Mild Stereoselective Synthesis of Fully Protected 1,6-Dioxaspiro[4.5]dec-3-ene Derivatives of Sugars

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Keywords: Spiro compounds / Carbohydrates / Lactones

Perbenzylated 1,6-dioxaspiro[4.5]dec-3-ene derivatives of sugars are prepared in three steps, starting from fully protected glycono-1,5-lactones. The procedure exploits a reagent previously devised in our laboratory, the 3-*C*-lithiated 5,6-dihydro-1,4-dithiin-2-yl[(4-methoxybenzyl)oxy]methane (**2**), that acts as an allylic alcohol anion equivalent leading to three carbon elongations by introduction of a fully protected hydroxypropenyl moiety. The attack of **2** on the starting glyconolactone occurs selectively from the β-face leading to a hemiacetal derivative, the spirocyclization of which is then accomplished by reaction with $BF_3{\cdot}Et_2O$. The fully protected unsaturated spiroacetals can be selectively desulfurized for any further elaboration of the free double bond.

Introduction

Semi-rigid dioxaspiroacetal units are widely found as sub-structures in many naturally occurring compounds from different sources, including insects, microbes, plants, fungi, and marine organisms.[1,2] The spiroacetal ring system is also an essential part of the complex structures of biologically active substances like the antiparasitic agents avermectin[3] and milbemycin,[4] or the polyether antibiotics of the monensin[5] and okadaic acid families.[6] The naturally occurring chiral spiroacetal sub-structures mostly include 1,7-dioxaspiro[5.5]undecane, 1,6-dioxaspiro[4.5]decane, and 1,6-dioxaspiro[4.4]nonane structural categories.

The spiroacetal synthesis is commonly accomplished by the acid-promoted spirocyclization of a suitable dihydroxy ketone precursor, generally leading to the correct configuration of the spiro carbon provided that it corresponds to the thermodynamically most stable form.[7] Recently, a new, elegant approach to the synthesis of unsaturated pyranose spiroacetals from perbenzylated glycono-1,5-lactones was reported.[8] It is based on the ring-closing metathesis reaction (RCM), in the presence of Grubbs ruthenium catalyst, of a terminal alkene-*O*-alkene arrangement created in three steps at the anomeric centre of sugars.

In this context we report here an alternative approach to the synthesis of perbenzylated 1,6-dioxaspiro[4.5]dec-3-ene derivatives of sugars that is accomplished in three steps from the same glycono-1,5-lactone precursors.

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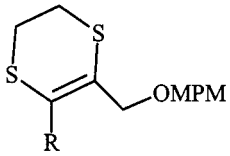
Results and Discussion

Our procedure exploits a reagent previously devised in our laboratory,[9] the 3-*C*-lithiated 5,6-dihydro-1,4-dithiin-2-yl[(4-methoxybenzyl)oxy]methane (**2**), that has been shown to act as an allylic alcohol anion equivalent, leading to three-carbon elongations of suitable electrophiles by introduction of a fully protected hydroxypropenyl moiety. Compound **2** is prepared in situ from its parent compound **1**, which is quite stable and can be stored in the refrigerator for months.

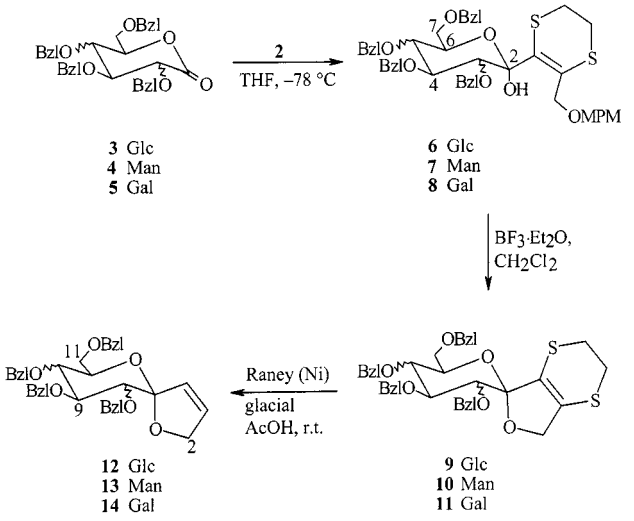


1 R = H
2 R = Li

Under our conditions, compound **2** was directly coupled with the proper glycono-1,5-lactone to afford the corresponding hemiacetal, as shown in Scheme 1. The formation of the sole thermodynamically more stable[10] hemiacetals **6**–**8** was confirmed by ^1H NMR spectroscopy.[11]

