Pergamon

Tetrahedron: *Asymmetry* 11 (2000) 765–771

TETRAHEDRON: *ASYMMETRY*

Two approaches to the enantioselective synthesis of (4*R*)-(−)-4-hydroxymethyl-4-thiobutyro-1,4-lactone

Patricia A. Zunszain and Oscar Varela *

CIHIDECAR-CONICET, Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina

Received 25 October 1999; accepted 24 November 1999

Abstract

Enantiomerically pure (4*R*)-4-hydroxymethyl-4-thiobutyro-1,4-lactone [(5*R*)-dihydro-5-(hydroxymethyl)-2(3*H*)-thiophenone (**12**)] and derivatives were synthesized by two enantiospecific sequences employing D-ribono-1,4-lactone (**1**) and L-glutamic acid (**6**) as chiral templates. The key step in the first approach was the SmI_2-promoted 2,3-deoxygenation of a 4-thio-L-lyxono-1,4-lactone derivative, prepared from **1**. The other strategy, which starts from **6**, involves the (5*S*)-dihydro-5-(*p*-tolylsulfonyloxymethyl)-2-(3*H*)-furanone (**8**) as chiral precursor. This was converted into a 4,5-thiirane derivative via the corresponding 4,5-epoxide. Regioselective opening of the thiirane ring by acetate followed by *O*-deacetylation gave **12** (40% overall yield from **8**). © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

In the last two decades a number of natural products containing a thiolactone ring have been isolated.[1–4] Many of them such as thiolactomycin,[1] thiotetromycin,[2] thiocoumarins,[3] and other thiolactones[4] displayed interesting biological activities. Small ring thiolactones have been prepared by addition of thioacetic acid to unsaturated, straight chain acids,[5] and from bismetallated derivatives of thioacids and carbonyl compounds.[6] Also, the reaction of *S*-(4-alkenyl)-dithiocarbonates with tri-*n*-butyltin hydride afforded 1,4-thiolactones.[7] More recently, saturated thiolactones have been prepared from ω-halo acid chlorides, by a sulfur transfer reaction mediated by benzyltriethylammonium tetrathiomolybdate,[8] and ω-carboxyacylsilanes have been used as precursors of unsaturated silylated thiolactones.[9] Also, activated carboxythiolactones have been synthesized as small molecules useful for the preparation of peptidil immunogen constructs.[10] Despite the importance of thiolactones, relatively little attention has been given to their synthesis in enantiomerically pure forms.[11,12] For example,

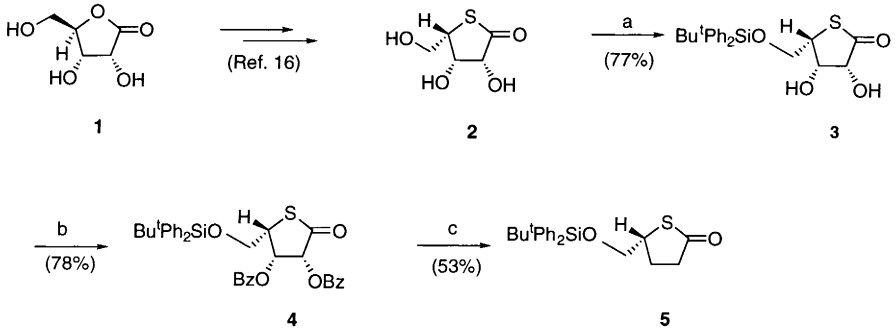
* Corresponding author. E-mail: varela@qo.fcen.uba.ar

0957-4166/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0957-4166(99)00568-6

thioascorbic acid,[13] thiolactomycin,[14] and the anticonvulsant agent thiolosigamone,[15] have been obtained as racemates. We considered that thiolactones having a stereocenter at C-4 as controlling element of asymmetry would be useful building blocks for the synthesis of natural products and their sulfur containing analogs. Thus, we have already reported a convenient procedure for the synthesis of optically pure aldopentono-1,4-thiolactones.[16] In connection with these studies and others on the synthesis and reactivity of 4-thiosugars,[16–21] we wish to report here two sequences for the preparation of (4*R*)-(−)-4-hydroxymethyl-4-thiobutyro-1,4-lactone (**12**) and derivatives, employing alternatively D-ribono-1,4-lactone (**1**) or L-glutamic acid (**6**) as chiral templates.

