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Carbohydrate Research 335 (2001) 63–70

CARBOHYDRATE RESEARCH

Note

DIBALH mediated reduction of the acetal moiety on perhydrofuro[2,3-*b*]pyran derivatives

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Received 23 May 2001; received in revised form 9 July 2001; accepted 10 July 2001

Abstract

The reaction of DIBALH with bis(heteroannulated)-pyranosides containing the perhydrofuro[2,3-*b*]pyran moiety is described. The hydride attack at the anomeric carbon (C-9a) resulted in the exclusive tetrahydrofuran ring opening. The selectivity of this reaction has been evaluated as other benzylidene acetals built on these substrates remain practically or partially unaltered in these conditions depending on the steric volume of the *O*-protecting group located at C-4 (TBDMS vs. Me). This protocol can be considered as a new entry for the synthesis of chiral and highly functionalized cyclopentanes.

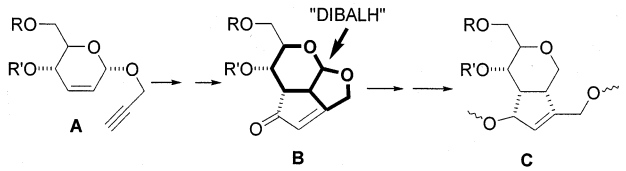
Keywords: DIBALH; Furo[2,3-*b*]pyrans; Reductive cleavage of benzylidene acetals

1. Introduction

A recent report on the reduction of spiroacetals in sugar templates,[1] prompts us to report here the results of the DIBALH mediated reduction of the acetal group incorporated in perhydrofuro[2,3-*b*]pyran derivatives (**B**)[2] obtained via Pauson–Khand reaction[3] on suitable functionalized 2-propynyl hex-2-enopyranosides (**A**). This protocol has resulted in a new entry for the synthesis of enantiomerically pure, highly functionalized cyclopentanes[4] (**C**) (Scheme 1) difficult to prepare by other strategies (see Chart 1).[5]

2. Results and discussion

In the course of our ongoing project,[2] we considered the reduction of ketone **1**[5] (Scheme 2) with DIBALH (1.0 M in toluene, 2.0 equiv) at −78 °C, in toluene as solvent. In these conditions, in addition to product **2** (69% yield), we isolated the unexpected allylic alcohol **3** in 9% yield (see Section 3). In both cases the ketone reduction proceeded stereoselectively from the less hindered β-face to give compounds with the absolute *S* configuration



Scheme 1. Reductive cleavage of perhydrofuro[2,3-*b*]pyrans.

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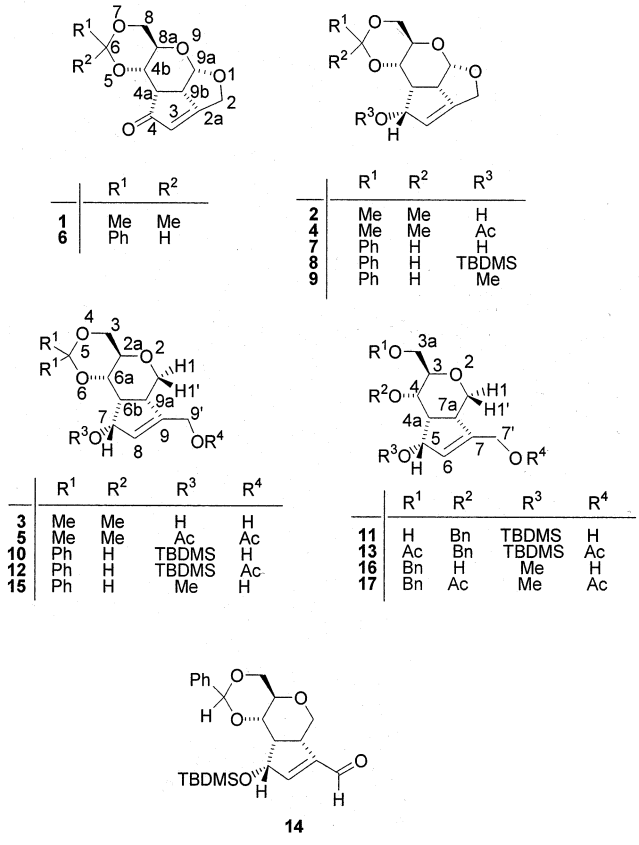
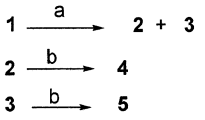


Chart 1.



