112. A Short Synthesis of (−)-Carbovir

by **Stefan Hildbrand**[1]), **Thomas Troxler**[2]), and **Rolf Scheffold***

Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH-3012 Bern

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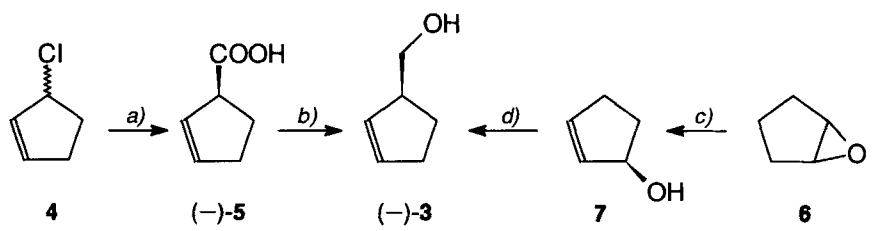
(−)-Carbovir ((−)-**1**) was synthesized *via* the cyclic carbonate **2** in four steps starting from enantiomerically enriched (−)-(*S*)-(cyclopent-2-enyl)methanol ((−)-**3**).

Introduction. – The carbocyclic 2′,3′-didehydro-2′,3′-dideoxyguanosine analogue (−)-carbovir (= 2-amino-1,9-dihydro-9-[4-(hydroxymethyl)cyclopent-2-en-1-yl]-6*H*-purin-6-one; (−)-**1**) proved to be a potent and selective inhibitor of HIV-1 *in vitro* [1] and is still of interest as a potential chemotherapeutic agent for the treatment of AIDS infections [2]. AIDS-Driven nucleoside chemistry [3] led to a number of different routes to **1**. Strategies employed were: *i*) synthesis from natural (−)-aristeromycin [4], *ii*) linear approaches with stepwise construction of the guanine moiety [1a] [5], and *iii*) convergent approaches with introduction of an intact guanine moiety [6]. Efficient and versatile variants of the convergent approach proved to be the Pd^0-catalyzed allylic substitution of optically pure cyclopent-2-enyl acetates or carbonates with guanine derivatives [7].

We report about a short and efficient synthesis of (−)-**1** *via* a new cyclic allylic carbonate **2**, which is easily accessible in optically pure form from (−)-(*S*)-(cyclopent-2-enyl)methanol ((−)-**3**).

Results and Discussion. – As starting material for the synthesis of (−)-**1**, enantiomerically enriched (*S*)-(cyclopent-2-enyl)methanol ((−)-**3**) was chosen. It was prepared by two different ways (*Scheme 1*). Cyclopentadiene was first converted to 3-chlorocyclopen-

Scheme 1



a) Mg^0, THF, then CO_2 [9]; recrystallization as (−)-(α-phenylethyl)amine salt [10]. *b*) $LiAlH_4$, Et_2O. *c*) Vitamin B_{12}, Zn/NH_4Cl, MeOH [12]. *d*) KH, then ICH_2SnBu_3, then BuLi, THF.

[1]) Part of the diploma work of *S. H.*, University of Bern, 1994.

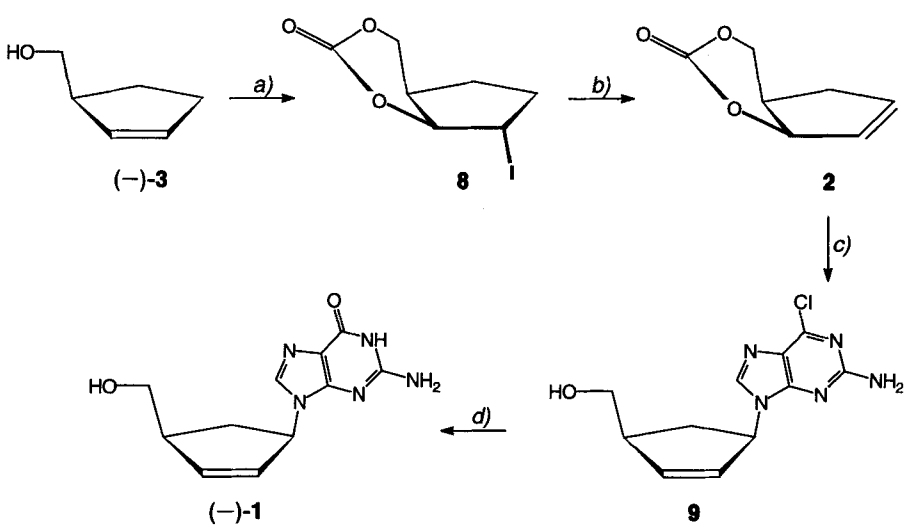
[2]) Part of the Ph. D. thesis of *T. T.*, University of Bern, 1993.

