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CHIRAL SYNTHESIS OF (S)-(+)-γ-HYDROXYMETHYL-γ-BUTYROLACTONE

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ABSTRACT

S-(+)-γ-hydroxymethyl-γ-butyrolactone has been synthesized from D-ribonolactone as chiral template.

INTRODUCTION

The importance of optically active 4-hydroxymethylbuten-2-olide[1] **8**, R = H and its protected derivatives[2] as building blocks[3-5] in the synthesis of optically active compounds comes from their high functionality confined in the five-membered ring. The preparation of butenolides can be achieved through several approaches[1,2], these produce in general one particular enantioner.

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Our interest in the synthesis of optically active 4-hydroxymethylbutenolides and related compounds, led us to explore the potential of D-ribonolactone **1** as a latent γ-hydroxymethyl-γ-butyrolactone, through different synthetic pathway to those already published[6-8]. Deoxygenation at both C-2 and C-3 would afford intermediate **8**, from which **11** could be obtained.

RESULTS AND DISCUSSION

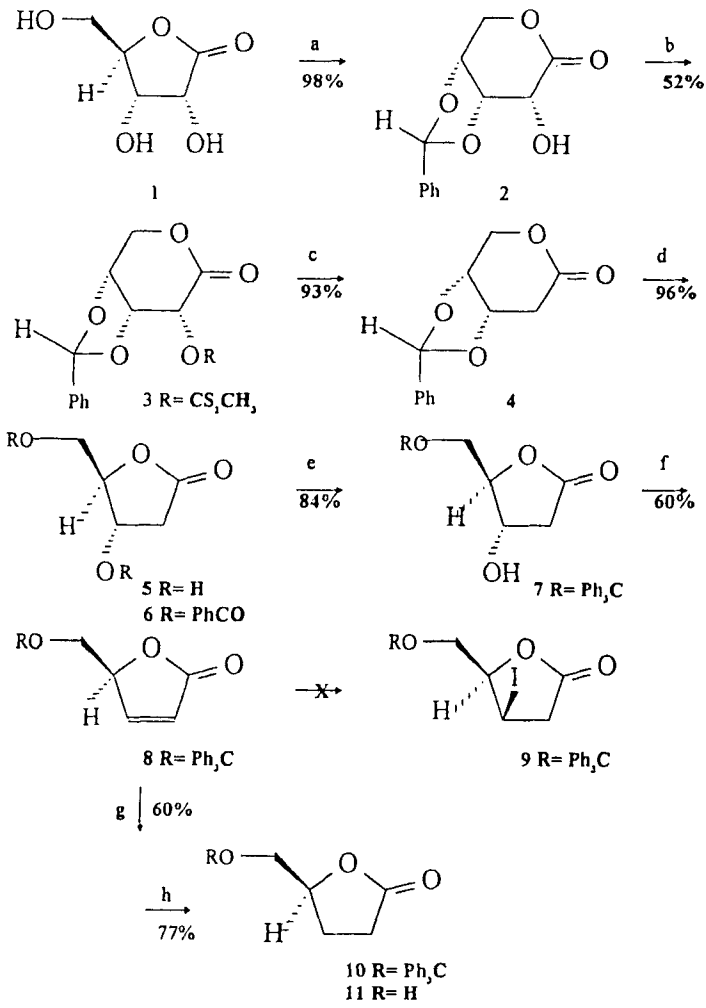
The product of the reaction of D-ribono-1,4-lactone with benzaldehyde and concentrated HCl has been shown by X-ray crystallography of its acetate to be 3,4-0-(R)-benzylidene-D-ribono-1,5-lactone[9]. Molecular mechanics calculations support a boat conformation for this lactone[10]. Therefore treatment of lactone **1** with benzaldehyde and concentrated HCl gave in high yield the crystalline benzylidine derivative[10] **2**, scheme, previously described as a 3,5-acetal[11-13]. Attempts to obtain xanthate **3**, as reported by Barton and Mc Combie[14], resulted in low yields. The reaction of **2** with carbon disulfide, in the presence of sodium hydride in dry N,N-dimethylformamide at -60°C, followed by alkylation with methyl iodide, gave xanthate **3** in reasonable yield[11]. Spectroscopic data for this compound is consistent with published data[11,12]. Deoxygenation of **3** with tri-n-butyltin hydride in the presence of initiator α,α'-azobisisobutyronitrile gave **4**. Compounds **2**, **3** and **4** show acetal proton chemical shifts in the range δ 5.76-5.83 as expected for 1,3-dioxolanes, supporting an endo-phenyl group assignment[13,15-18]. Deprotection of the 2-deoxy compound **4** with 50% aqueous trifluoroacetic acid in chloroform at 70°C for 10 h gave **5** which