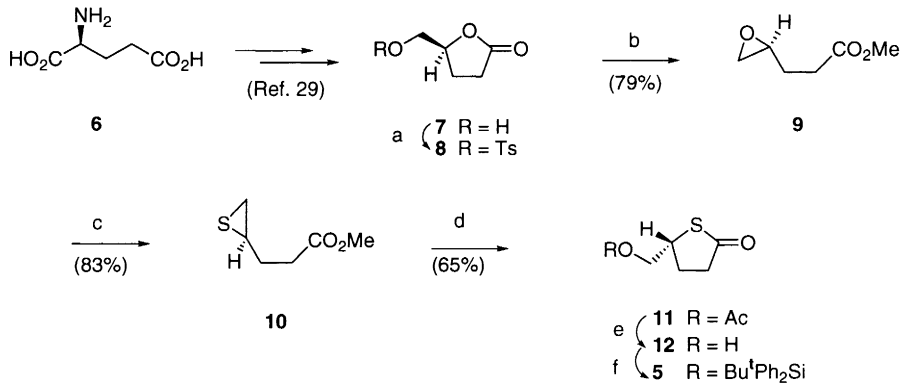
2. Results and discussion

4-Thio-L-lyxono-1,4-lactone (**2**) constitutes a suitable precursor for the synthesis of (4*R*)-4-hydroxymethyl-4-thiobutyro-1,4-lactone (**12**). Compound **2** was readily prepared,[16] and in good yield, starting from D-ribono-1,4-lactone (**1**). α,β-Deoxygenation of **2** would lead to the desired dideoxythiolactone **5**. Samarium iodide (SmI_2) has been successfully employed for the deoxygenation and unsaturation of common aldonolactone derivatives. Inanaga and co-workers[22] described an easy access to 2-deoxysugar lactones by SmI_2-promoted deacetoxylation of per-*O*-acetyl aldonolactone derivatives. Hanessian et al.[23] employed SmI_2 in THF for the 2,3-unsaturation of per-*O*-benzoyl derivatives of aldonolactones. Similarly, we have observed that 5-*O*-silyl derivatives of 2,3-di-*O*-acyl-D-ribonolactone reacted with SmI_2–THF to give the corresponding butenolides.[24] Such butenolides could be readily hydrogenated to the corresponding 2,3-dideoxylactone derivatives, or they might even undergo the SmI_2-induced reduction of analogous α,β-unsaturated carbonyl compounds.[25] This reaction takes place in the presence of *t*-butanol–*N*,*N*-dimethylacetamide[26] or just hexamethylphosphoramide.[27] In order to apply these procedures to the synthesis of **5**, 2,3-di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-4-thio-L-lyxono-1,4-lactone (**4**) was prepared (Scheme 1). Treatment of **2** with 1.1 molar equivalent of *t*-butylchlorodiphenylsilane in DMF, and in the presence of imidazole, selectively afforded the 5-*O*-silyl derivative **3** in 77% yield. Conventional benzoylation of **3** gave the dibenzoate **4**, which was treated with a freshly prepared solution of SmI_2 in THF,[28] under a variety of conditions. The crude products were monitored by ^1H NMR, and it was observed that the 4-thiobutenolide was accompanied by variable proportions of the dideoxythiolactone **5**. When the reaction was performed in the presence of *t*-butanol as proton source, no thiobutenolide was formed and compound **5** was isolated by column chromatography in 53% yield.



Scheme 1. (a) Bu^{t}Ph$_2$SiCl (1.1 molar equiv.), $C_3H_4N_2$, DMF; (b) PhCOCl (BzCl), C_5H_5N; (c) 0.1 M SmI_2 (3 molar equiv.), THF, 0°C, 5 min; 0.1 M SmI_2 (2 molar equiv.), THF, Bu^{t}OH (2.5 molar equiv.), 0→25°C, 2 h

