201. The Stereoselectivity of the Alkylation of the Dianion of Ethyl 2-Hydroxy-6-methylcyclohexanecarboxylates: Control of Stereochemistry at Three Adjacent Stereogenic Centers

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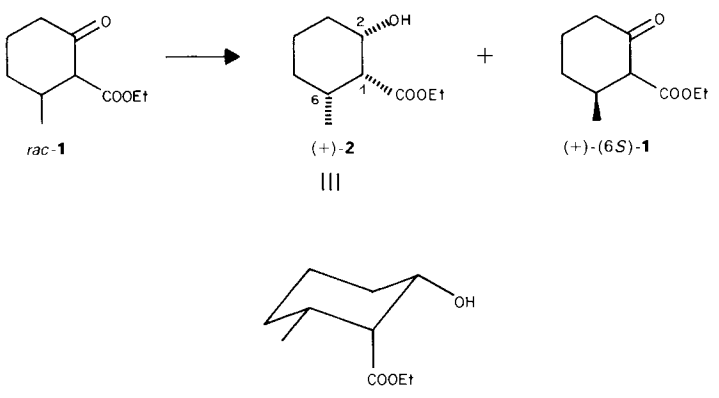
(10.X.89)

Yeast reduction of *rac*-ethyl 2-methyl-6-oxocyclohexanecarboxylate (*rac*-**1**) yielded selectively (+)-ethyl 2-hydroxy-6-methylcyclohexane carboxylate (+)-**2** *(Scheme 1)* which has been alkylated with 5-iodo-2-methylbut-2-ene by the dianion method to furnish the 4-methylbut-3-enyl derivat **3** *(Scheme 3)*. $NaBH_4$ reduction of (+)-**1** led to three hydroxy-carboxylates (−)-**2**, (+)-**5**, and (−)-**6** *(Scheme 4)*. Allylation of the dianion of (+)-**5** afforded (+)-**7**.

Introduction. – A recent publication of *Herradón* and *Seebach* [1] motivated us to complete some work started ten years ago. We consider it supplementary to *Seebach*'s contribution [1] as well as to our own work in this field [2] [3]. After having investigated the alkylation of the dianion of ethyl (1*R*,2*S*)-2-hydroxycyclohexanecarboxylate, obtained from the yeast reduction of the corresponding cyclohexanone [2] [3], it is of considerable interest to investigate both yeast reduction and alkylation in case of an additional Me group at C(6).

Results and Discussion. – Reduction of the *rac*-ethyl 2-methyl-6-oxocyclohexanecarboxylate (*rac*-**1**) [4] with baker's yeast furnished one hydroxy-carboxylate (+)-(1*R*,2*S*,6*R*)-**2** *(Scheme 1)* in 27% yield with 82% e.e. and unreacted starting material (+)-(6*S*)-**1** in 36% yield. The configuration of (+)-**2** can be deduced from the ^{1}H-NMR spectrum on the basis of $J(2,1) \approx 4$ Hz and $J(2,3ax) \approx 9$ Hz, which are conclusive for the

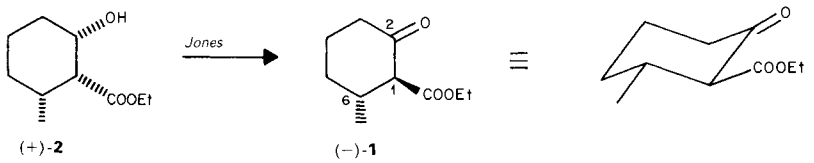
Scheme 1



axial position of the ester and the equatorial position of the OH group in (+)-**2**. On the other hand difference NOE studies revealed a NOE between H_{ax}–C(2) and H_{ax}–C(6), indicating that the Me group adopts an equatorial position.

The absolute configuration of (+)-**2** was established by oxidation of (+)-**2** leading to (−)-**1**. Keto-ester (−)-**1** was shown by ^{1}H-NMR, to be a mixture of ketone and the corresponding tautomers (*ca.* 6:4) which furthermore indicated that both COOEt and Me groups are in pseudoequatorial positions. Compound (−)-**1** displays a relatively weak positive CD effect ($\Delta\varepsilon$ (288 nm) = +0.26) clearly indicating the (1*S*,6*R*)-configuration *(Scheme 2)*.

