Supporting informations

An Unexpected Stereochemistry in the "Lithium Salt Catalyzed" Ring Expansion of non Racemic Oxaspiropentanes. Formal Synthesis of (-)-(4*R*,5*R*)-Muricatacin and the Pheromone (*R*)-Japonilure.

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(2*R*)-2-[(4*S*)-2,2-Dimethyl-[1,3]dioxolan-4-yl-cyclobutanone. (*R,S*)-3. A solution of the oxaspiropentane **(*R,R*)-2** (200 mg**,** 1.2 mmol), with a catalytic amount (1%) of LiI in CH_2Cl_2 (10mL) was refluxed for 5 h. The solution after cooling and filtration was evaporated under vacuum to give the crude cyclobutanone which was purified by flash chromatography (silica gel, diethyl ether / light petroleum, 1/1). Colourless oil. Yield 81 %. $[\alpha]_D^{23}$ = + 5.38 (c, 0.14, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: 1.35 (s, 6H), 1.91-2.22 (m, 2H), 2.99 (t, 2H, *J* = 8.4 Hz), 3.39-3.46 (m, 1H), 3.81 (t, 1H, *J* = 8.1 Hz)), 3.91 (dd, 1H, *J* = 8.1 Hz and *J* = 6 Hz), 4.15-4.19 (m, 1H). ^{13}C NMR δ: 13.53, 25.56, 26.12, 45.32, 61.12, 66.50, 74.24, 109.15, 208.56. IR (neat, cm^{-1}): 1780. MS m/z: 155 (M^+ -15 (2)), 113 (17), 95 (4), 84 (26), 72(25), 43 100).. Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.64; H, 8.24**.**

(2*S*)-2-[(4*S*)-2,2-Dimethyl-[1,3]dioxolan-4-yl-cyclobutanone. (*S,S*)-3. A solution of the oxaspiropentane **(*S,R*)-2** (200 mg**,** 1.2 mmol), with $LiClO_4$ (254 mg, 2.4 mmol) in benzene (10 mL) was refluxed for 24 h. The solution after cooling and filtration, was evaporated under vacuum to give a 10 : 90 mixture of **(*R,S*)-3** and **(*S,S*)-3**. Repeated chromatographies (silica gel, diethyl ether / light petroleum 1/1) gave a pure sample of **(*S,S*)-3** as a colourless oil. Yield 85 %. $[\alpha]_D^{23}$ = -6.55 (c, 0.61, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: 1.33 (s, 3H), 1.35 (s, 3H), 2.08-2.14 (m, 2H), 294-3.03 (m, 2H), 3.43-3.47 (m, 1H), 3.61 (t, 1H, *J* = 7.8 Hz), 4.05 (dd, 1H, *J* = 6.6 Hz and *J* = 7.8 Hz), 4.37 (q, 1H, *J* = 6.6 Hz). ^{13}C NMR δ: 12.77, 25.34, 26.46, 45.61, 62.53, 67.43, 73.32, 109.21, 208.57. IR (neat, cm^{-1}): 1780. MS m/z: 155 (M^+- 15 (5)), 113. (25), 95 (4), 84 (26), 72 (25), 43 (100).. Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.44; H, 8.19.

(4'*R*,5*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,5-dihydro-2(3H)-furanone. (*R,R*)-4. To a stirred solution of the cyclobutanone **(*R,S*)-3** (1g, 5.9 mmol) in CH_2Cl_2 (30mL) at 0°C was added 1.44 g of MCPBA (5.9 mmol). The resulting white suspension was stirred at room temperature for 2 h and then diluted with CH_2Cl_2, filtered and washed with 10 % $NaHCO_3$ solution. The organic solution was dried and concentrated under vacuum to give the crude lactone which was purified by column chromatography (silica gel, diethyl ether / light petroleum, 3/1). Colourless oil. Yield 68 %. $[\alpha]_D^{24}$ = -18 (c 7.71, $CHCl_3$). Lit[37]: $[\alpha]_D^{19}$ = -20 (c 1.0, $CHCl_3$).

(4*R*,5*R*)-5,6-Dihydroxy-4-hexanolide (5). A mixture of the γ-lactone **(*R,R*)-4** (200 mg, 1.07 mmol) and $FeCl_3$-SiO_2 reagent (21 mg) in CH_2Cl_2 (12 mL) was stirred at room temperature for 48 h. Filtration of the organic layer and evaporation of the solvent under vacuum left a residue that was purified by column chromatography on silica gel (dichloromethane/methanol, 10/1) to give the product **(*R,R*)-5**. Colourless oil. Yield 96 %.$[\alpha]_D^{23}$ = - 38.62 (c, 1.86, CH_3OH). Lit.[26a] $[\alpha]_D$ = - 43.38 (c 0.9, CH_2Cl_2).

(1*S*,4*R*,5*S*)-1-Methoxy-2-oxabicyclo[3.2.0]-2-eptanol (8). A solution of **(*R,S*)-3** (1 g**,** 6.2 mmol) in methanol with a catalytic amount of p-toluensulfonic acid was refluxed for 3 h. The solution was then washed with 10 % $NaHCO_3$, dried and evaporated. The crude product was chromatographed on silica gel (diethyl ether / light petroleum, 3/1). Colourless oil. Yield 68 %. $[\alpha]_D^{29}$ = + 14 (c 7.93, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 1.66-1.89 (m, 2H), 2.08-2-36 (m, 3H, 1H exchange with D_2O), 2.90 (q, 1H, *J* = 7.2 Hz), 3.22 (s, 3H), 3.76 (dd,1H, *J* = 6 Hz and *J* = 9.3 Hz), 4.19 (dd, 1H, *J* = 6 Hz and *J* = 9.3 Hz), 4.55 (q, 1H, *J* = 7.2Hz). ^{13}C NMR ($CDCl_3$) δ: 8.76, 30.19, 45.92, 49.97, 71.45, 73.86, 109.57. IR (neat, cm^{-1}): 3430. MS m/z: 145 (M^+-15 (6)), 127 (38), 113 (76), 99(100). Anal. Calcd. For $C_7H_{12}O_3$: C, 58.33; H, 8.33. Found: C, 57.93, H, 8.38.

(5*R*)-5-Hydroxymethyl-2-oxotetrahydrofuran (10). To a stirred suspension of silica gel (4g) in CH_2Cl_2 (32 mL) a solution of $NaIO_4$ (428 mg, 2 mmol) in water (4 mL) was added dropwise at room temperature. Then a solution of **(*R,R*)-5** (300 mg, 2 mmol) in CH_2Cl_2 (4 mL) was added dropwise to the suspension at 0°C. The mixture was stirred for 30 minutes at same temperature and then diluted with CH_2Cl_2 and the produced solid was filtered off. The organic solvent was dried and concentrated under vacuum to give the crude aldehyde **9** which was used immediately for the next step.

$NaBH_4$ (64 mg, 1.7 mmol) was added in small portions to an ice cooled solution of crude **9** (220 mg, 1.7 mmol) in CH_3OH (10 mL) and the mixture was stirred for 10 min. Then the reaction was quenched with sat. $KHSO_4$ and evaporated under vacuum to remove CH_3OH. The residue was extracted with THF and the organic layer dried and concentrated to afford the crude alcohol **10** which was purified by column chromatography (silica gel, CH_2Cl_2 / CH_3OH, 20/1). Colourless oil. Yield 40 % for the two steps. $[\alpha]_D^{24}$ = -5.9 (c 1.5, EtOH). IR, ^{1}H NMR and ^{13}C NMR spectra were in good agreement with those reported in ref 40 for this compound.