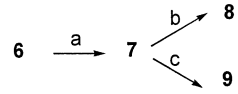
Scheme 2. (a) DIBALH, −78 °C, toluene; (b) Ac_2O, py, rt.

at the newly formed stereocenters.[2] After acetylation, compounds **2** and **3** gave acetate **4** (99%) and diacetate **5** (46%), respectively. Particularly significant in product **5** was the absence of the anomeric proton, substituted by two protons at 3.38 ppm (t, $J_{1,1'} = J_{1,9a}$ 11.5 Hz, H-1) and at 4.17 ppm (ddd, $J_{1,1'}$ 11.5, $J_{1',9a}$ 6.6, J 0.5 Hz, H-1′), a fact which led us to conclude that **3** was the product resulting after hydride attack at C-9a and subsequent tetrahydrofuran ring opening, the formation of the alternative product having a secondary alcohol after a possible tetrahydropyran ring opening, being excluded.

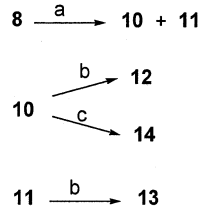
This interesting result prompted us to prepare new related derivatives in order to address the selectivity of the reduction regarding other functional groups, as well as the scope and limitations of this protocol. In connection with our current synthetic interests[2] we considered products **8** and **9**, containing a benzylidene acetal at positions O–C-5/O–C-7. In fact, reductive opening of carbohydrate benzylidene acetals with $AlCl_3$–$LiAH_4$,[6] $NaCNBH_3$–HCl[7] or DIBALH[8] is a very well known and exploited method for the regioselective cleavage of *O*-benzylidene acetals leading to *O*-benzyl ethers.

Products **8** and **9** have been easily prepared from compound **6**[5] after mild ketone reduction followed by standard *O*-protection (**8**: 87, **9**: 86%; Scheme 3) (see Section 3).

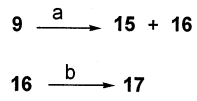
The reduction of compound **8** in toluene as solvent, at −78 or at −40 °C afforded alcohol **10** in 26 or 57% yield, respectively. Using methylene chloride at −78 °C, alcohol **10** (21%) was again obtained. Finally, when the DIBALH mediated reduction was carried out at −40 °C in methylene chloride, a clean and complete reaction occurred affording product **10** in good yield (79%) along with minor amounts of product **11** (8% yield) (Scheme 4). The analytical and spectroscopic data of **10** clearly showed that this product was the result of the exclusive and regioselective cleavage of the glycosidic bond followed by tetrahydrofuran ring opening, as we could demonstrate by additional chemical manipulation of compound **10** giving acetate **12** (99%), and aldehyde **14** (82%) after oxidation (Scheme 4). Substrate **11** was the result of the cleavage of the glycosidic bond followed by tetrahydrofuran ring opening plus the reduction of the benzylidene group. Very interestingly, in



Scheme 3. (a) DIBALH, −78 °C, toluene[5]; (b) ClTBDMS, imidazole, CH_2Cl_2, rt; (c) NaH, ICH_3, THF, rt.



Scheme 4. (a) DIBALH, −40 °C, CH_2Cl_2; (b) Ac_2O, py, rt; (c) PCC, CH_2Cl_2, rt.