Scheme 2



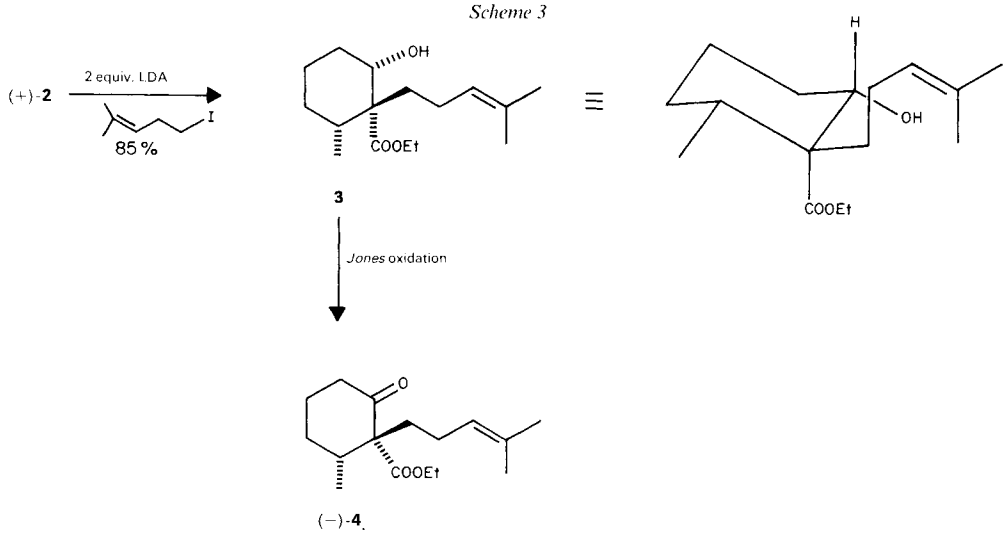
(+)-**2** (−)-**1**

The optical purity of (+)-**2** was determined in the presence of Eu(hfc)$_3$: both the *d* of the CH_3–C(6) and the *t* of CH_3CH_2O groups of the enantiomers separated into two pairs of signals in a ratio of 91:9.

Thus, the yeast reduction of **1** turned out to be analogous to that of ethyl 2-oxocyclohexanecarboxylate [3][5] (see also [6]). Both give the (1*R*,2*S*)-configurated hydroxy-carboxylate with very high diastereoselectivity.

Alkylation of the dianion of (+)-**2** in analogy to earlier work [2] [3] [7] *(Scheme 3)* furnished, in a high yield (85%), compound **3**, which happened to exhibit no optical activity at the Na D-line. The equatorial position of *HO*–C(2) and CH_3–C(6) in **3** is easily established by ^{1}H-NMR on the basis of the large *J*(ax,ax) value of 10 Hz for H–C(2) and H–C(6). The configuration on C(1), *i.e.* the stereochemical mode of the alkylation was deduced with the help of a differential NOE experiment between the