A crucial step in the overall conversion of glycono-1,5-lactones into the corresponding spiroacetals is the induction of an electrophilic centre at the allylic methylene position of the 1,4-dithiinyl moiety to be attacked by the free hemiacetal hydroxyl group. This was achieved by $BF_3{\cdot}Et_2O$ catalysis, under conditions that did not affect the hemiacetal hydroxyl group. In this way we could prepare the three unsaturated spiroacetals **9**–**11** with the double bond still protected by the dimethylene-disulfur bridge in good yields. The usual conditions to remove the MPM protection[12,13]

  1434–193X/02/0203–0534 $ 17.50+.50/0 *Eur. J. Org. Chem.* **2002**, 534–536



Scheme 1

− treatment with either $NaBH_3CN$ or DDQ − led invariably to the free primary alcohol that could be isolated as such.[14]

Desulfurization with Raney-Ni in glacial acetic acid[15] eventually afforded the 1,6-dioxaspiro[4.5]dec-3-ene derivatives **12**−**14** of the starting glycono-1,5-lactones **3**−**5**, respectively.

The whole procedure is very simple, and is characterized by clean and high yielding reactions. The double bond in the final sulfur-free unsaturated spiroacetals can be easily saturated by catalytic hydrogenation, and hydroxylated under stereocontrolled conditions as well, to synthesise other more complex dioxaspiroacetal-based compounds.

Experimental Section

General: ^1H (in C_6D_6) and ^{13}C (in $CDCl_3$) NMR spectra: Bruker DRX-400 spectrometer, chemical shifts in ppm (δ), TMS internal standard. Optical rotations (in $CHCl_3$): Jasco P-1010 (1.0 dm cell). Combustion analyses: Perkin−Elmer Series II 2400, CHNS analyzer. TLC analyses: silica gel Merck 60 F_{254} plates (0.2 mm layer thickness). Column chromatography: Merck Kieselgel 60 (70−230 mesh). Dry solvents were distilled immediately before use.