tene **4** by addition of gaseous HCl [8]. *Grignard* reaction of **4** using *Rieke*-Mg [9] and quenching with CO_2 yielded the racemic acid (±)-**5** (85%) which, after optical resolution *via* recrystallization as its (−)-(α-phenylethyl)amine salt and liberation of the acid, afforded the enantiomer (−)-**5** in 16% yield [10]. The unwanted, enriched (+)-enantiomer was recycled to (±)-**5** by double deprotonation with lithium diisopropylamide (LDA) in THF/1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU) 2:1 at −70° to the racemic dianion, followed by kinetically controlled protonation with 0.1M HCl at −70°. The alcohol (−)-**3** was then obtained by $LiAlH_4$ reduction of (−)-**5** in 64% yield (ee 98%) [11].

An alternative route to (−)-**3** involves the vitamin-B_{12}-catalyzed isomerization of 1,2-epoxycyclopentane (**6**) to optically active (*R*)-cyclopent-2-en-1-ol (**7**; 66%; ee 56%) [12]. Consecutive treatment of **7** with KH in THF, ICH_2SnBu_3 [13], and BuLi led to the formation of (−)-**3** *via* a clean [2,3]-sigmatropic *Wittig* rearrangement (49%; ee 54%).

Sequential treatment of the homoallylic alcohol (−)-**3** at room temperature with BuLi (1 h), CO_2 (1 h), and I_2 (13 h, dark) in THF [14] led to the crystalline cyclic iodocarbonate **8** (*Scheme 2*). The pure (+)-enantiomer of **8** was easily obtained by recrystallization in 53% (rel. to optically resolved (−)-**3** (ee 98%)) or 18% yield (rel. to the *Wittig* rearrangement product (−)-**3** (ee 54%)), respectively. The *cis*-configuration at the ring junction of **8** was established by NOE studies. No *trans*-isomer could be found in the reaction mixture. Elimination of HI from **8** was effected with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under a vigorous stream of CO_2. The cyclic allylic carbonate **2** was obtained after column chromatography in 63% yield. If the reaction was conducted in absence of CO_2, formation of **3**, *via* reductive opening of **8** by I^- ions and decarboxylation was predominant.

Scheme 2



a) BuLi, then CO_2, then I_2, THF. *b*) DBU, CO_2, toluene, 90°. *c*) 2-Amino-6-chloro-1*H*-purine, allylpalladium chloride dimer, PPh_3, THF/DMSO. *d*) 0.33M NaOH [7b].

Reaction of **2** with 2-amino-6-chloro-1*H*-purine in THF/DMSO with 10% Pd^0 catalyst (prepared *in situ* from allylpalladium chloride dimer and PPh_3) yielded, after column chromatography, the known (−)-carbovir precursor **9** in 59% yield. NMR, IR, and MS were identical with reported data [1a]. Hydrolysis of **9** with 0.33M NaOH for 3 h [7b] gave, after column chromatography, the title compound (−)-**1** in 71% yield.