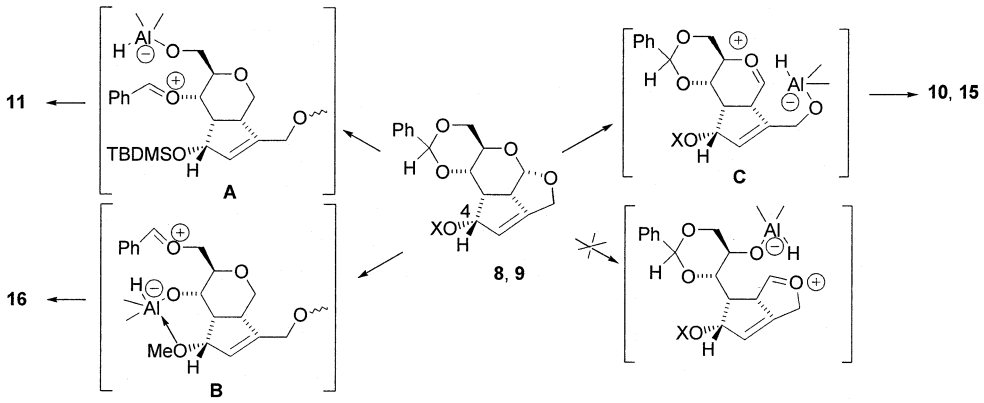


Scheme 5. (a) DIBALH, −40 °C, CH_2Cl_2; (b) Ac_2O, py, rt.

product **11**, the resulting *O*-benzyl group was located at the secondary carbon (C-4), in good agreement with similar trends observed for the reduction of benzylidene groups.[6] As expected, diol **11** gave diacetate **13** (7% overall yield from precursor **8**) in the usual conditions.

The reduction of product **9** using DIBALH at −40 °C, in methylene chloride, afforded two compounds in good overall yield: alcohol **15** (32%) and diol **16** (34%) (Scheme 5). Their analytical data and the comparison of their spectroscopic data with those of compounds **10** and **11** (see above) clearly supported and confirmed these structures (see Section 3). Particularly interesting in this case was, first of all, the preferred glycosidic reduction giving tetrahydrofuran ring opening molecules; secondly, the absence of selectivity, as an almost equimolecular ratio of the unreduced benzylidene acetal **15** and the reduced benzylidene acetal **16** having the *O*-benzyl group at C-3a resulted. This was confirmed after peracetylation of **16** giving diacetate **17** (90%). The structure of this product has been inequivocally demonstrated by detailed spectroscopic analysis and by comparison of these data with those of compound **16**. It was observed that in **16**, H-4 appeared at 3.85 ppm, and in **17** at 5.13 ppm ($\Delta\delta = +1.28$), while protons at C-3a in compound **16** or in **17** practically remained at the same field. In the ^{13}C NMR spectra, we could also detect the same trends: in **16**, C-4 was observed at 67.5 ppm, and in **17** at 69.3 ppm ($\Delta\delta = +1.8$).

In summary, the most interesting result of this work is the preferred reduction of the acetal at the glycosidic bond with regard to the benzylidene acetal in these perhydrofuro[2,3-*b*]pyrans. From the mechanistic point of view, it is proposed that in the DIBALH reduction, coordination of the aluminum reagent to the oxygens induced the formation of the oxonium intermediates followed by rapid intramolecular capture of the oxonium ion by the hydride source (see Scheme 6). Comparing the reactivity of **8** and **9**, it appears that the presence of a more sterically demanding group at O–C-4 in compound **8** directs the preferential, regioselective cleavage at the acetal moiety of the glycosidic bond, and regarding the reductive opening of the benzylidene acetal, the formation of the 4-*O*-benzyl protected cyclopentane-annulated pyranoside (**11**) (intermediate **A**, Scheme 6). As a result, the ratio of products **10**/**11** is above that in compounds **15**/**16**. Presumably, the less sterically demanding methyl ether in compound **9** allows a possible aluminum coordination with the oxygens at O–C-5/O–C-4 which should result in the hydride delivery giving rise to compound **16** with the *O*-benzyl ether in C-3a via intermediate **B** (Scheme 6). In this analysis, we cannot exclude a concerted bond breaking and hydride transfer versus the oxy-cationic DIBALH complexes in rapid equilibrium, as discussed. Regardless of the exact mechanism of the process, the bond breaking should be the rate determining step