A more direct, and higher yielding, sequence for the synthesis of the 4-thiolactone was attempted, employing, in this case, L-glutamic acid (**6**) as chiral template (Scheme 2). Nitrous acid deamination of **6** afforded the (4*S*)-(+)-4-carboxy-1,4-butyrolactone, which was reduced with borane in THF to give **7**.[29] Tosylation of the free HO group of **7** with tosyl chloride in dry chloroform containing about 2 molar equivalents of pyridine[30] gave the tosylate **8** (83% yield from **7**). On treatment with sodium methoxide in methanol, compound **8** underwent opening of the lactone ring by methanolysis, followed by nucleophilic attack of the resulting C-4 alkoxide to C-5, with displacement of the tosylate, affording the oxirane **9**. The formation of the oxirane ring was evidenced by the spectral data of **9**. Its ^{13}C NMR spectrum showed a strong upfield shifting (> 20 ppm) for the signals of C-4 and C-5, which are now incorporated within the three-membered oxirane ring, relative to the same signals of **8**. Reaction of **9** with thiourea in methanol produced the replacement of the ring oxygen atom by sulfur, to give 83% yield of the thiirane having inverted configuration at C-4. The ^{13}C NMR spectrum of **10** showed that the signals of the carbons involved in the thiirane ring (C-4 and C-5) underwent a further upfield displacement (≈20 ppm).



Scheme 2. (a) TsCl (1.5 molar equiv.), C_5H_5N (2 molar equiv.), $CHCl_3$, 0°C, 12 h (83%); (b) NaOMe, MeOH, 25°C, 50 min; (c) $(NH_2)_2CS$ (2 molar equiv.), MeOH, 25°C, 72 h; (d) KOAc (10 molar equiv.), 1:1 DMF:AcOH, reflux temp, 18 h; (e) 2:1 THF:6% aq. HCl, 35°C, 16 h (92%); (f) Bu^tPh_2SiCl (1.1 molar equiv.), $C_3H_4N_2$, DMF (90%)

In order to promote the thiolactonization, compound **10** was dissolved in a mixture of KOAc in AcOH−DMF, and heated at the reflux temperature. Under these conditions, opening of the thiirane ring took place by regioselective nucleophilic attack of the acetate ion to C-5, with simultaneous thiolactonization, to give **11** in 65% yield. Removal of the acetyl group of **11** by acid hydrolysis afforded the free (4*R*)-4-hydroxymethyl-4-thiobutyrolactone (**12**) in 92% yield. The ^{13}C NMR spectrum of **12** showed the signal characteristic of a thiolactone carbonyl at 208.7 ppm, which was strongly shifted downfield with respect to that of the lactone carbonyl of **7**. Conversely, the C-4 resonance of **12** showed an intense upfield shifting relative to the same signal in **7**. Silylation of **12** was performed as described for **2**, affording compound **5**, which showed the same spectral and physical properties as the product previously synthesized from **1**.

In summary, we describe herein two alternative routes for the enantiospecific synthesis of (4*R*)-4-hydroxymethyl-4-thiobutyro-1,4-lactone (**12**) and derivatives. The sequence that starts from L-glutamic acid (**6**) was simple, direct and efficient, as **12** was obtained in about 40% yield from **8**. Furthermore, the enantiomer of **12**, which possesses opposite configuration at C-4, could be prepared similarly starting from 4-thio-D-ribono-1,4-lactone[16] or from D-glutamic acid.

3. Experimental

3.1. General methods

Solvents were dried and purified by appropriate standard procedures. Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.2 mm silica gel 60 F_{254} (Merck) aluminum supported plates. Detection was effected by exposure to UV light or charring with 10% H_2SO_4 (v/v) in EtOH. Column chromatography was performed with silica gel 60 (230–400 mesh, Merck). Optical rotations were measured with a Perkin–Elmer 343 polarimeter at 25°C. Nuclear magnetic resonance (NMR) were recorded on a Bruker AC 200 spectrometer (^{1}H at 200 MHz, ^{13}C at 50 MHz) in $CDCl_3$ with TMS as an internal standard.