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Experimental Part

General. Chemicals and solvents: 2-Amino-6-chloropurine (97%) from *Aldrich*; KH, *Fluka pract., ca.* 20% in oil; BuLi, *Fluka pract., ca.* 1.6M in hexane; ICH_2SnBu_3 was prepared following the reported procedure [13]; allylpalladium chloride dimer, *Fluka purum* (> 98%); Et_2O, pentane, and toluene from *Siegfried*, distilled over NaH before use; THF from *Siegfried*, distilled over K before use; all other reagents were *Fluka purum* and all other solvents *Fluka puriss.p.a.* and were used as purchased. Flash column chromatography (FC): silica gel (30–60 μm) from *Baker*. Anal. GC: *Hewlett-Packard-5794* gas chromatograph; 20-m *Duran*-glass cap. column coated with *SE-54* (*df* 0.15 μm); temp. program from 40 to 250°, 3°/min; flame-ionization detector (FID). Enantioselective GC (t_R in min): *Hewlett-Packard-5890* with modified cyclodextrins as chiral stationary phase; column *A*: 10 m, 20% heptakis{2,3-di-*O*-propyl-6-*O*-[(*tert*-butyl)dimethylsilyl]}-β-cyclodextrin in *OV-1701*; column *B*: 10 m, 20% heptakis{2,3-di-*O*-methyl-6-*O*-[(*tert*-butyl)dimethylsily]}-β-cyclodextrin in *OV-1701*; ee's were determined from the % of relative intensities of base-line-separated peaks of enantiomers and checked by analogous measurements of the corresponding racemic compounds. M.p. (uncorrected): *Büchi 510*. $[\alpha]_D$: *Perkin-Elmer-241* polarimeter. IR: *Perkin-Elmer-782* spectrometer. ^{1}H-NMR: *Bruker-AC-300* (300 MHz) spectrometer; δ in ppm with respect to Me_4Si (= 0 ppm) or (D_6)DMSO (= 2.49 ppm) as internal standard. ^{13}C-NMR: *Bruker-AC-300* (75 MHz) spectrometer; Me_4Si (= 0 ppm) or (D_6)DMSO (= 39.7 ppm) as internal standard. MS (*m*/*z* (%)): *Varian-MAT-CH-7A*, ionization energy 70 eV; only peaks with intensities > 3% of the base peak are given. Elemental analyses: Mikroelementaranalytisches Laboratorium, ETH, Zürich.

(S)-(Cyclopent-2-enyl)methanol ((−)-**3**). To a soln. of allylic alcohol (*R*)-**7** (2.82 g, 33.5 mmol; ee (GC) 56.1% [12]) in THF (60 ml) was added KH (1.60 g, 40 mmol) at r.t. under Ar and the suspension stirred for 30 min. A soln. of ICH_2SnBu_3 (20.2 g, 47 mmol) in THF (20 ml) was added dropwise during 30 min. After stirring for 1 h at r.t., the mixture was cooled to −78° and BuLi (89 ml, 134 mmol) added dropwise within 30 min. The mixture was warmed up to r.t. over 1 h, Et_2O (100 ml), ice (50 ml), and H_2O (100 ml) were added, and the soln. was extracted with Et_2O (3 × 60 ml). The combined org. phase was dried ($MgSO_4$), the solvent removed, and the residual yellow liquid (30 ml) diluted with hexane (100 ml). This soln. was extracted with MeCN (3 × 50 ml). From the combined MeCN extracts, the solvent was distilled off over a 10-cm *Vigreux* column at 1 atm. Purification of the residue by FC (silica gel, Et_2O/pentene 1:1) yielded (−)-**3** (1.62 g, 49%). Clear colourless oil. $[\alpha]_D^{20} = -59.7$ (neat). Enantioselective GC (column *A*, 60°): t_R 9.55 (22.39%; (+)-**3**), 10.55 (75.19%; (−)-**3**); 54.1% ee. IR (film): 3320 (br.), 3050*s*, 2900*s*, 1615*w*, 1460*m*, 1440*m*, 1370*m*, 1285*w*, 1210*w*, 1155*w*, 1120*w*, 1080*s*, 1030*s*, 960*m*, 930*w*, 910*w*, 850*w*, 720*s*, 615*m*. ^{1}H-NMR ($CDCl_3$): 1.51–1.66 (*m*, 1 H); 1.92–2.08 (*m*, 1 H); 2.22–2.45 (*m*, 2 H); 2.80–2.97 (*m*, 2 H); 3.52 (*d*, *J* = 6.2, 2 H); 5.63–5.71 (*m*, 1 H); 5.78–5.87 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 132.9, 131.5, 66.4, 48.5, 32.1, 26.1. MS: 99 (1), 98 (23, M^+) 83 (4), 81 (14), 80 (68), 79 (37), 77 (12), 70 (3), 69 (6), 68 (42), *67* (100), 66 (51), 65 (47), 63 (4), 57 (10), 55 (6), 53 (8), 51 (5), 43 (4), 42 (4), 41 (42), 40 (8), 39 (28), 31 (9), 29 (4), 28 (6), 27 (5), 18 (21).