Hemiacetal Formation. (2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-Tri(benzyloxy)-6-[(benz-yloxy)methyl]-5,6-dihydro-2-{3-[(4-methoxybenzyloxy)-methyl]-1,4-dithiin2-yl}tetrahydro-2*H*-2-pyranol (6). Typical Procedure: 1.6 M BuLi in hexane (0.9 mL, 1.4 mmol) was added dropwise over 10 min to a stirred solution of 5,6-dihydro-1,4-dithiin-2-yl-[(4-methoxybenzyl)oxy]methane (**1**) (0.32 g, 1.2 mmol) in anhydrous THF (5 mL), at −78 °C under an N_2 atmosphere. After 40 min, D-gluconolactone (**3**) (0.54 g, 1.0 mmol) dissolved in the same solvent (2 mL) was added dropwise with a cannula. The reaction mixture was kept for 3 h at −78° C, then quenched with 10% aq NH_4Cl (5 mL), and extracted with EtOAc (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and the solvents evaporated under reduced pressure. Chromatography on silica gel (light petroleum ether/EtOAc 7:3) of the crude residue finally afforded the pure hemiacetal **6** (0.73 g, 90%) as an oil. $[\alpha]_D^{25}$ = +84.4 (*c* = 0.6). $C_{47}H_{50}O_8S_2$ (807.0): calcd. C 69.95, H 6.24; found C 69.15, H 6.15. ^1H NMR: δ = 2.38−2.50 (m, 2 H, SCH_2CH_2S), 2.54−2.60 (m, 1 H, SCH_2CHHS), 2.85−2.92 (m, 1 H, SCH_2CHHS), 3.38 (s, 3 H, OMe), 3.67 (d, *J* = 10.0 Hz, 1 H, 7-Ha), 3.72 (d, *J* = 11.3 Hz, 1 H, Bzl_i-H_a), 3.96 (dd, *J* = 2.1, 8.9 Hz, 1 H, 7-H_b), 4.02 (t, *J* = 9.1 Hz, 1 H, 5-H), 4.22 (d, *J* = 2.6 Hz, 1 H, 3-H), 4.28 (m, 1 H, 6-H), 4.32 (m, 3 H, CH_2C= and 4-H), 4.54 (d, *J* = 12.2 Hz, 1 H, Bzl_{ii}-H_a), 4.71 (d, *J* = 10.5 Hz, 1 H, Bzl_{iv}-H_a), 4.76 (d, *J* = 12.2 Hz, 1 H, Bzl_{ii}-H_b), 4.80 (d, *J* = 11.3 Hz, 1 H, Bzl_{iii}-H_a), 4.98 (m, 4 H, $CH_2C_6H_4OMe$, Bzl_{iv}-H_b and Bzl_{iii}-H_b), 5.47 (d, *J* = 11.3 Hz, 1 H, Bzl_i-H_b), 5.58 (br. s, 1 H, O*H*), 6.79 (d, J_{ortho} = 8.7 Hz, 2 H, H_{arom}), 7.45−7.17 (m, 22 H, H_{arom}). ^{13}C NMR: δ = 26.5, 30.4, 54.8, 59.9, 68.2, 71.6, 72.1, 73.0, 74.5, 75.1, 75.4, 77.7, 82.1, 82.9, 99.7, 113.8.

The following hemiacetals were also obtained under the same conditions.

(2*R*,3*S*,4*S*,5*R*,6*R*)-3,4,5-Tri(benzyloxy)-6-[(benzyloxy)methyl)]-5,6-dihydro-2-{3-[(4-methoxybenzyloxy)methyl]-1,4-dithiin-2-yl}-tetrahydro-2*H*-2-pyranol (7) from D-Mannonolactone (4): Yield: 87%. Oil. $[\alpha]_D^{25}$ = −19.2 (*c* = 0.2). $C_{47}H_{50}O_8S_2$ (807.0): calcd. C 69.95, H 6.24; found C 69.50, H 6.30. ^1H NMR: δ = 2.42−2.58 (m, 3 H, SCH_2CHHS), 2.71−2.85 (m, 1 H, SCH_2CHHS), 3.36 (s, 3 H, OMe), 3.75−3.83 (m, *J* = 3.6 Hz, 2 H, H-7), 4.19 (d, *J* = 11.3 Hz, 1 H, Bzl_i-H_a), 4.21−4.34 (m, 1 H, H-6), 4.38−4.55 (m, 6 H, CH_2C=C and H-3 and H-4 and H-5, and Bzl_{ii}-H_a), 4.57−4.64 (m, 4 H, Bzl_{ii}-H_b, Bzl_{iii}-H_a and $CH_2C_6H_4OMe$), 4.97 (d, *J* = 11.1 Hz, 1 H, Bzl_{iv}-H_a), 5.03 (d, *J* = 11.4 Hz, 1 H, Bzl_{iii}-H_b), 5.24 (d, *J* = 11.1 Hz, 1 H, Bzl_{iv}-H_b), 5.41 (d, *J* = 11.3 Hz, 1 H, Bzl_i-H_b), 6.78 (d, J_{ortho} = 8.7 Hz, 2 H, H_{arom}), 7.18−7.59 (m, 22 H, H_{arom}). ^{13}C NMR: δ = 27.7, 31.4, 55.0, 69.6, 69.9, 71.7, 72.6, 73.8, 74.6, 74.9, 76.4, 77.6, 79.5, 81.6, 100.6, 113.6.