Scheme 3

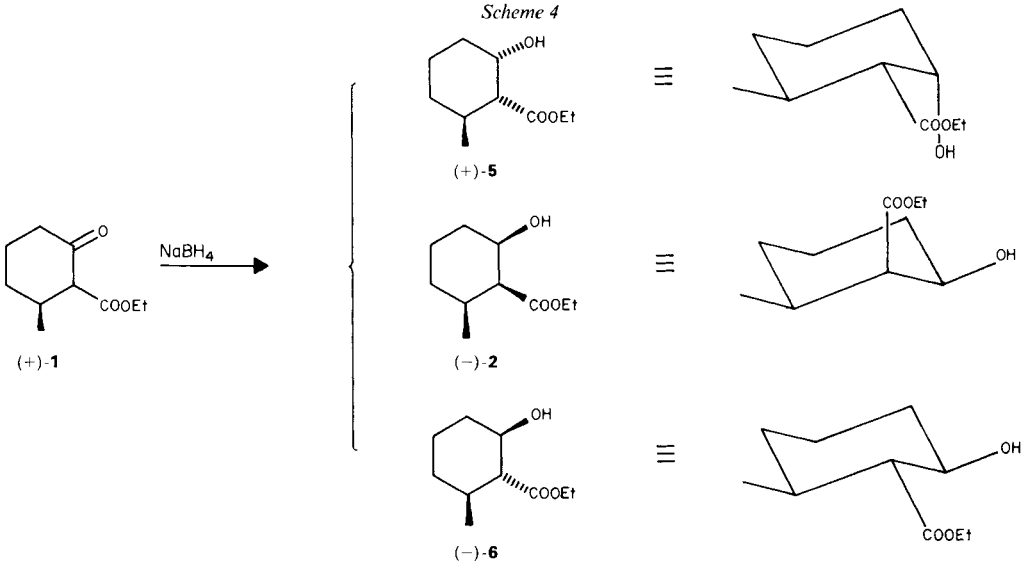


(−)-**4**

H_{ax}–C(2) and α H–C(2′) of the side chain. *Jones* oxidation of the alkylation product **3** yielded the cyclohexanone (−)-**4**[1]).

Reduction of (+)-**1**[2]), *i.e.* the starting material which was recovered after reduction with baker's yeast (*vide supra*), with $NaBH_4$ gave a mixture of three products, (+)-**5**, (−)-**2**, and (−)-**6** in the ratio of *ca.* 4:3:3 (*Scheme 4*). The main product is (+)-**5** with two equatorial Me and COOEt groups and an axial OH group (for ^{1}H-NMR, see *Exper. Part*).

Scheme 4



The second alcohol eluted from the column is (−)-**2**, which is identical to the yeast-reduction product except for its optical rotation. The $[\alpha]_D^{20}$ value of −2.29 indicates a 28% e.e., relative to the measured $[\alpha]_D^{20}$ value of +6.65° for (+)-**2** with 82% e.e. This has been confirmed by optishift experiments. The most polar alcohol turns out to be (−)-**6** with equatorial arrangement of all substituents. This follows from its ^{1}H-NMR spectrum. The $[\alpha]_D^{20}$ values are dependent on the concentration (see *Exper. Part*).

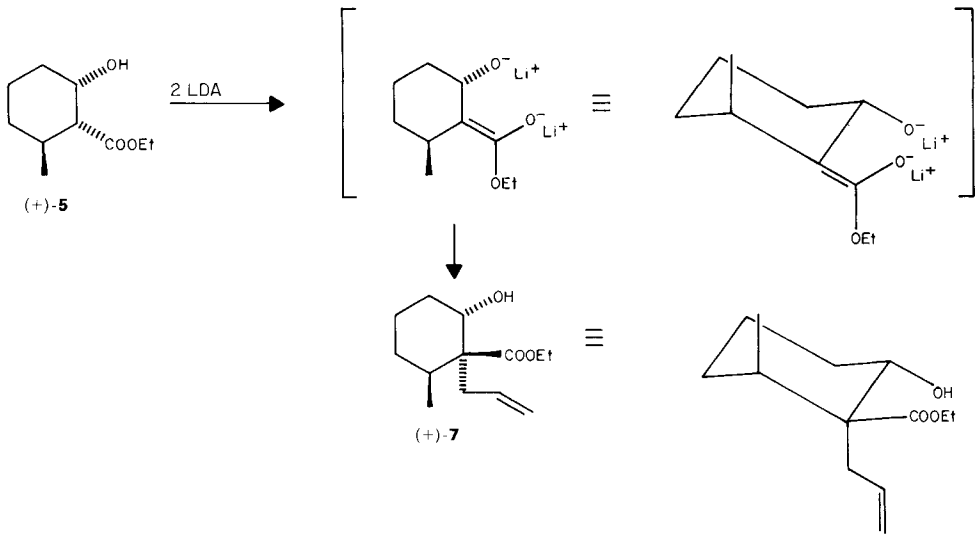
Among these three alcohols, the relative configuration of *HO*–C(2) and CH_3–C(6) in (+)-**5** is *trans*, and *cis* in (−)-**2** and in (−)-**6**. Thus, it was of interest to know, how the dianion of (+)-**5** would behave in the reaction with allyl bromide. The reaction was sluggish but otherwise clean, yielding (+)-**7** with high stereoselectivity (98:2) and in moderate yield (30%; 38% of starting material were recovered). Compound (+)-**7** was in all aspects analogous to the corresponding methyl ester described by *Herradón* and *Seebach* [1] (*Scheme 5*).