The same alcohol (−)-**3** was obtained *via* **4** → **5** in an ee (enantioselective GC) of 98% [9] [10].

(4aR,7S,7aS)-Hexahydro-7-iodocyclopenta[d][1,3]dioxin-2-one (**8**). To a soln. of (−)-**3** (1.10 g, 11.2 mmol; ee 98%) in THF (20 ml) under Ar at 0° was added dropwise BuLi (8.2 ml, 13 mmol). The mixture was stirred for 1 h at r.t. A vigorous stream of CO_2 (dried over $CaSO_4$) was bubbled through the soln., first for 10 min at 0°, then for 50 min at r.t. A soln. of I_2 (6.27 g, 24.7 mmol) in THF (30 ml) was added dropwise within 20 min and the mixture stirred for 13 h in the dark. To the brown soln., AcOEt (45 ml) was added and the dark soln. washed with 20% aq. $Na_2S_2O_3$ soln. (2 × 35 ml). The aq. phase was extracted with AcOEt (30 ml), the combined org. phase dried (Na_2SO_4), the solvent distilled off, and the residual brown solid (2.50 g) crystallized from AcOEt: **8** (1.58 g, 53%). Enantioselective GC (column *B*, 140°): t_R 39.0; ee > 99%. Brown crystals. M.p. 122.5–123.5°. $[\alpha]_D^{23} = 54$ (*c* = 0.16, MeOH). A sample was chromatographed (silica gel, cyclohexene/AcOEt 10:9). White solid. M.p. 128–129°. IR

(KBr): 2975*w*, 2950*w*, 2920*w*, 1750*s*, 1720*s*, 1470*w*, 1445*w*, 1405*s*, 1360*m*, 1290*w*, 1245*s*, 1200*s*, 1175*m*, 1140*m*, 1125*s*, 1090*m*, 1070*m*, 1045*m*, 1015*w*, 930*w*, 780*w*, 765*w*, 555*w*. ^{1}H-NMR ($CDCl_3$): 1.77–1.92 (*m*, 1 H); 2.12–2.23 (*m*, 1 H); 2.24–2.45 (*m*, 2 H); 2.98–3.10 (*m*, 1 H); 4.25 (*dd*, *J* = 11.4, 3.3, 1 H); 4.37–4.43 (*m*, 1 H); 4.50 (*dd*, *J* = 11.4, 3.7, 1 H); 5.12 (*dd*, *J* = 6.2, 1.5, 1 H). ^{13}C-NMR ($CDCl_3$): 148.9, 90.7, 68.5, 35.6, 33.4, 28.3, 25.7. MS: 269 (6), 268 (48, M^+), 154 (31), 142 (8), *141* (100), 128 (10), 127 (9), 97 (50), 80 (4), 79 (53), 77 (10), 69 (59), 68 (6), 67 (74), 66 (12), 65 (10), 57 (4), 55 (20), 53 (6), 43 (28), 42 (4), 41 (68), 40 (5), 39 (17), 28 (8), 28 (6), 18 (7). Anal. calc. for $C_7H_9IO_3$ (268.05): C 31.37, H 3.38, I 47.34, O 17.91; found: C 31.59, H 3.38, I 47.18, O 17.69.

The alcohol (−)-**3** (ee 54%) from the *Wittig* rearrangement **7** → **3** gave, by the same procedure and after recrystallization from (i-Pr)$_2$O/MeOAc, then from H_2O/THF, enantiomerically pure **8** (18%).