was characterized as the solid dibenzoyl derivative[19] **6**. Compound **5** was readily converted into the 5-O-tritylether **7**. Attempted conversion of **7** into the 3-iodo-lactone **9**, by treatment with diethylazodicarboxylate, triphenylphosphine and methyl iodide[20], as a suitable intermediate for reductive dehalogenation, afforded butenolide **8**, whose spectral properties were in agreement with those reported in the literature[3,21]. The favourable position for elimination of the 3-alkoxytriphenylphosphonium salt intermediate of **7** was demonstrated by the facility and high yield by which the elimination occurred when **7** was subjected to the same reaction in the absence of methyl iodide[22]. The large steric effect of the trityl group hinders nucleophilic attack at C-3 of triphenylphosphonium salt of **7**, which undergoes elimination instead of substitution. Catalytic hydrogenation of **8** led to a convenient production of compound **10**. Removal of the trityl ether of **10** with p-toluenesulfonic acid in methanol gave the desired lactone **11**, whose specific rotation is in good agreement with that described by Camps[21] for this compound.

In conclusion, a method is presented for the synthesis of chiral(S)-(+)-γ-hydroxymethyl-γ-butyrolactone, in 8 steps which uses D-(+)-Ribonolactone as chiral template.

EXPERIMENTAL

Routine gas liquid chromatography (gc) analyses were run on a Varian 1400 flame ionization gas chromatograph, with packed glass columns containing 3% OV-17 on Chromosorb W. Analytical (0.25 mm) thin layer chromatography (tlc) plates were prepared from silica gel GF_{254} (E.



Scheme. Reagents and conditions: a) PhCHO, HCl, r.t.; b) NaH, -60°C, 5h, CS_2, -30, -10°C, 2h, MeI, r.t., 30 min; c) n-Bu_3SnH, AIBN, toluene, reflux; d) CF_3CO_2H, H_2O, $CHCl_3$, 70°C, 10h; e) Ph_3CCl, pyridine, r.t., 4h; f) Ph_3P, DEAD, MeI, benzene, r.t., 24h; g) H_2, 5% Pd/EtOH; h) p-TsOH, MeOH, r.t., 5h.

Merck, Darmstadt). Column chromatography was performed by the flash chromatography method[23], on silica gel Kieselgel 60, (40-63 μm. E. Merck, Darmstadt). Chromatographic solvents were distilled before use. Low boiling (30°-60°C) petroleum ether was used for chromatography. IR spectra were determined on a Perkin-Elmer 599B spectrophotometer. Samples were run as neat films on NaCl plates, as KBr pellets or as solutions in a cell with NaCl windows. ^{1}H-NMR were recorded on a Varian EM-360 (60 MHz) or a Bruker 400 (400 MHz) NMR spectrometer. Chemical shifts are reported in δ units, referenced to an internal standard (TMS) or to an internal (deuterium) lock signal. Splitting patterns are described as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and combinations thereof. Coupling constants are reported in Hertz (Hz). Low resolution mass spectra were obtained with direct insertion probe or gc-ms samples on a Hewlett-Packard 5985 B coupled gas chromatograph-mass spectrometer. All samples were run using electron impact ionization (70 eV). Relative abundances are expressed as percentages of the abundance of the base peak. Elemental analyses were carried out on a Perkin Elmer Model 240 elemental analyzer. Optical rotations were measured with a Rudolph Model 70 polarimeter, using either a 1 dm x 4 mm id. sample cell or a 1 dm x 1.5 mm i.d. sample cell. Concentrations are reported in g/100 mL solvent. All reactions requiring anhydrous and/or oxygen-free conditions were run under a positive pressure of nitrogen or argon.