(2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-Tri(benzyloxy)-6-[(benzyloxy)methyl]-5,6-dihydro-2-{3-[(4-methoxybenzyloxy)methyl]-1,4-dithiin-2-yl}-tetrahydro-2*H*-2-pyranol (8) from D-Galactonolactone (5): (89%), oil, $[\alpha]_D^{25}$ = +16.4 (*c* = 0.7). $C_{47}H_{50}O_8S_2$ (807.0): calcd. C 69.95, H 6.24; found C 69.78, H 6.17. ^1H NMR: δ = 2.44−2.52 (m, 2 H, SCH_2CH_2S), 2.58−2.64 (m, 1 H, SCH_2CHHS), 2.71−2.81 (m, 1 H, SCH_2CHHS), 3.38 (s, 3 H, OMe), 3.70 (dd, *J* = 5.3, 8.9 Hz, 1 H, 7-H_a), 3.95 (m, 2 H, 7-Hb and Bzl_i-H_a), 4.05 (dd, *J* = 2.7, 9.7 Hz, 1 H, 4-H), 4.08−4.13 (m, 1 H, 5-H), 4.26−4.42 (m, 4 H, 3-H, Bzl_{ii}-H_a, CH_2C=), 4.46−4.54 (m, 1 H, 6-H), 4.55 (d, *J* = 11.8 Hz, 1 H, $CHHC_6H_4OMe$), 4.64 (d, *J* = 11.8 Hz, 1 H, $CHHC_6H_4OMe$), 4.78 (t, *J* = 11.3 Hz, 2 H, Bzl_{iii}-H), 4.87 (d, *J* = 10.7 Hz, 1 H, Bzl_{iv}-H_a), 4.98 (m, 2 H, O*H* and Bzl_{ii}-H_b), 5.15 (d, *J* = 10.7 Hz, 1 H, Bzl_{iv}-H_b), 5.41 (d, *J* = 11.3 Hz, 1 H, Bzl_i-H_b), 6.81(d, J_{ortho} = 8.6 Hz, 2 H, H_{arom}), 7.13−7.50 (m, 22 H, H_{arom}). ^{13}C NMR: δ = 27.7, 29.8, 55.2, 64.9, 68.1, 70.3, 70.8, 71.5, 72.4, 72.7, 73.4, 74.7, 75.7, 80.5, 96.5, 114.1.

Spirocyclization of Hemiacetal 6 to Compound 9. Typical Procedure: A solution (3% v/v in CH_2Cl_2) of $BF_3{\cdot}Et_2O$ (0.2 mL) was added carefully to a magnetically stirred solution of hemiacetal **6** (0.81 g, 1.0 mmol) in CH_2Cl_2 (14 mL) at room temperature. After 1 h, the reaction mixture was quenched with Et_3N (0.03 mL, 0.2 mmol) and then washed with water. The organic layer was dried (Na_2SO_4) and the solvents evaporated under reduced pressure to afford a crude residue, the chromatographic separation of which on a silica gel column (light petroleum ether/EtOAc: 8:2) afforded the pure spiroacetal **9** (0.58 g, 87%), oil, $[\alpha]_D^{25}$ = +21.1 (*c* = 0.6). $C_{39}H_{40}O_6S_2$ (668.7): calcd. C 70.03, H 6.03; found C 70.30, H 6.07. ^1H NMR: δ = 2.22−2.51 (m, 4 H, SCH_2CH_2S), 3.60 (dd, *J* = 1.7 and 11.2 Hz, 1 H, 11-H_a), 3.79 (dd, *J* = 3.4 and 11.2 Hz, 1 H, 11-H_b), 3.90 (t, *J* = 9.2 Hz, 1 H, 8-H), 3.94 (d, *J* = 10.3 Hz, 1 H, Bzl_i-H_a), 4.15−4.25 (m, 2 H, 7-H and 9-H), 4.32 (d, *J* = 10.3 Hz, 1 H, Bzl_i-H_b), 4.40 (d, *J* = 12.2 Hz, 1 H, Bzl_{ii}-H_a), 4.57 (d, *J* = 12.2 Hz, 1

H, Bzl_{ii}-H_b), 4.63 (m, 3 H, 10-H and Bzl_{iii}-H), 4.81−5.01 (m, 4 H, Bzl_{iv}-H and 2-H), 6.98−7.37 (m, 20 H, H_{arom}). ^{13}C NMR: δ = 25.3, 26.0, 68.5, 73.2, 74.7, 75.1, 75.4, 77.7, 80.9, 83.3, 95.9, 113.2, 117.9, 124.4.