3.2. 5-O-tert-Butyldiphenylsilyl-4-thio-L-lyxono-1,4-lactone (3)

To a solution of compound **2**[16] (113 mg, 0.69 mmol) in anhydrous DMF (0.5 mL), imidazole (102 mg, 1.48 mmol) and *tert*-butylchlorodiphenylsilane (0.20 mL, 0.76 mmol) were added. The mixture was stirred at room temperature for 5 h and then poured into water and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated to a syrup, which was chromatographed with 4:1 hexane:EtOAc. Fractions containing the product of R_f 0.90 (EtOAc) were concentrated to afford compound **3** (214 mg, 77%); $[\alpha]_D=-54$ (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 7.70–7.32 (m, 10H), 4.53 (dd, 1H, *J*=4.0, 3.0 Hz), 4.32 (d, 1H, *J*=4.0 Hz), 4.2–3.9 (m, 3H), 1.03 (s, 9H); ^{13}C NMR δ 204.8, 135.5, 132.7, 130.0, 127.8, 80.9, 78.3, 62.9, 49.7, 26.9, 19.4. Anal. calcd for $C_{21}H_{26}O_4SSi$: C, 62.65; H, 6.51. Found: C, 62.52; H, 6.50.

3.3. 2,3-Di-O-benzoyl-5-O-tert-butyldiphenylsilyl-4-thio-L-lyxono-1,4-lactone (4)

A solution of **3** (78 mg, 0.194 mmol) in anhydrous pyridine (0.8 mL), cooled at 0°C, was stirred with benzoyl chloride (0.4 mL, 3.4 mmol) for 1 h, when TLC indicated complete transformation of **3** into a less polar product (R_f 0.20, 15:1 hexane:EtOAc). The mixture was poured into ice-water and stirred for an additional 12 h. It was then extracted with CH_2Cl_2, and successively washed with 5% HCl, H_2O, saturated aqueous $NaHCO_3$, and water. The organic extract was dried ($MgSO_4$) and concentrated to a syrup, which was chromatographed with 30:1 hexane:EtOAc, to afford compound **4** (92 mg, 78%); ^{1}H NMR δ 7.93–7.10 (m, 20H), 6.22 (dd, 1H, *J*=3.4, 4.0 Hz), 5.94 (d, 1H, *J*=4.0 Hz), 4.37 (dt, 1H, *J*=3.4, 7.5 Hz), 4.07 (dd, 1H, *J*=10.2, 7.5 Hz), 3.88 (dd, 1H, *J*=7.5, 10.2 Hz), 0.98 (s, 9H); ^{13}C NMR δ 197.3, 165.1, 164.9, 135.6, 135.4, 130.1, 130.0, 128.7, 128.0, 127.8, 78.3, 69.5, 62.3, 47.8, 26.7, 19.1.

3.4. (4R)-4-(tert-Butyldiphenylsilyloxymethyl)-4-thiobutyro-1,4-lactone (5) ((5R)-dihydro-5-(tert-butyldiphenylsilyloxymethyl)-2(3H)-thiophenone)

To a solution of **4** (65 mg, 0.11 mmol) in recently distilled, dry THF (0.5 mL) cooled at 0°C was added under Ar a freshly prepared[28] 0.1 M solution of SmI_2 in THF (3.3 mL, 0.33 mmol). The solution changes immediately from the deep blue color to yellow, and *t*-butanol (0.021 mL, 0.22 mmol) and an additional amount of 0.1 M SmI_2 in THF (2.8 mL, 0.28 mmol) were added. The mixture was allowed to reach room temperature, and after 2 h of stirring it was diluted with CH_2Cl_2 and washed with 5% HCl, H_2O, saturated aqueous $NaHCO_3$, and H_2O. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography with 30:1 hexane:EtOAc, to give **5** (20 mg, 53%); $[\alpha]_D=-49.6$ (*c* 0.5; $CHCl_3$); ^{1}H NMR δ 7.67–7.36 (m, 10H), 4.03 (m, 1H, $J\approx6.3$ Hz), 3.83 (d, 2H, $J\approx6.0$ Hz), 2.53

(m, 2H), 2.29 (dq, 1H, $J\approx$7.0, 13.0 Hz), 2.08 (dq, 1H, $J\approx$6.5, 13.0 Hz), 1.06 (s, 9H); ^{13}C NMR δ 207.0, 135.6, 130.0, 127.9, 127.8, 66.6, 51.9, 40.8, 27.5, 26.8, 19.3. Anal. calcd for $C_{21}H_{26}O_2SiS$: C, 68.06; H, 7.07. Found: C, 68.25; H, 7.34.