Scheme 6. Proposed mechanism for the DIBALH-mediated reduction of acetals **8** and **9**.

and, in consequence, the key point here should be the quality of the leaving group. In this regard, the allylic oxy group should be a better leaving group than the benzyloxy carbenium intermediate. The exclusive bond cleavage of the pseudoaxial OR group exo to the tretrahydropyran ring is probably a consequence of the resulting highly stabilized α-pyranosyl carbenium intermediate (**C**) (Scheme 6). But one cannot exclude the release of strain in these perhydrofuro[2,3-*b*]pyran derivatives as an additional fact operating also in the same sense. In fact, simple, differently substituted α-methyl glycosides are stable to the hydride mediated reduction of benzylidene acetals.[6]

Finally, from the synthetic point of view, these results have afforded a new and simple protocol for the synthesis of chiral and highly polyfunctionalized cyclopentanes.

3. Experimental

General methods.—Reactions were monitored by TLC using precoated silica gel aluminum plates containing a fluorescent indicator (E. Merck, 5539). Detection was done by UV (254 nm) followed by charring with sulfuric–AcOH spray, 1% aq $KMnO_4$ solution or 0.5% phosphomolybdic acid in 95% EtOH. Anhydrous Na_2SO_4 was used to dry organic solutions during work-ups and the removal of solvents was carried out under diminished pressure with a rotary evaporator. Flash column chromatography was performed using Silica Gel 60 (230–400 mesh, E. Merck) and hexane–EtOAc mixtures as eluent unless otherwise stated. ^{1}H spectra were recorded with a Varian VXR-300(400)S spectrometers, using tetramethylsilane as internal standard and ^{13}C NMR spectra were recorded with a Bruker WP-200-SY. Values with (*) can be interchanged.

General method for DIBALH reduction.—The compound to be reduced was dissolved (0.15 M) and cooled in dry toluene (-78 °C) or CH_2Cl_2 (-40 °C) at the selected temperature. Thus DIBALH (1.1 equiv, 1.0 M in toluene) was added and after 3 h, a further amount of DIBALH (1.9 equiv) was added. When the reaction was complete (3 h), MeOH was added to destroy the excess of reagent and the mixture was warmed at rt. The suspension was filtered over Celite, the solvent removed and the crude reaction mixture was submitted to chromatography.

General method for acetylation.—The compound was treated with a mixture of 1:1 Ac_2O–pyridine at rt overnight. The solvent was evaporated and the residue was submitted to chromatography.