The following spiroacetals were also obtained under the same conditions.

Compound 10, from Hemiacetal 7: Yield: 85%, oil. $[\alpha]_D^{25}$ = +22.3 (*c* = 0.7). $C_{39}H_{40}O_6S_2$ (668.7): calcd. C 70.03, H 6.03; found C 70.16, H 5.98. ^1H NMR: δ = 2.23−2.57 (m, 4 H, SCH_2CH_2S), 3.82 (dd, *J* = 1.8 and 11.6 Hz, 1 H, 11-Ha), 3.93 (d, *J* = 2.39 Hz, 1 H, 10-H), 4.08 (dd, *J* = 3.8 and 11.6 Hz, 1 H, 11-H_b), 4.25−4.31 (m, 1 H, 7-H), 4.38 (dd, *J* = 2.4, 9.3 Hz, 1 H, 9-H), 4.47 (d, *J* = 12.2 Hz, 1 H, Bzl_i-H_a), 4.58 (t, *J* = 9.3 Hz, 1 H, 8-H), 4.62 (d, *J* = 11.9 Hz, 1 H, Bzl_{ii}-H_a), 4.64−4.74 (m, 3 H, 2-H and Bzl_i-H_b), 4.77 (d, *J* = 11.4 Hz, 1 H, Bzl_{iii}-Ha), 4.92−5.06 (m, 3 H, Bzl_{ii}-H_b, Bzl_{iii}-H_b and Bzl_{iv}-H_a), 5.18 (d, *J* = 11.3 Hz, 1 H, Bzl_{iv}-Hb), 7.14−7.36 (m, 20 H, H_{arom}). ^{13}C NMR: δ = 25.7, 25.9, 68.7, 72.2, 73.1, 73.8, 74.2, 74.6, 74.8, 75.9, 77.1, 78.6, 81.3, 113.4, 123.1.

Compound 11, from Hemiacetal 8: Yield: 82%, oil. $[\alpha]_D^{25}$ = +4.7 (*c* = 0.3). $C_{39}H_{40}O_6S_2$ (668.7): calcd. C 70.03, H 6.03; found C 70.21, H 5.98. ^1H NMR: δ = 2.32−2.47 (m, 3 H, SCH_2C*H*HS), 2.52−2.62 (m, 1 H, SCH$_2$CH*H*S), 3.74 (dd, *J* = 8.8, 5.4 Hz, 1 H, 11-H_a), 3.90 (t, *J* = 8.8 Hz, 1 H, 11-H_b), 4.10−4.16 (m, 1 H, 8-H), 4.22 (dd, *J* = 2.8, 9.9 Hz, 1 H, 9-H), 4.28 (d, *J* = 11.9 Hz, 1 H, Bzl_i-H_a), 4.34 (d, *J* = 11.9 Hz, 1 H, Bzl_i-H_b), 4.47−4.52 (m, 1 H, 7-H), 4.55 (d, *J* = 11.8 Hz, 1 H, Bzl_{ii}-H_a), 4.61 (d, *J* = 9.9 Hz, 1 H, Bzl_{ii}-H_b), 4.68 (d, *J* = 9.9 Hz, 1 H, 2-H), 4.72−4.83 (m, 3 H, 2-H and Bzl_{iv}-H_a), 4.92 (d, *J* = 11.1 Hz, 1 H, Bzl_{iii}-H_a), 5.05 (d, *J* = 11.1 Hz, 1 H, Bzl_{iii}-H_b), 5.17 (d, *J* = 11.8 Hz, 1 H, Bzl_{iv}-H_b), 7.11−7.50 (m, 20 H, H_{arom}). ^{13}C NMR: δ = 25.6, 26.2, 68.4, 71.6, 72.8, 73.4, 74.3, 74.5, 75.4, 76.6, 77.9, 80.9, 96.1, 113.4, 118.5, 124.2.