3.5. *(4S)-(+)-4-Hydroxymethyl-1,4-butyrolactone (7) ((5S)-dihydro-5-(hydroxymethyl)-2-(3H)-furanone)*

It was prepared from L-glutamic acid (**6**) via *(4S)*-(+)-4-carboxy-1,4-butyrolactone as already described.[29]

3.6. *(4S)-(+)-4-(p-Tolylsulfonyloxymethyl)-1,4-butyrolactone (8) ((5S)-(+)-dihydro-5-(p-tolyl-sulfonyloxymethyl)-2(3H)-furanone)*

To a solution of **7** (1.38 g, 11.9 mmol) in dry $CHCl_3$ (12 mL), cooled at 0°C, pyridine (1.9 mL, 24.5 mmol) and tosyl chloride (3.43 g, 18 mmol) were added. After 12 h of stirring at 0°C, water (10 mL) was added dropwise, and the stirring was maintained for 0.5 h. The mixture was diluted with CH_2Cl_2 and it was successively washed with 0.5 N HCl, water, saturated aqueous $NaHCO_3$, and water. The organic extract was dried ($MgSO_4$) and concentrated to give a crystalline residue. Compound **8** (R_f 0.44, 2:1 toluene:EtOAc) was recrystallized from EtOH (2.68 g, 83%); mp 85–86°C; $[\alpha]_D$=+46.2 (*c* 1.0, $CHCl_3$); lit.[29] mp 85–87°C; $[\alpha]_D$=+47.

3.7. *Methyl (4S)-4,5-epoxipentanoate (9)*

Compound **8** (603 mg, 2.2 mmol) was added to a solution prepared by dissolving sodium (54 mg, 2.3 mmol) in anhydrous methanol (8.5 mL). The mixture was stirred at room temperature for 50 min, when a single spot, faster migrating than **8** (R_f 0.67, 2:1 toluene:EtOAc), was detected by TLC. Evaporation of the solvent afforded a residue which was extracted with CH_2Cl_2. The extract was concentrated and the resulting syrup dissolved in hexane and filtered. Upon evaporation of the solvent, compound **9** was obtained as a chromatographically homogeneous oil (228 mg, 79%); $[\alpha]_D$=−18 (*c* 1.1, $CHCl_3$); lit.[31] $[\alpha]_D$=−17.9; ^{13}C NMR δ 173.2, 51.6, 51.1, 46.9, 30.1, 27.5.

3.8. *Methyl (4R)-4,5-epithiopentanoate (10)*

To a solution of **9** (0.37 g, 2.8 mmol) in dry methanol (44 mL) was added thiourea (0.47 g, 5.5 mmol). The resulting solution was stirred at room temperature for 72 h, when TLC showed a single spot (R_f 0.73, 2:1 toluene:EtOAc) less polar than the starting **9**. Evaporation of the solvent afforded a residue which was extracted with ether. The extract was concentrated and the resulting syrup was dissolved in hexane and filtered. Concentration of the solution gave chromatographically homogeneous, oily compound **10** (0.34 g, 83%); $[\alpha]_D$=+83 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 3.69 (s, 3H), 2.95 (dddd, 1H, J=5.1, 5.5, 6.1, 8.0 Hz), 2.53 (t, 2H, $J\approx$7.2 Hz), 2.51 (dd, 1H, J=1.2, 6.1 Hz), 2.30 (dddd, 1H, J=5.1, 7.2, 8.0, 14.0 Hz), 2.19 (dd, 1H, J=1.2, 5.6 Hz), 1.65 (ddt, 1H, J=7.2, 8.0, 14.0 Hz); ^{13}C NMR δ 173.1, 51.5, 34.7, 33.3, 31.5, 25.7. Anal. calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89. Found: C, 48.92; H, 6.51.

*3.9. (4R)-Acetoxymethyl-4-thiobutyro-1,4-lactone (**11**) ((5R)-dihydro-5-(acetoxymethyl)-2(3H)-thiophenone)*