Reduction of ketone (**1**).—Following the method in Section 3.2, **1** (358 mg, 1.42 mmol) was treated with DIBALH (1.6 mL, 1.1 equiv, 1.0 M in toluene). After 1 h, a further portion of DIBALH (1.3 mL, 0.9 equiv) was added. After usual work-up and flash chromatography of the crude product (from hexane to 3:2 hexane–EtOAc), we obtained compounds (4*S*,4a*R*,4b*S*,8a*R*,9a*S*,9b*S*)-6,6′-dimethyl-4,4a,4b,6,8,8a,9a,9b-octahydro-2*H*-1,5,7,9-tetraoxacyclohexa[g]cyclopenta[cd]indene-4-ol (**2**) (249 mg, 69%) and **3** (33.2 mg, 9%), characterized as its diacetate {(2a*R*,6a*S*,6b*R*,7*S*,9a*S*)-7-acetyloxy-5,5′-dimethyl-1,2a,3,5,6a,6b,7,9a-octahydro-4,6-dioxacyclohexa[e]cyclopenta[c]-pyran-9-methanol acetate} (**5**). **2**: mp 101–104 °C; $[\alpha]_D^{25}$ $-6°$ (*c* 0.04, $CHCl_3$); IR (BrK) *ν* 3390, 1360, 1080, 990, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 5.83–5.79 (m, 1 H, H-3), 5.43–5.37 (m, 1 H, H-4), 5.35 (d, $J_{9a,9b}$ 5.5 Hz, 1 H, H-9a), 5.30 (d, $J_{OH,4}$ 6.4 Hz, 1 H, OH), 4.54 (ddd, $J_{2,2'}$ 13.0, *J* 3.5, *J* 1.8 Hz, 1 H, H-2), 4.21 (ddt, $J_{2',2}$ 13.0, *J* 4.0, *J* 2.2 Hz, 1 H, H-2′), 4.16 (ddd, $J_{8a,4b}$ 10.3, $J_{8a,8}$ 9.4, $J_{8a,8'}$ 5.5 Hz, 1 H, H-8a), 4.06 (dd, $J_{4b,8a}$ 10.3, $J_{4b,4a}$ 7.5 Hz, 1 H, H-4b), 3.88 (dd, $J_{8',8}$ 11.2, $J_{8',8a}$ 5.5 Hz, 1 H, H-8′), 3.51 (dd, $J_{8,8'}$ 11.2, $J_{8,8a}$ 9.4 Hz, 1 H, H-8), 3.32–3.26 (m, 1 H, H-9b), 3.16 (dt, $J_{4a,4b}$ 7.5, $J_{4a,4} = J_{4a,9b}$ 6.6 Hz, 1 H, H-4a), 1.46, 1.42 [s, s, 2 × 3 H, $OC(CH_3)_2O$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 144.0 (C-2a), 127.3 (C-3), 100.1 (C-6), 95.6 (C-9a), 86.4 (C-4), 72.8 (C-4b), 64.1 (C-2), 63.4 (2 C, C-8a, C-8), 51.7 (C-9b), 39.5 (C-4a), 29.0, 18.3 [$OC(CH_3)_2O$]; EIMS: *m*/*z* 153 (54), 124 (22), 107 (53), 101 (26), 79 (100), 43 (93). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.41; H, 7.13. Found: C, 61.72; H, 7.40. **5** [obtained from **3** (33 mg, 0.13 mmol) following the method in Section 3.3 after flash chromatography of the crude (4:2

hexane–EtOAc): **5** (17.9 mg, 46%)]: mp 74–77 °C; $[\alpha]_D^{25}$ +210° (*c* 0.74, $CHCl_3$); IR (BrK): *v* 1737, 1380, 1234, 1108, 1073, 1029, 867 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.92–5.91 (m, 1 H, H-7), 5.89–5.88 (m, 1 H, H-8), 4.68 (d, $J_{9'A,9'B}$ 14.3 Hz, 1 H, H-9′A), 4.58 (d, $J_{9'A,9'B}$ 14.3 Hz, 1 H, H-9′B), 4.17 (ddd, $J_{1',1}$ 11.5, $J_{1',9a}$ 6.6, *J* 0.5 Hz, 1 H, H-1′), 4.01 (dd, $J_{6a,2a}$ 9.9, $J_{6a,6b}$ 6.6 Hz, 1 H, H-6a), 3.89 (dd, $J_{3',3}$ 9.9, $J_{3',2a}$ 4.4 Hz, 1 H, H-3′), 3.71 (td, $J_{2a,6a} = J_{2a,3}$ 9.9, $J_{2a,3'}$ 4.4 Hz, 1 H, H-2a), 3.62 (t, $J_{3,3'} = J_{3,2a}$ 9.9 Hz, 1 H, H-3), 3.38 (t, $J_{1,1'} = J_{1,9a}$ 11.5 Hz, 1 H, H-1), 2.94 (dt, $J_{9a,1}$ 11.5, $J_{9a,6b} = J_{9a,1'}$ 6.6 Hz, 1 H, H-9a), 2.67 (q, $J_{6b,6a} = J_{6b,7} = J_{6b,9a}$ 6.6 Hz, 1 H, H-6b), 2.09, 2.08 (s, s, 2 × 3 H, 2 $OCOCH_3$), 1.50, 1.35 [s, s, 2 × 3 H, $OC(CH_3)_2O$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.9 (2 C, $OCOCH_3$), 147.6 (C-9), 127.8 (C-8), 99.6 (C-5), 75.5 (C-7), 71.4 (C-1), 71.0 (2 C, C-6a, C-2a), 70.8 (C-3), 61.6 (C-9′), 45.0 (C-9a), 41.5 (C-6b), 29.2, 18.7 [$OC(CH_3)_2O$], 21.6, 20.8 (2 C, $OCOCH_3$); EIMS: *m*/*z* 239 (20), 137 (20), 134 (25), 91 (100), 43 (51). Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 59.67; H, 6.95.