3,4-O-(R)-Benzylidene-D-ribono-1,5-lactone[11] (2).

A mixture of D-(+)-ribonolactone[8] **1** (30 g, 0.20 mol), freshly distilled benzaldehyde 300 mL and concentrated hydrochloric acid 30 mL was

stirred at ambient temperature for 7 h. Ether 350 mL was added to precipitate the product, which was collected by filtration. The crude product was washed successively with 5% aqueous sodium bicarbonate 100 mL, water 100 mL and petroleum ether 200 mL. The white product was dried (P_2O_5) and recrystallized from acetone-petroleum ether to afford **2** as white needles (47 g, 98%). m.p. = 234-235°C, $[\alpha]_D^{23}$ = -171° (C 2.70, DMF). Lit.[8], m.p. = 233-235.5°C, $[\alpha]_D^{23}$ = -174.1° (C 2.26, DMF). IR(KBr): ν = 3430, 3380, 2935, 2890, 1750, 1460, 1410, 1180, 1140, 1078, 1055, 1045, 1010, 952, 770, 720 cm^{-1}. ^{1}H-NMR (acetone-d_6):

δ = 4.44 (d, 1H, H_5, $J_{5,5'}$ = 13.5), 4.48 (d, 1H, OH, $J_{2\text{-}OH,2}$ = 7, D_2O exchangeable), 4.52 (dd, 1H, $H_{5'}$, $J_{5,5'}$ = 13.5, $J_{4,5'}$ = 3.25), 4.7 (dd, 1H, H_2, $J_{2\text{-}OH,2}$ = 7, $J_{2,3}$ = 3.25), 4.75 (dq, 1H, H_3, $J_{3,4}$ = 8, $J_{2,3}$ = 3.25, $J_{3,5}$ = 1), 4,85 (ddd, 1H, H_4, $J_{3,4}$ = 8, $J_{4,5'}$ = 3.25, $J_{4,5}$ = 1.5), 5.8 (s, 1H, øCH-), 7.3-7.6 (m, 5H, C_6H_5-). MS: m/z (%) = 236 (31), 235 (50), 218 (1), 130 (54), 105 (93), 91 (30), 89 (20), 79 (55), 78 (48), 77 (100).

$C_{12}H_{12}O$ (236.22)

Calcd	C 61.02	H 5.12
Found	C 61.21	H 5.03

3,4-0-(R)-Benzylidine-2-0-[(methylthio)-thiocarbonyl]-D-ribono-1,5-lactone (3).

To a stirred solution of **2** (30 g, 0.127 mol) in dry DMF 200 mL, kept at 60°C, was added NaH (7.30 g, 0.152 mol, 50% dispersion in mineral oil) and the stirring was continued at -60°C for 5 h. CS_2 (11.6 g, 0.152 mol) was added and the stirring continued for a further 2 h between -30 to