The comparison of the respective molecular rotations suggests a 30% e.e. for (+)-**7**, whereas optishift experiments lead to a lower value of *ca.* 25% e.e., in good agreement with the 28% e.e. for (−)-**2**. It is obvious from the ^{1}H-NMR-spectra, that *H*–C(2) is in an

[1]) Synthesis of (−)-**4** demonstrates the practicability of this strategy also for other analogues (*cf.* [8] [9]).

[2]) Because of the keto-enol tautomers, the concentrations of which are dependent on trace amounts of H_2O and acid, the $[\alpha]_D^{20}$ value is not a measure of e.e.

Scheme 5



axial and *H*–C(6) in an equatorial position. Differential NOE experiments confirmed the axial orientation of the allyl group at the quaternary center C(1). Thus, (+)-**7** prefers a conformation with the two alkyl substituents in an axial and the two polar groups in an equatorial position.

Finally, (+)-**1** has been alkylated (NaH, DMF) with homoprenyl iodide to yield (+)-**4** ($[\alpha]_D^{20} = +14.1$ ($CHCl_3$, $c = 1.5$)). This mode of selectiveness, *i.e.* alkylation from the opposite side with respect to the Me group at C(6) has already been observed [8] [9]. The comparison of the $[\alpha]_D^{20}$ values of (+)- and (–)-**4** implies a 23% e.e. for (+)-**1**.

Conclusion. – It has been shown that yeast reduction of *rac*-**1** is reasonably enantioselective with respect to the starting material. The enantiomer with (6*R*)-configuration is reduced about 10 times faster than the one with (6*S*)-configuration. This gives rise to the reduced product with *ca.* 82% e.e.

Moreover, the yeast reduction is completely product-specific, *i.e.* completely diastereoselective, yielding only one stereoisomer, (+)-**2**, in contrast to the reduction with $NaBH_4$ (*Scheme 4*). This seems to be a useful alternative for the enantioselective elaboration of three consecutive stereocenters, even with the moderate yield of 30%.

Alkylation of the dianion of (+)-**2** with homoprenyl iodide proceeded analogously to the desmethyl compound [2], but with even higher stereoselectivity, under formation of a valuable quaternary center in **3**.

Alkylation of the dianion of the stereoisomer (+)-**5** occurs sluggishly but highly selectively (98:2), leading to (+)-**7**. In (+)-**7** and in **3**, the relative configuration of the COOEt group and the CH_3–C(6) is the same, *i.e. cis*, whereas the relative configuration of the COOEt and the *OH*–C(2) group is *trans* in (+)-**7** and *cis* in **3**.

We thank Dr. *K. Noack* (*F. Hoffmann-La Roche AG*, Basel) for the CD spectra and Mr. *J. Märki* for the NMR spectra.

Experimental Part

General. See [10].