*(4a*R*,7a*R*)-4,4a,5,7a-Tetrahydrocyclopenta[* d*][1,3]dioxin-2-one* (**2**). A vigorous stream of CO_2 was bubbled through a suspension of **8** (1.50 g, 5.60 mmol) and DBU (2.55 g, 16.8 mmol) in toluene (60 ml). The suspension was immersed in a pre-heated oil bath (90°) and stirred for 50 min (additional toluene was added from time to time). The white precipitate (DBU·HI) was filtered off and washed with Et_2O (2 × 10 ml). Removal of the solvent from the combined filtrate at 90°/100–200 Torr and FC (silica gel (120 g), Et_2O) of the residual dark oil afforded **2** (493 mg, 63%). Colourless oil, solidifying at 4°. M.p. 32.0–33.0°. $[\alpha]_D^{22} = -192$ (*c* = 0.06, MeOH). IR (film): 3060*w*, 2920*m*, 2860*m*, 1755*s*, 1620*m*, 1470*m*, 1445*m*, 1395*s*, 1365*s*, 1250*s*, 1180*s*, 1110*s*, 1030*s*, 980*m*, 930*m*, 900*m*, 835*m*, 780*m*, 720*m*, 680*w*, 605*w*, 460*m*. ^{1}H-NMR ($CDCl_3$): 2.38–2.49 (*m*, 1 H); 2.63–2.75 (*m*, 1 H), 2.92–3.03 (*m*, 1 H); 4.06 (*dd*, *J* = 11.1, 5.9, 1 H); 4.37 (*dd*, *J* = 11.1, 4.4, 1 H); 5.52–5.58 (*m*, 1 H); 5.83–5.89 (*m*, 1 H); 6.13–6.17 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 151.6, 137.5, 128.9, 87.5, 68.3, 35.1, 33.8. MS: 141 (4), 140 (35, M^+), 96 (22), 95 (47), 83 (8), 81 (40), 79 (42), 78 (78), 77 (20), 69 (22), 68 (86), 67 (71), *66* (100), 65 (48), 64 (5), 63 (11), 57 (4), 56 (13), 55 (81), 54 (12), 53 (35), 52 (8), 51 (13), 50 (5), 44 (12); 43 (4), 42 (12), 41 (44), 40 (36), 39 (49), 38 (9), 31 (5), 29 (12), 28 (6), 27 (23), 18 (8).

*[(1*S*,4*R*)-4-(2′-Amino-6′-chloro-9′*H*-purin-9′-yl)cyclopent-2-enyl]methanol* (**9**). A soln. of allylpalladium chloride dimer (57.4 mg, 0.16 mmol) and PPh_3 (165 mg, 0.63 mmol) in THF (5 ml) was stirred under Ar for 1 h. A soln. of 2-amino-6-chloro-1*H*-purine (532 mg, 3.14 mmol) in DMSO (8 ml, flushed with Ar) was added at r.t. and the resulting yellow soln. stirred for 15 min. After cooling to 0°, a soln. of **2** (440 mg, 3.14 mmol) in THF (7 ml, flushed with Ar) was added dropwise within 5 min. After 2 h, the yellow soln. was allowed to warm up to r.t. and the mixture stirred for 46 h at r.t. The solvents were distilled off (80°/10^{-2} Torr), and the residual yellow oil was purified by FC (silica gel (160 g), hexane/AcOEt 1:1 (250 ml) then AcOEt/MeOH 15:1). The white solid was dissolved in CH_2Cl_2 (8 ml), filtered through *Celite*, and the solvent distilled off affording **9** (492 mg, 59%). White solid. A sample was crystallized from H_2O/MeOH. White solid. M.p. 160–162°. $[\alpha]_D^{23} = -95$ (*c* = 0.22, MeOH; [7b]: $[\alpha]_D^{24} = -75$ (*c* = 0.9, MeOH)). IR (KBr; characteristic absorptions): 3600–2600 (br.), 1620*m*, 1575*m*. ^{1}H-NMR ((D$_6$)DMSO): 1.62 (*dt*, *J* = 14.0, 5.5, 1 H); 2.61 (*dt*, *J* = 14.0, 8.8, 1 H); 2.80–2.93 (*m*, 1 H); 3.38 (*s*, *ca.* 6 H, H_2O); 3.44 (*t*, *J* = 5.1, 2 H); 4.74 (*t*, *J* = 5.1, –OH); 5.39–5.50 (*m*, 1 H); 5.85–5.93 (*m*, 1 H); 6.10–6.16 (*m*, 1 H); 6.86–6.95 (*s*, NH_2); 8.02 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 160.2, 154.2, 149.8, 141.6, 139.4, 129.7, 124.1, 64.3, 59.5, 48.2, 34.4. MS: 268 (16), 267 (55, M^+), 266 (43), 265 (76), 264 (5), 249 (5), 248 (8), 247 (13), 237 (28), 236 (22), 235 (47), 234 (28), 230 (6), 211 (11), 210 (9), 209 (32), 208 (7), 199 (5), 198 (17), 197 (13), 196 (6), 183 (5), 174 (5), 173 (12), 172 (52), 171 (71), 170 (76), *169* (100), 168 (20), 144 (6), 143 (5), 141 (11), 135 (26), 134 (60), 133 (19), 117 (7), 115 (6), 114 (6), 108 (9), 107 (24), 106 (10), 97 (17), 96 (23), 95 (19), 92 (16), 86 (5), 81 (6), 80 (17), 79 (37), 78 (9), 77 (21), 69 (7), 68 (10), 67 (35), 66 (28), 65 (22), 55 (8), 54 (8), 53 (10), 43 (12), 41 (20), 40 (5), 39 (10), 31 (12), 28 (9), 18 (6).