*(4*S*,4a*R*,4b*S*,8a*R*,9a*S*,9b*S)-6,6′-Dimethyl-4,4a,4b,6,8,8a,9a,9b-octahydro-2*H*-1,5,7,9-tetraoxacyclohexa[g]cyclopent[cd]indene-4-ol acetate* (**4**).—Following the method in Section 3.3 from **2** (23.3 mg, 0.077 mmol), compound **4** (23 mg, 99%)] was obtained after flash chromatography (3:1 hexane–EtOAc): mp 141–144 °C; $[\alpha]_D^{25}$ −91° (*c* 0.1, $CHCl_3$); IR (KBr) *v* 1733, 1241, 1115, 1015, 863 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.27–6.23 (m, 1 H, H-4), 5.70–5.67 (m, 1 H, H-3), 5.42 (d, $J_{9a,9b}$ 4.0 Hz, 1 H, H-9a), 4.54 (dm, $J_{2,2'}$ 13.0 Hz, 1 H, H-2), 4.26 (dm, 1 H, H-2′), 4.15 (ddd, $J_{8a,4b}$ 10.1, $J_{8a,8}$ 9.1, $J_{8a,8'}$ 5.9 Hz, 1 H, H-8a), 3.91 (ddm, $J_{4b,8a}$ 10.1, $J_{4b,4a}$ 6.5 Hz, 1 H, H-4b), 3.88 (dd, $J_{8',8}$ 11.5, $J_{8',8a}$ 5.9 Hz, 1 H, H-8′), 3.54 (dd, $J_{8,8'}$ 11.5, $J_{8,8a}$ 9 Hz, 1 H, H-8), 3.39–3.36 (m, 2 H, H-4a, H-9b), 2.08 (s, 3 H, $COOCH_3$), 1.44, 1.36 [s, s, 2 × 3 H, $OC(CH_3)_2O$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6 ($OCOCH_3$), 147.1 (C-2a), 122.7 (C-3), 99.3 (C-6), 95.1 (C-9a), 84.3 (C-4), 70.0 (C-4b), 63.9 (C-8a), 63.6 (C-8), *63.5 (C-2), *53.9 (C-9b), 39.5 (C-4a), 28.8, 18.5 [2 C, $OC(CH_3)_2O$], 21.4 ($OCOCH_3$); EIMS: *m*/*z* 281 (4), 195 (17), 178 (13), 107 (40), 101 (28), 91 (15), 79 (88), 43 (100). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.64; H, 6.62.