Desulfurization. Formation of (5*R*,7*R*,8*R*,9*S*,10*R*)-8,9,10-Tri(benzyloxy)-7-[(benzyloxy) methyl]-1,6-dioxaspiro[4.5]dec-3-ene (12). Typical Procedure: A solution of spiroacetal **9** (0.1 g, 0.15 mmol) in glacial acetic acid (3 mL) was added in one portion to a stirred suspension of Raney-Ni (W2) (1.5 g, wet) in the same solvent (2 mL) at room temperature. The suspension was stirred for 35 min (TLC monitoring). The solid was then filtered off and washed with EtOAc. The filtrate was neutralized with saturated aq Na_2CO_3 and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with water until neutral, dried (Na_2SO_4), and the solvents evaporated under reduced pressure to afford a crude residue. Chromatography of the latter on a silica gel column (light petroleum ether/EtOAc: 8:2) gave the pure sulfur-free spiroacetal **12** (0.07 g, 77%) as an oil. $[\alpha]_D^{25}$ = +30.1 (*c* = 0.2). $C_{37}H_{38}O_6$ (578.3): calcd. C 76.79, H 6.62; found C 76.85, H 6.48. ^1H NMR: δ = 3.62 (dd, *J* = 1.9 and 10.8 Hz, 1 H, 11-H_a), 3.80 (dd, *J* = 3.2 and 10.8 Hz, 1 H, 11-H_b), 3.91−4.05 (m, 2 H, 8-H and Bzl_i-H_a), 4.17−4.53 (m, 8 H, 2-H, 7-H, 9-H, 10-H, Bzl_{ii}-H and Bzl_i-H_b), 4.60−5.01 (m, 4 H, Bzl_{iii}-H and Bzl_{iv}-H), 5.43 (dt, *J* = 6.1, 2.4 Hz, 1 H, 3-H), 5.62 (dt, *J* = 1.2, 6.1 Hz, 1 H, 4-H), 7.12−7.39 (m, 20 H, H_{arom}). ^{13}C NMR: δ = 68.7, 72.4, 73.4, 74.8, 75.7, 76.3, 76.7, 78.5, 81.4, 83.7, 96.1, 109.5, 112.1.

The following desulfurized spiroacetals were also obtained under the same conditions.

(5*R*,7*R*,8*R*,9*S*,10*S*)-8,9,10-Tri(benzyloxy)-7-[(benzyloxy)methyl]-1,6-dioxaspiro[4.5]dec-3-ene (13) from Spiroacetal 10: Yield: 70%, oil. $[\alpha]_D^{25}$ = +10.2 (*c* = 0.04). $C_{37}H_{38}O_6$ (578): calcd. C 76.79, H 6.62; found C 76.31, H 6.12. ^1H NMR: δ = 3.89 (d, *J* = 11.6 Hz, 1 H, 11-H_a), 3.98 (br. s, 1 H, 10-H), 4.08 (dd, *J* = 4.0, 11.6 Hz, 1 H, 11-H_b), 4.25−4.42 (m, 2 H, 7-H and 9-H), 4.30 (d, *J* = 12.2 Hz, 2 H, Bzl_i-H_a), 4.52−4.81 (m, 6 H, 2-H, 8-H, Bzl_i-H_b, Bzl_{ii}-H_a and Bzl_{iii}-H_a), 4.88−5.05 (m, 3 H, Bzl_{ii}-H_b, Bzl_{iii}-H_b and Bzl_{iv}-H_a), 5.18 (d, *J* = 10.9 Hz, 1 H, Bzl_{iv}-H_a), 5.72 (dt, *J* = 6.14 and 2.39 Hz, 1 H, 3-H), 5.89 (d, *J* = 6.14 Hz, 1 H, 4-H) 7.11−7.36 (m, 20 H, H_{arom}). ^{13}C NMR: δ = 68.5, 70.2, 73.85, 73.6, 73.7, 74.5, 74.9, 80.1, 82.1, 82.4, 103.9, 111.4. 113.4.