Compound **10** (0.21 g, 1.39 mmol) was dissolved in a mixture of DMF (7 mL), AcOH (7 mL), and KOAc (1.4 g, 14.4 mmol) and heated to the reflux temperature, under nitrogen. After 18 h the reaction mixture showed by TLC a main spot (R_f 0.48, 2:1 toluene:EtOAc); it was diluted with CH_2Cl_2 (60 mL) and successively washed with water, saturated aqueous $NaHCO_3$, and water. The organic extract was dried ($MgSO_4$) and concentrated to a syrup, which was chromatographed using 20:1 hexane:EtOAc. From the column unreacted starting **10** (50 mg) was recovered, and the fractions containing the product of R_f 0.48 were pooled and concentrated to afford the thiolactone **11** (0.12 g, 65% yield based on reacted **10**). It had $[\alpha]_D=-87$ (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 4.37 (dd, 1H, *J*=6.3, 11.1 Hz), 4.22 (dd, 1H, *J*=6.6, 11.1 Hz), 4.11 (tdd, 1H, *J*=6.3, 6.6, ≈7.0 Hz), 2.71 (dq, 1H, *J*≈7.5, 17.0 Hz), 2.55 (dq, 1H, *J*≈7.5, 17.0 Hz), 2.38 (dq, 1H, *J*≈7.0, 13.0 Hz), 2.10 (s, 3H), 2.06 (dq, 1H, *J*≈7.0, 13.0 Hz); ^{13}C NMR δ 207.0, 170.5, 66.3, 48.1, 40.6, 27.9, 20.7. Anal. calcd for $C_7H_{10}O_3S$: C, 48.26; H, 5.78. Found: C, 48.26; H, 6.02.

*3.10. (4R)-Hydroxymethyl-4-thiobutyro-1,4-lactone (**12**) ((5R)-dihydro-5-(hydroxymethyl)-2(3H)-thiophenone) and its* tert*-butyldiphenylsilyloxy derivative **5***

Compound **11** (115 mg, 0.69 mmol) was dissolved in a mixture of THF (5 mL) and 6% aqueous HCl (2.5 mL), and the resulting solution was stirred at 35°C for 16 h. The reaction mixture, which showed by TLC a main spot having R_f 0.66 (EtOAc), was concentrated and the resulting syrup was purified through a short column of silica gel with 2:1 hexane:EtOAc. Evaporation of the solvent led to the free thiolactone **12** (80 mg, 92%): $[\alpha]_D=-106$ (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 4.04 (dq, 1H, *J*=5.3, ≈7.0 Hz), 3.78 (dd, 1H, *J*=5.3, 12.5 Hz), 3.66 (dd, 1H, *J*=7.0, 12.5 Hz), 2.88 (bs, 1H, OH), 2.61 (dq, 1H, *J*≈7.0, 17.6 Hz), 2.57 (dq, 1H, *J*≈7.5, 17.6 Hz), 2.28 (dq, 1H, *J*≈7.5, 12.5 Hz), 1.97 (dq, 1H, *J*≈7.5, 12.5 Hz); ^{13}C NMR δ 208.7, 65.3, 52.1, 41.1, 27.4. Anal. calcd for $C_5H_8O_4S$: C, 36.58; H, 4.91; S, 19.53. Found: C, 36.71; H, 4.71; S, 19.49.

Silylation of **12** (127 mg, 0.96 mmol) with *tert*-butylchlorodiphenylsilane (293 mg, 106 mmol) in anhydrous DMF (2 mL), and in the presence of imidazole (147 mg, 2.1 mmol), was performed as described for **2**. After column chromatography with 40:1 hexane:EtOAc, syrupy compound **5** (321 mg, 90%) was obtained; $[\alpha]_D=-48.2$ (*c* 0.9, $CHCl_3$). It showed the same spectral properties as the product **5** obtained from **2**.

Acknowledgements

Financial support from ANPCYT (National Agency for Promotion of Science and Technology, PICT 01698) and from the University of Buenos Aires (Project TW70) is gratefully acknowledged. O.V. is a Research Member of the National Research Council of República Argentina (CONICET).

References

1. (a) Oishi, H.; Noto, T.; Sasaki, H.; Suzuki, K.; Hayashi, T.; Okazaki, H.; Ando, K.; Sawada, M. *J. Antibiotics* **1982**, *35*, 391. (b) Sasaki, H.; Oishi, H.; Hayashi, T.; Matsuura, I.; Ando, K.; Sawada, M. *J. Antibiotics* **1982**, *35*, 396. (c) Noto, T.;