*(1′*R*,4′*S*)-2-Amino-1,9-dihydro-9-[4-(hydroxymethyl)]cyclopent-2-enyl]-6*H*-purin-6-one* (*= (−)-Carbovir;* (−)-**1**) [7b]. A suspension of **9** (90 mg, 0.34 mmol) in 0.33M NaOH (4.6 ml) under Ar was heated for 3 h. The resulting clear soln. was allowed to cool to r.t., neutralized (pH *ca.* 7.5) with 0.5M HCl, and H_2O distilled off *in vacuo*. The solid was dissolved in MeOH (10 ml), silica gel (1 g) added, and MeOH evaporated. The powder was then placed on the top of a column (silica gel (5 g)) and chromatographed with CH_2Cl_2/MeOH 9:1: (−)-**1** (59.7 mg, 71%). White solid. M.p. 205–210° (dec.; [7b]: 210–220° (dec.)). $[\alpha]_D^{23} = -65$ (*c* = 0.2, MeOH; [7b]: $[\alpha]_D^{24} = -66$ (*c* = 0.4, MeOH)). IR (KBr; characteristic absorptions): 3600–2600 (br.), 1690*s*, 1635*m*. ^{1}H-NMR ((D$_6$)DMSO): 1.48–1.63 (*m*, 1 H); 2.50–2.65 (*m*, 1 H); 2.77–2.90 (*m*, 1 H); 3.36–3.47 (*m*, 2 H); 3.39 (*s*, H_2O, *ca.* 4 H); 4.69–4.83 (*m*, OH); 5.27–5.38 (*m*, 1 H); 5.80–5.90 (*m*, 1 H); 6.05–6.13 (*m*, 1 H); 6.49 (*s*, NH_2); 7.58 (*s*, 1 H); 10.70 (*s*, NH). ^{13}C-NMR ((D$_6$)DMSO): 157.1, 153.7, 151.0, 138.5, 135.3, 129.8, 116.8, 64.2, 58.7, 47.9, 34.5. MS: 248 (25), 247 (76, M^+), 230 (7), 229 (11), 218 (8), 217 (46), 216 (13), 191 (30), 174 (10), 153 (14), 162 (67), *151* (100), 150 (14), 135 (32), 134 (34), 124 (9), 123 (7), 122 (5), 111 (6), 110 (45), 109 (49), 108 (39), 107 (12), 106 (5), 97 (6), 96 (20), 95 (17), 92 (6), 91 (8), 83 (8), 82 (8), 81 (14), 80 (10), 79 (35), 78 (20), 77 (25), 69 (11), 68 (8), 67 (33), 66 (31), 65 (24), 55 (9), 54 (12), 53 (9), 51 (6), 44 (8), 43 (21), 41 (17), 40 (6), 39 (12), 31 (5), 28 (8), 18 (8).

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