(5*R*,7*R*,8*S*,9*S*,10*R*)-8,9,10-Tri(benzyloxy)-7-[(benzyloxy)methyl]-1,6-dioxaspiro[4.5]dec-3-ene (14) from Spiroacetal 11: Yield: 69%, oil. $[\alpha]_D^{25}$ = +25 (*c* = 0.2). $C_{37}H_{38}O_6$ (578.3): calcd. C 76.79, H 6.62; found C 76.87, H 6.20. ^1H NMR: δ = 3.77 (dd, *J* = 8.8, 5.4 Hz, 1 H, 11-H_a), 3.95 (t, *J* = 8.8 Hz, 1 H, 11-H_b), 4.10−4.15 (m, 1 H, 8-H), 4.18−4.51 (m, 3 H, 9-H and Bzl_i-H), 4.55−4.60 (m, 4 H, 2-H, 7-H and Bzl_{ii}-H_a), 4.65−4.90 (m, 5 H, 10-H, Bzl_{ii}-H_b, Bzl_{iii}-H and Bzl_{iv}-H_a), 5.02 (d, *J* = 11.2 Hz, 1 H, Bzl_{iv}-H_b), 5.55 (dt, *J* = 5.9, 2.5 Hz, 1 H, 3-H), 5.62 (d, *J* = 5.9 Hz, 1 H, 4-H), 7.16−7.39 (m, 20 H, H_{arom}). ^{13}C NMR: δ = 69.8, 70.8, 71.5, 72.9, 73.3, 74.9, 75.4, 77.1, 77.2, 81.6, 96.1, 109.6, 110.5.

Acknowledgments

^1H and ^{13}C NMR spectra, and Amber3 calculations, were performed at the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli Federico II.

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[10] From Amber3 calculations, Δ*E* between axially and equatorially oriented anomeric hydroxyl group turned out to be −19.2 *k*J mol^{-1} (compound **6**), −14.6 *k*J mol^{-1} (compound **7**), and −21.1 *k*J mol^{-1} (compound **8**).
[11] The 4-H resonance signal in compounds **6**, **7**, and **8** was shifted downfield, according to: F. Nicotra, L. Panza, G. Russo, *Tetrahedron Lett.* **1991**, *32*, 4035−4038.
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[14] Most of the experiments aimed to devise proper cyclization conditions were performed with compound **6** as a model, and the relevant ^1H NMR peaks of the corresponding free primary alcohol were: δ = 2.30−2.82 (m, 4 H, SCH_2CH_2S), 3.51 (d, *J* = 11.0 Hz, 1 H, 7-H_a), 3.62−3.70 (m, *J* = 11.3 Hz, 2 H, 6-H and 7-H_b), 3.72−3.82 (m, 2 H, 3-H and 5-H), 4.18 (t, *J* = 9.0 Hz, 1 H, 4-H), 4.49 (d, *J* = 12.0 Hz, 1 H, CH_aOH), 4.55−4.70 (m, 4 H, CH_bOH and Bzl-H), 4.81 (d, *J* = 11.0 Hz, 1 H, Bzl_i-H_a), 4.84 (d, *J* = 11.0 Hz, 1 H, Bzl_i-H_b), 4.90 (d, *J* = 12.2 Hz, 1 H, Bzl_{ii}-H_a), 4.97 (d, *J* = 12.2 Hz, 1 H, Bzl_{ii}-H_b), 4.99 (d, *J* = 11.0 Hz, 1 H, Bzl-H), 7.03−7.49 (m, 20 H, H_{arom}).
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Received July 20, 2001
[O01360]