(+)-Ethyl (1R,2S,6R)-2-Hydroxy-6-methylcyclohexanecarboxylate ((+)-**2**). *Ethyl 2-methyl-6-oxocyclohexanecarboxylate* (**1**; 100 g, 0,54 mol) 1 kg of baker's yeast, 1.5 kg of sucrose in 10 l of H_2O were stirred during 65 h. Usual workup [2] yielded 85 g of oil, which, upon chromatography on silica gel, gave 36.4 g (36.4%) of starting material (+)-**1** ($[\alpha]_D^{20} = +1.15$ ($CHCl_3$, $c = 1.0$)) and 28 g (27%) of (+)-**2**. The latter was distilled at 75–80° 0.05 Torr. $[\alpha]_D^{22} = +6.65$ ($CHCl_3$, c = 1.0). IR (film): 3450, 1725. ^{1}H-NMR. 4.24–4.50 (*AB*, CH_3CH_2); 3.90–3.84 (*ddd*, $J = 9$, H_{ax}–C(2)); 2.795 (*dd*, $J_1 \approx J_2 \approx 4$, H_{eq}–C(1)); 1.95–1.79 (*m*, H_{eq}–C(4), H_{ax}–C(3), H_{ax}–C(6)); 1.69–1.61 (*m*, H_{eq}–C(3)); 1.58–1.48 (*m*, H_{ax}–C(5)); 1.46–1.39 (*m*, H_{eq}–C(5)); 1.35–1.28 (*m*, H_{ax}–C(4)); 1.28 (*t*, CH_3CH_2); 1.03 (*d*, CH_3–C(6)). Differential NOE: 3.90–3.84 (H_{ax}–C(2))→2.8 (H_{eq}–C(1)); 1.95–1.75 (H_{ax}–C(6)), 1.89–1.61 (H_{eq}–C(3)); 1.03 (CH_3–C(6))→2.8 (H_{eq}–C(1)); 1.95–1.75 (H_{ax}–C(6)), 1.58–1.48 (H_{ax}–C(5)), 1.46–1.39 (*m*, H_{eq}–C(5)). ^{1}H-NMR experiments in the presence of optishift reagent showed both the *t* of CH_3 and the *d* of CH_3 separated in a ratio of *ca.* 10:1, thus the compound (+)-**2** displays an e.e. value of *ca.* 82%. ^{13}C-NMR: 173.4 (*s*); 70.1 (*d*); 59.8 (*t*); 51.57 (*d*); 32.5 (*d*); 29.8 (*t*); 29.0 (*t*); 21.5 (*t*); 18.7 (*q*); 14.1 (*q*). MS: 186 (2, M^+), 168 (8), 158 (21), 143 (16), 141 (16), 123 (14), 115 (100), 95 (73), 87 (96), 69 (66), 55 (44), 41 (66). Anal. calc. for $C_{10}H_{18}O_3$ (186.25): C 64.49, H 9.47; found: C 64.46, H 9.87.

(−)-Ethyl (1S,6R)-6-Methyl-2-oxocyclohexanecarboxylate ((−)-**1**). Ester (+)-**2** (900 mg, 4.8 mmol) was dissolved in 10 ml of Et_2O and oxidized with *Jones'* reagent in acetone. Usual workup and chromatography on silica gel yielded an oil, which, upon distillation (bulb-to-bulb) at *ca.* 90°/0.03 Torr, furnished 0.5 g (55%) of pure (−)-**1**. $[\alpha]_D^{20} = -1.9$ ($CHCl_3$, $c = 1.0$). $\Delta\varepsilon$(288 nm) = 0.26 (EtOH); $\Delta\varepsilon$(290.8) = +0.29 (cyclohexane). ^{1}H-NMR (ketone and enol in a 2:1 ratio): 12.4 (OH); 4.3–4.15 (*m*, CH_3CH_2); 3.3 (*dd*, $J \approx 11$, 0.5, H–C(1) (ketone)); 2.74–2.66 (*m*, H–C(6) (enol)); 2.51–2.43 (*dm*, $J \approx 14$, H_{eq}–C(3) (ketone)); 2.34–2.23 (*m*); 2.09–2.0 (*m*); 1.96–1.88 (*m*); 1.9–1.4 (*m*); 1.32, 1.28 (2*t*, CH_3CH_2); 1.07, 1.04 (2*d*, CH_3–C(6)). MS: 184 (26, M^+), 169 (49), 156 (21), 141 (23), 139 (28), 123 (100), 114 (17), 101 (16), 95 (23), 87 (19), 82 (44), 69 (58), 55 (92), 41 (60).