-10°C. Methyl iodide (21.6 g, 0.152 mol) was added at -10°C and the reaction was allowed to reach room temperature in 30 min. The reaction mixture was then diluted with water 200 mL. The aqueous layer was extracted with methylene chloride (4 x 50 mL), washed with a saturated sodium chloride solution (150 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was crystallized twice from anhydrous ethanol to give crystalline **3** (21.5 g, 52%); m.p. 147-148.5°C, $[\alpha]_D^{23}$ = -317.0° (C 1.1, $CHCl_3$). Lit.[8], m.p. = 145-146°C, $[\alpha]_D^{23}$ = -314.3° (C 2.0, $CHCl_3$). IR ($CHCl_3$): ν = 2995, 2890, 1790, 1450, 1410, 1390, 1190, 1160, 1120, 1085 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 2.65 (s, 3H, CH_3S), 4.45 (dd, 1H, H_5, $J_{5,5'}$ = 13.5, $J_{4,5}$ = 1.8), 4.65 (d, 1H, $H_{5'}$, $J_{5,5'}$ = 13.5), 4.77 (qdd, 1H, H_3, $J_{3,4}$ = 8, $J_{2,3}$ = 2, $J_{3,5}$ = 0.8), 4.99 (ddd, 1H, H_4, $J_{3,4}$ = 8, $J_{4,5}$ = 3, $J_{4,5'}$ = 0.8), 5.83 (s, 1H, øCH), 6.47 (d, 1H, H_2, $J_{2,3}$ = 3), 7.35 - 7.55 (m, 5H, C_6H_5-); MS: m/z(%) = 328 (4), 327 (4), 326 (23), 279 (8), 235 (8), 233 (10), 219 (15), 105 (82), 91 (100), 89 (16), 79 (56), 78 (30), 77 (85).

$C_{14}H_{14}O_5S_2$ (326.29)

Calcd	C 51.52	H 4.32
Found	C 51.62	H 4.22

3,4-0-(R)-Benzylidene-2-deoxy-D-erythro-ribono-1,5-lactone (4).

To a solution of xanthate **3** (7.6 g, 0.023 mol) in dry toluene 100 mL was added tri-*n*-butyltin hydride (13.6 g, 0.047 mol) and AIBN (0.5 g) under an argon atmosphere. The mixture was refluxed under argon overnight. The solution was cooled to room temperature and the insoluble product

was collected by filtration. Recrystallization from toluene afforded **4** (5.6 g, 93%) as needles; m.p. = 139-141°C, $[\alpha]_D^{24}$ = -175° (C 0.5, $CHCl_3$). Lit.[8,12], m.p. = 139-139.5°C, $[\alpha]_D$ = -172.3° (C 1.7, $CHCl_3$). IR (KBr): ν = 2940, 2880, 1745, 1413, 1395, 1348, 1270, 1160, 1102, 1065, 1048, 1030, 975, 785, 762 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 2.65 (dd, 1H, H_2, $J_{2,2'}$ = 16, $J_{2,3}$ = 3.8), 3.06 (dd, 1H, $H_{2'}$, $J_{2,2'}$ = 16, $J_{2',3}$ = 2.5), 4.24 (dd, 1H, H_5, $J_{5,5'}$ = 13, $J_{4,5}$ = 2), 4.58 (ddd, 1H, H_4, $J_{3,4}$ = 8, $J_{4,5}$ = 2, $J_{4,5'}$ = 1.5), 4.60 (dd, 1H, $H_{5'}$, $J_{5,5'}$ = 13, $J_{4,5'}$ = 1.5), 4.80 (ddd, 1H, H_3, $J_{3,4}$ = 8, $J_{2,3}$ = 3.8, $J_{2',3}$ = 2.5), 5.76 (s, 1H, øCH), 7.35-7.55 (m, 5H, C_6H_5); MS: m/z (%) = 220 (38), 219 (100), 105 (97), 91 (16), 79 (25), 78 (63), 77 (73), 51 (22).

$C_{12}H_{24}O_4$ (232.32)

Calcd	C 65.45	H 5.49
Found	C 65.46	H 5.60

2-Deoxy-D-erythro-pentono-1,4-lactone (5).

