystal-Structure Determinations of **17** *and (±)*-epi-**32**[2]). All measurements were conducted on a *Nonius KappaCCD* diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1* and *2*. For **17**, the structure was solved by direct methods using SHELXS97 [14]. The non-H-atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2Ueq of its parent C-atom. The absolute configuration could not be determined crystallographically due to the absence of significant anomalous scatterers in the compound. Instead, the enantiomer used in the refinement was based on the known (*R*)-configuration at the Ph-substituted C-atom which was derived from the (+)-L-mandelic acid used in the synthesis. For (±)-*epi*-**32**, the structure was solved by direct methods with SIR92 [15]. The Si-atom and its attached Me and *t*-Bu groups are disordered. Two positions were defined for each of the affected atoms. The best results were obtained when the site occupation factor of the major conformation was set to 0.63, although some of the C–C distances in the

Table. *Crystallographic Data for Compounds* **17** *and (±)*-epi-**32**

	17	(±)-*epi*-**32**
Crystallized from	THF	EtOH
Empirical formula	$C_{14}H_{18}O_3$	$C_{20}H_{33}NO_6Si$
Formula weight [g mol^{-1}]	234.29	411.56
Crystal color, habit	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.20 × 0.23 × 0.23	0.13 × 0.25 × 0.25
Temp. [K]	298(1)	160(1)
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	*Pbca*
Z	4	8
Reflections for cell determination	1762	4565
2θ Range for cell determination [°]	5–55	4–50
Unit cell parameters a [Å]	5.9263(1)	11.2988(2)
b [Å]	10.2524(2)	10.6558(1)
c [Å]	21.3223(4)	38.0316(6)
V [Å^3]	1295.52(4)	4578.9(1)
D_x [g cm^{-3}]	1.201	1.194
μ(MoK_α) [mm^{-1}]	0.0831	0.135
Scan type	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	55	50
Total reflections measured	21650	44013
Symmetry independent reflections	2979	4042
Reflections used [$I > 2\sigma(I)$]	2388	2462
Parameters refined	155	264
Final R	0.0416	0.0736
wR	0.0529	0.0739
Weights: p in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$	0.023	0.010
Goodness-of-fit	1.472	3.484
Secondary extinction coefficient	$9(1) \times 10^{-6}$	–
Final Δ_{max}/σ	0.0002	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.14; −0.14	0.33; −0.31

[2]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-181625 and 181626 for **17** and (±)-*epi*-**32**, resp. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

model for the disordered region of the molecule are quite poor, particularly for the minor conformation. The O-atoms of the NO_2 group are also disordered over two positions, with the major conformation again having a site occupation factor of 0.63. The non-H-atoms were refined anisotropically, except for the disordered C-atoms of both conformations and the disordered O-atoms of the minor conformation, which were refined only isotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2Ueq of its parent atom. The orientation of the OH group was defined so that the idealized O–H vector pointed in the direction of a peak located in a difference electron-density map.

The refinement of each structure was carried out on F by full-matrix least-squares procedures which minimized the function $\Sigma w(|F_o|-|F_c|)^2$. A correction for secondary extinction was applied only in the case of **17**. Neutral-atom-scattering factors for non-H-atoms were taken from [16], and the scattering factors for H-atoms from [17]. Anomalous dispersion effects were included in F_c [18]; the values for f' and f'' were those of *Creagh* and *McAuley* [19], and the values of the mass-attenuation coefficients were those of [20]. All calculations were performed using the teXsan crystallographic software package [21], and the crystallographic diagrams were drawn with *ORTEPII* [22].

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