Ethyl (1R,2S,6R)-1-(4-Methylpent-3-enyl)-2-hydroxy-6-methylcyclohexanecarboxylate (**3**). To the soln. of 0.23 mol of LDA in 120 ml of THF, prepared from 23.1 g (0.23 mol) of $(i\text{-}Pr)_2NH$, 19.6 g (0.105 mol) of (+)-**2** were added at −50° in quick succession. After stirring for 10 min at −50°, the soln. of 33.2 g (0.16 mol) of homoprenyl iodide in 70 ml HMPTA was added within 10 min and the temp. was left to rise to 20°. The mixture was refluxed for 10 min and then worked up as usual. The crude product (31 g) was chromatographed on silica gel (700 g) with hexane/Et_2O 1:1 yielding 22.6 g (80%) of **3** (100% pure GLC). Bulb-to-bulb distillation at 100°/0.005 Torr. $[\alpha]_D^{20} = 0$ ($CHCl_3$, $c = 1.4$). IR (film): 3540, 1735, 1720. ^{1}H-NMR: 5.18–5.05 (*m*, H–C(3′)); 4.26–4.13 (*m*, CH_3CH_2); 3.91–3.86 (*m*, H_{ax}–C(2); becomes *dd*, $J \approx 12.5$, upon treatment with D_2O); 3.35 (*d*, $J \approx 10$, OH); 2.02–1.54 (*m*, 10 H); 1.68, 1.595 (2 br. *s*, 2 CH_3–C(4′)); 1.41–1.30 (*m*, 1 H_{ax}); 1.32 (*t*, CH_3CH_2); 1.14 (*d*, CH_3–C(6)). Double resonance: 1.96 (2 H–C(2′))→5.18–5.05 (br. *s*, H–C(3′)); 1.14 (CH_3–C(6))→1.64 (*dd*, $J_1 \approx 10$, 3, H–C(6)). Differential NOE: 3.91–3.86 (H_{ax}–C(2))→2.02–1.85 (2 H–C(2)). MS: 268 (1, M^+), 205 (6), 199 (5), 186 (13), 184 (14), 168, (68), 153 (15), 140 (16), 125 (26), 95 (34), 82 (100), 69 (42) 55 (53), 41 (76). Anal. calc. for $C_{16}H_{28}O_3$ (268, 40): C 71.60, H 10.52; found: C 71.35, H 10.54.

(−)-Ethyl (1R,6R)-1-(4-Methylpent-3-enyl)-2-oxo-6-methylcyclohexanecarboxylate ((−)-**4**). To the soln. of 21 g (0.078 mol) of **3** in 250 ml of Et_2O has been treated, at 3°, with the soln. of 23 g (0.078 mol) of $Na_2Cr_2O_7$, and 23 g (0.23 mol) of conc. H_2SO_4 in 70 ml of H_2O. After usual workup and distillation at 90°/0.03 Torr, 17.3 g (85%) of (−)-**4** were isolated. $[\alpha]_D^{22} = -53.2$ ($CHCl_3$, $c = 1.08$). $\Delta\varepsilon$ (300.3 nm) = −0.91 (EtOH). IR (film): 1740, 1735 (sh), 1715. ^{1}H-NMR: 5.16–5.09 (*m*, H–C(3′)); 4.19–4.11 (*m*, CH_3CH_2); 2.73–2.62 (*ddd*, $J \approx 15$, 15, 8, H_{ax}–C(3)); 2.47–2.39 (*dm*, $J \approx 15$, H_{eq}–C(3)); 2.1–1.6 (*m*, 9 H); 1.68, 1.62 (2 br. *s*, 2 CH_3–C(4′)); 1.26 (*t*, CH_3CH_2); 1.16 (*d*, CH_3–C(6)). Double resonance: 1.16 (CH_3–C(6))→1.90 (*dd*, $J_1 \approx 11$, 4, H_{ax}–C(6)). MS: 221 (4, M^+ − OEt), 184 (24), 169 (100), 123 (47), 82 (32), 69 (16). Anal. calc. for $C_{16}H_{26}O_3$ (266.38): C 72.14, H 9.84; found: C 72.06, H 9.78.