The 2-deoxy compound **4** (5.6 g, 0.026 mol) was deprotected with 50% aqueous trifluoroacetic acid 20 mL in chloroform 20 mL at 70°C for 10 h. The aqueous layer was separated and the organic layer was extracted with water (2 x 10 mL). The combined water extracts were evaporated to dryness and the residue was evaporated with toluene (5 x 10 mL) to give **5** (3.3 g, 96%) as a viscous, colourless oil. The product, which was pure by tlc, was characterized as the di-benzoyl derivative **6**, and was used without further purification.

3,5-di-0-benzoyl-2-deoxy-D-erythro-pentono-1,4-lactone (6).

Compound **6** was prepared in 40% yield, as described by Bock, Lundt

and Pedersen; m.p. = 98-100°C, $[\alpha]_D^{23}$ = +19.3° (C 3.0, ethyl acetate). Lit.[19], m.p. = 99-100°C, $[\alpha]_D^{25}$ = +19°C (C 3.3, ethyl acetate).

5-0-Trityl-2-deoxy-D-erythro-pentono-1,4-lactone (7).

To a stirred solution of **5** (1.26 g, 9.54 mmol) in pyridine 20 mL, was added freshly-prepared triphenylmethyl chloride (3.2 g, 11.45 mmol) at room temperature and stirring was continued for 4 h. Most of the pyridine was evaporated at 50-60°C and the residue was dissolved in dichloromethane 40 mL, washed thoroughly with brine (5 x 20 mL) and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure left a colourless oil which, after column chromatography with ether/petroleum ether (1:1), afforded **7** as a crystalline solid (3g, 84%); m.p. = 131-133°C, $[\alpha]_D^{23}$ = +336° (C 4.25, methanol). IR (KBr): ν = 3560, 3520, 3100, 3070, 3040, 2950, 2930, 2888, 2820, 1780, 1600, 1490, 1455, 1220, 1200, 1160, 1100 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 1.23 (d, 1H, OH), 2.5 (dd, 1H, H_2, $J_{2,2'}$ = 18, $J_{2,3}$ = 6.5), 3.06 (dd, 1H, H_5, $J_{5,5'}$ = 11, $J_{4,5}$ = 3), 3.2 (dd, 1H, $H_{2'}$, $J_{2,2'}$ = 18, $J_{2',3}$ = 2.75), 3.53 (dd, 1H, $H_{5'}$, $J_{5,5'}$ = 11, $J_{4,5'}$ = 3.75), 4.4-4.5 (m, 2H, H_3, H_4), 7.2-7.5 (m, 15H, C_6H_5); MS: m/z (%) = 375 (12), 357 (1), 259 (19), 258 (23), 243 (78), 242 (8), 166 (15), 165 (100), 115 (13), 105 (38), 91 (8), 79 (5), 78 (10), 77 (25).

$C_{24}H_{22}O_4$ (374.44)

Calcd	C 76.99	H 5.92
Found	C 76.70	H 6.17

(S)-5-Trityloxymethyl-(5H)-furan-2-one (8).

To a stirred solution of **7** (1.5 g, 4 mmol) and tryphenylphosphine (1.3 g,

4.8 mmol) in benzene 20 mL under argon was added diethyl azodicarboxylate (0.83 g, 4.8 mmol) in benzene (2 mL) and the mixture was stirred at room temperature for 24 h. The solvent was then removed under reduced pressure, leaving a yellow syrup, and was replaced by toluene 20 mL. Methyl iodide (0.68 g, 4.8 mmol) was added and, after 30 min at room temperature, the mixture was refluxed for 24 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel by eluting with methylene chloride, yielding **8** (0.87 g, 60%), which solidified upon standing; m.p. = 155-157°C, $[\alpha]_D^{23}$ = -106° (C 3.01, $CHCl_3$). Lit.[24], m.p. = 152-154°C, $[\alpha]_D^{20}$ = -95.1° (C 3.42, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 3.41 (dd, 1H, H_5, $J_{5,5'}$ = 13.5, $J_{4,5}$ = 5), 3.42 (dd, 1H, $H_{5'}$, $J_{5,5'}$ = 13.5, $J_{4,5'}$ = 5), 5.1 (ttd, 1H, H_4, $J_{4,5}$ = 5, $J_{4,5'}$ = 5, $J_{3,4}$ = 2), 6.2 (dd, 1H, H_2, $J_{2,3}$ = 6, $J_{2,4}$ = 2), 7.2-7.5 (m, 16H, C_6H_5, H_3).