Miyakawa, S.; Oishi, H.; Endo, H.; Okazaki, H. *J. Antibiotics* **1982**, *35*, 401. (d) Miyakawa, S.; Suzuki, K.; Noto, T.; Harada, H.; Okazaki, H. *J. Antibiotics* **1982**, *35*, 411.
2. (a) Omura, S.; Iwai, Y.; Nakagawa, A.; Iwata, R.; Takahashi, Y.; Shimizu, H.; Tanaka, H. *J. Antibiotics* **1983**, *36*, 109. 11. (b) Omura, S.; Nakagawa, A.; Iwata, R.; Hatano, A. *J. Antibiotics* **1983**, *36*, 1781; Dolak, L. A.; Castle, T. M.; Truesdell, S. E.; Sebek, O. K. *J. Antibiotics* **1986**, *39*, 26.
3. (a) Panetta, J. A.; Rapoport, H. *J. Org. Chem.* **1982**, *47*, 2626. (b) Li, A.-H.; Moro, S.; Forsyth, N.; Melman, N.; Ji, X.-d.; Jacobson, K. A. *J. Med. Chem.* **1999**, *42*, 706.
4. Cruz-Almanza, R.; Hernández-Quiroz, T.; Breña-Valle, L. J.; Pérez Flores, F. *Tetrahedron Lett.* **1997**, *38*, 183.
5. Stevens, C. M.; Tarbell, D. S. *J. Org. Chem.* **1954**, *19*, 1996.
6. Sarpeshkar, A. M.; Gossick, G. J.; Wemple, J. *Tetrahedron Lett.* **1979**, 703.
7. Crich, D. *Tetrahedron Lett.* **1988**, *29*, 5805.
8. Bhar, D.; Chandrasekaran, S. *Tetrahedron* **1997**, *53*, 11835.
9. Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *Synlett* **1999**, 486.
10. Garbiras, B. J.; Marburg, S. *Synthesis* **1999**, 270.
11. Chambers, M. S.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1989**, 23.
12. Yang, Z. Y.; Xia, P.; Cosentino, L. M.; Lee, K. H. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1483.
13. Stachel, H.-D.; Schachtner, J. *Tetrahedron* **1993**, *49*,4871.
14. Wang, C.-L.; Salvino, J. M. *Tetrahedron Lett.* **1984**, *25*, 5243.
15. Schachtner, J. E.; Stachel, H.-D.; Chatterjee, S. S.; Hauer, H.; Polborn, K. *Eur. J. Med. Chem*. **1998**, *33*, 665.
16. Varela, O.; Zunszain, P. A. *J. Org. Chem*. **1993**, *58*, 7860.
17. Varela, O.; Cicero, D.; Lederkremer, R. M. *J. Org. Chem*. **1989**, *54*, 1884.
18. Cicero, D.; Varela, O.; Lederkremer, R. M. *Tetrahedron* **1990**, *46*, 1131.
19. Cicero, D.; Varela, O.; Lederkremer, R. M. *Carbohydr. Res.* **1991**, *211*, 295.
20. Cicero, D.; Varela, O. *Tetrahedron* **1990**, *46*, 8019.
21. Zunszain, P. A.; Varela, O. *Carbohydr. Res.* **1991**, *222*, 131.
22. Inanaga, J.; Katsuki, J.; Yamaguchi, M. *Chem. Lett.* **1991**, 1025.
23. Hanessian, S.; Girard, C.; Chiara, J. L. *Tetrahedron Lett.* **1992**, *33*, 573.
24. Zunszain, P. A.; Varela, O. *An. Asoc. Quím. Argent.* **1998**, *86*, 151.
25. Fujita, Y.; Fukuzumi, S.; Otera, J. *Tetrahedron Lett.* **1997**, *38*, 2121. For a review on reactions of SmI_2, see: Molander, G. A.; Harris, C. R. *Tetrahedron* **1998**, *54*, 334.
26. Inanaga, J.; Sakai, S.; Handa, Y.; Yamaguchi, M.; Yokoyama, Y. *Chem. Lett.* **1991**, 2117.
27. Cabrera, A.; Alper, H. *Tetrahedron Lett.* **1992**, *33*, 5007.
28. Fukuzawa, S.; Nakanishi, A.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1669
29. Ravid, U.; Silverstein, R. M.; Smith, L. R. *Tetrahedron* **1978**, *34*, 1449.
30. Kabalka, G. W.; Varma, M.; Varma, R. S.; Srivastava, P. C.; Knapp Jr., F. F. *J. Org. Chem.* **1986**, *51*, 2386.
31. Ho, P.-T.; Davies, N. *Synthesis* **1983**, 462.