$NaBH_4$ Reduction of (+)-Ethyl (1R,6S)-6-Methyl-2-oxocyclohexanecarboxylate ((+)-**1**) *to (+)-Ethyl (1R,2S,6S)-* ((+)-**5**), *(−)-Ethyl (1S,2R,6S)-* ((−)-**2**) *and (−)-Ethyl (1R,2R,6S)-2-Hydroxy-6-methylcyclohexanecarboxylate* ((−)-**6**). To the soln. of 50 g (0.27 mol) of (+)-**1** in 250 ml of EtOH 15 g (0.4 mol) of $NaBH_4$ were added slowly at 10–15°. After 1 h the mixture was worked up as usual, and 41.6 g of a crude alcohol mixture were isolated. The GLC indicated three isomers in the ratio of 40:30:30. Chromatography on silica gel with hexane/*t*-BuOMe 2:1 furnished 13 g of (+)-**5**, 6.9 g of (−)-**2**, and 4 g of (−)-**6**. (+)-**5**: $[\alpha]_D^{20} = +6.13$ ($CHCl_3$, $c = 1.14$); $[\alpha]_D^{20} = +6.78$ ($CHCl_3$, $c = 5$). IR (film): 3500 (br.), 1735, 1705. The ^{1}H-NMR was measured in C_6D_6 because of much better separation of signals compared to the spectrum in $CDCl_3$. ^{1}H-NMR (C_6D_6): 4.10–4.06 (br. *s*, H_{eq}–C(2)); 4.0–3.85 (*ABm*, CH_3CH_2); 3.52–3.49 (br. *s*, OH); 2.24–2.12 (*m*, H_{ax}–C(6); ⚡ at 0.84→*ddd*,

$J_1 \approx J_2 \approx 11$, $J_3 \approx 3$); 1.99–1.85 (*m*, 3 H); 1.93 (*dd*, $J \approx 11$, 2, H_{ax}–C(1)); 1.55–1.48 (*dm*, $J_{gem} \approx 13$, H_{eq}–C(5)); 1.33–1.25 (*m*, 1 H); 1.11–1.0 (*ddm*, 1 H); 0.94 (*t*, CH_3CH_2); 0.84 (*d*, CH_3–C(6)); 0.725 (*dddd*, $J_{gem} \approx 13$, J(5ax,6ax) ≈ 11, J(5ax,4eq) ≈ 3, H_{ax}–C(5)). ^{13}C-NMR: 175.8 (*s*); 66.3 (*d*); 60.2 (*t*); 54.0 (*d*); 33.9 (*t*); 31.3 (*t*); 28.3 (*d*); 20.15 (*q*); 19.1 (*t*); 13.9 (*q*). MS: 168 (2, $M^+ - H_2O$), 158 (18, $M - C_2H_4$), 141 (5), 123 (7), 115 (100), 95 (32), 87 (63), 69 (29), 58 (18), 55 (15), 43 (74).

(–)-**2**: $[\alpha]_D^{20} = -2.29°$ ($CHCl_3$, $c = 1$), *i.e.* 28% e.e.