(S)-(+)-δ-Trityloxy-γ-valerolactone (10).

Catalytic hydrogenation of (S)-5-trityloxymethyl-(5H)-furan-2-one[24] **8** (3.1 g, 8.7 mmol) in ethanol 100 mL at room temperature and atmospheric pressure (1013 mbars) with 5% palladium on charcoal (310 mg) for 12 h gave, upon filtration and evaporation of the solvent, crystalline **10**. Two recrystallizations of **10** from boiling methanol gave the lactone derivative (1.86 g, 60%); m.p. = 146-148°C, $[\alpha]_D^{26}$ = +24.6° (C 2.36, $CHCl_3$), Lit.[25], m.p. = 153-154°C, $[\alpha]_D$ = +26.6° (C 1, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ = 2.05 (m, 1H, H_2), 2.25 (m, 1H, $H_{2'}$), 2.52 (ddd, 1H, H_3, $J_{3,3'}$ = 18, $J_{2',3'}$ = 10, $J_{2,3'}$ = 7), 2.70 (ddd, 1H, $H_{3'}$, $J_{3,3'}$ = 18, $J_{2',3'}$ = 10, $J_{2,3'}$ = 7), 3.17 (dd, 1H, H_5, $J_{5,5'}$ = 10.5, $J_{4,5}$ = 4.5), 3.43 (dd, 1H, $H_{5'}$,

$J_{5,5'}$ = 10.5, $J_{4,5'}$ = 3.5), 4.65 (m, 1H, H_4), 7.2-7.5 (m, 15H, C_6H_5).

$C_{24}H_{22}O_3$ (358.44)

Calcd	C 80.26	H 6.24
Found	C 80.01	H 6.29

(S)-(+)-δ-Hydroxy-γ-valerolactone (11)

Detritylation of **10** (2 g, 5.6 mmol) was accomplished with p-toluenesulfonic acid (200 mg) in methanol (20 mL) at room temperature for 5 h. The reaction mixture was diluted with water 20 mL and extracted with methylene chloride (3 x 20 mL). The combined organic layers were washed with brine and dried (Na_2SO_4). Column chromatography with 7% ethanol in chloroform as eluant gave **11** (500 mg, 77%) as a colorless oil; $[\alpha]_D^{25}$ = +31.8° (C 8.35, ethanol). Lit.[26], $[\alpha]_D^{26}$ = +31.3° (C 2.92, ethanol). IR (neat film): ν = 3450, 1770 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 2.15 (m, 1H, H_3), 2.26 (m, 1H, $H_{3'}$, 2.45 (t, broad, 1H, OH, D_2O exchangeable), 2.5-2.7 (m, 2H, H_2, $H_{2'}$), 3.65 (ddd, 1H, H_5, $J_{5,5'}$ = 12.5, $J_{5,5\text{-OH}}$ = 6, $J_{4,5}$ = 4.5), 3.92 (ddd, 1H, $H_{5'}$, $J_{5,5'}$ = 12.5, $J_{5',5\text{-OH}}$ = 6, $J_{4,5'}$ = 2.75), 4.65 (dddd, 1H, H_4, $J_{3',4}$ = 7, $J_{3,4'}$ = 7, $J_{4,5}$ = 4.5, $J_{4,5'}$ = 2.75); MS: m/z (%) = 116 (1), 85 (100), 57 (32), 56 (12).

$C_5H_8O_3$ (116.12)

Calcd	C 51.73	H 6.95
Found	C 51.51	H 7.21

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