(–)-**6**: $[\alpha]_D^{20} = -2.01$ ($CHCl_3$, $c = 1.04$); $[\alpha]_D^{20} = -3.2$ ($CHCl_3$, $c = 5.1$). IR (film): 3430 (br.), 1730, 1710. ^{1}H-NMR: 4.25–4.14 (*ABm*, CH_3CH_2); 3.77 (*ddd*, $J_1 \approx J_2 \approx 11$, J(2ax,2eq) ≈ 4, H_{ax}–C(2)); 2.28–1.18 (br., OH); 2.04–1.97 (*dm*, H_{eq}–C(3)); 1.94 (*dd*, J(1,2) $\approx J$(1,6) ≈ 11; H_{ax}–C(1)); 1.78–1.62 (*m*, 3 H); 1.44–1.20 (*m*, 2 H_{ax}); 1.29 (*t*, CH_3CH_2); 1.0–0.89 (*dddd*, 1 H_{ax}); 0.91 (*d*, CH_3–C(6)). ^{13}C-NMR: 174.9 (*s*); 71.5 (*d*); 59.99 (*t*); 59.6 (*d*); 34.15 (*d* + *t*); 33.3 (*t*); 23.38 (*t*); 19.65 (*q*); 14.0 (*q*). MS: 168 (3, $M - H_2O$), 158 (15, $M - C_2H_4$), 141 (10), 115 (100), 95 (42), 87 (58), 69 (35), 55 (19), 41 (33).

*(+)-Ethyl (1*S*,2*S*,6*S*)-1-Allyl-2-hydroxy-6-methylcyclohexanecarboxylate* (**7**). Compound (+)-**5**, (3.7 g, 0.02 mol) dissolved in 10 ml THF, was added dropwise at –70° to the soln. of 0.1 mol of LDA in 80 ml of THF. Within 5 min, the soln. became slightly yellow, and the temp. rose to –30°. Then, the soln. of 3.6 g (0.03 mol) allyl bromide in 20 ml HMPTA was added quickly (–30° → 0°), and the mixture was stirred for 10 min at 0°. After the usual workup, 6.1 g of a crude product was isolated. GLC and TLC indicated a mixture of *ca.* 55% of the starting material and *ca.* 45% of two new compounds in the ratio of *ca.* 98:2. Chromatography on silica gel with hexane/*t*-BuOMe 2:1 yielded 1.3 g (29%) of **7** and 1.5 g (38%) of (+)-**5**. $[\alpha]_D^{20} = +25.3$ ($CHCl_3$, $c = 1.09$). Optishift experiment showed a *ca.* 62:38 ratio, *i.e.* 24% e.e. IR (film): 3540, 3450 (sh), 3070, 1715, 1635. ^{1}H-NMR: 6.04–5.93 (*m*, H–C(2′)); 5.08–4.98 (*m*, 2 H–C(3)); 4.26–4.20 (*m*, H_{ax}–C(2)); 4.22–4.14 (*m*, CH_3CH_2); 3.0–2.96 (br. *s*, OH); 2.675, 2.38 (2*ddt*, 2 H–C(1′)); 2.18–2.09 (*ddq*, H_{eq}–C(6)); 1.89–1.82 (*m*, H_{eq}–C(3)); 1.7–1.54 (*m*, 4 H); 1.29 (*t*, CH_3CH_2); 1.33–1.26 (*m*, 1 H); 0.945 (*d*, CH_3–C(6)). ^{13}C-NMR: 176.0 (*s*, CO); 135.3 (*d*, C(2′)); 116.4 (*t*, C(3′)); 68.2 (*d*, C(2)); 59.8 (*t*, CH_3CH2); 54.0 (*s*, C(1)); 36.4 (*t*, C(1′)); 34.5 (*d*, C(6)); 28.2 (*t*, C(3)); 27.5 (*t*, C(5)); 19.0 (*t*, C(4)); 15.8 (*q*, CH_3–C(6)); 13.8 (*q*, CH_3CH_2). Differential NOE: 0.945 (CH_3–C(6)) → 4.26–4.20 (H_{ax}–C(2)); 2.18–2.09 (H_{eq}–C(6)); 4.22–4.14 (CH_3CH_2); 2.675, 2.38 (H_{eq}–C(1′)) → 6.04–5.93 (H–C(2′)); 5.08–4.98 (H–C(3′)); 2.18–2.09 (H_{eq}–C(6)). MS: 226 (12, M^+), 211 (2), 208 (5), 198 (6), 185 (13), 180 (12), 169 (15), 155 (75), 135 (25), 127 (100), 109 (87), 93 (45), 81 (70), 67 (39), 55 (78), 41 (79).

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