*(4*S*,4a*R*,4b*S*,8a*R*,9a*S*,9b*S)-4-O-[(1,1-Dimethylethyl)dimethylsilyloxy]-4,4a,4b,6,8,8a,9a,9b-octahydro-6-phenyl-2*H*-1,5,7,9-tetraoxacyclohexa[g]cyclopent[cd]indene* (**8**).—To a solution of alcohol **7** (151 mg, 0.5 mmol) in dry CH_2Cl_2 (4.2 mL, 0.12 M) cooled in an ice-bath (0 °C), under Ar and stirring, imidazole (37 mg, 0.55 mmol, 1.1 equiv), *tert*-butyldimethylsilyl chloride (88 mg, 0.55 mmol, 1.1 equiv) and 4-DMAP (cat.) were added. The mixture was warmed at rt for 5 h; then, more imidazole (31 mg, 0.45 mmol, 0.9 equiv), *tert*-butyldimethylsilyl chloride (68 mg, 0.45 mmol, 0.9 equiv) were added. After 24 h the operation was repeated again. Finally, after 48 h the mixture was diluted with CH_2Cl_2, extracted with aq satd $NaHCO_3$ solution and brine. The organic phase was dried (Na_2SO_4), filtered, evaporated and submitted to flash chromatography (9:1 hexane–EtOAc) to give **8** (180 mg, 87%): mp 61–64 °C; $[\alpha]_D^{25}$ +28° (*c* 0.29, $CHCl_3$); IR (KBr) *v* 1371, 1104, 1092, 1071, 1028, 985, 891, 855 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.28 (m, 5 H, C_6H_5), 5.66 (s, 1 H, H-3), 5.47–5.43 (m, 1 H, H-4), 5.42 (d, $J_{9a,9b}$ 4.4 Hz, 1 H, H-9a), 5.39 (s, 1 H, H-6), 4.52 (dm, $J_{2,2'}$ 12.5 Hz, 1 H, H-2), 4.39 (td, $J_{8a,4b} = J_{8a,8}$ 10.0, $J_{8a,8'}$ 5.5, 1 H, H-8a), 4.31 (dd, $J_{8,8'}$ 10.0, $J_{8',8a}$ 5.5 Hz, 1 H, H-8′), 4.23 (dm, $J_{2,2'}$ 12.5 Hz, 1 H, H-2′), 3.88 (dd, $J_{4b,8a}$ 10.0, $J_{4b,4a}$ 5.9 Hz, 1 H, H-4b), 3.47 (t, $J_{8,8'} = J_{8,8a}$ 10.0 Hz, 1 H, H-8), 3.36–3.33 (m, 1 H, H-9b), 3.23 (dt, $J_{4a,4}$ 8.8, $J_{4a,4b} = J_{4a,9b}$ 5.9 Hz, 1 H, H-4a), 0.74 [s, 9 H, $Si(CH_3)_2C(CH_3)_3$], 0.03, −0.28 [s, s, 2 × 3 H, $Si(CH_3)_2C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5 (C-2a) 137.7–126.3 (C_6H_5), 127.7 (C-3), 101.9 (C-6), 95.3 (C-9a), 84.4 (C-4), 77.9 (C-4b), 70.9 (C-8), 63.7 (C-2), 63.4 (C-8a), 54.3 (C-9b), 41.4 (C-4a), 26.0 [$Si(CH_3)_2C(CH_3)_3$], 18.5 [$Si(CH_3)_2C(CH_3)_3$], −5.2, −5.5 [2 C, $Si(CH_3)_2C(CH_3)_3$]; EIMS: *m*/*z* 359 (49), 225 (43), 207 (58), 181 (35), 161 (38), 129 (35), 105 (36), 91 (100). Anal. Calcd for $C_{23}H_{32}O_5Si$: C, 66.32; H, 7.74. Found: C, 66.08, H, 7.45.

(4S,4aR,4bS,8aR,9aS,9bS) - 4 - Methoxy-4,4a,4b,6,8,8a,9a,9b - octahydro - 6 - phenyl - 2H-1,5,7,9-tetraoxacyclohexa[g]cyclopent[cd]indene (**9**).—To a solution of **7** (110 mg, 0.36 mmol) in dry DMF (2.4 mL, 0.15 M) cooled at 0 °C, under Ar and stirring, NaH (66 mg, 1.1 mmol, 3 equiv, 60% dispersion in oil) and methyl iodide (0.07 mL, 1.1 mmol, 3 equiv) were added. The mixture was warmed at rt in 6 h. The solvent was removed and the crude reaction mixture was diluted with EtOAc (20 mL), and extracted with aq satd NaCl solution. The organic phase was dried (Na_2SO_4), filtered, and the solvent was evaporated and the crude reaction mixture was submitted to flash chromatography (3:2 hexane–EtOAc) to give **9** (99 mg, 86%): oil; $[\alpha]_D^{25}$ −26° (*c* 0.29, $CHCl_3$); IR (KBr) *v* 1372, 1125, 1037, 1014, 976, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.32 (m, 5 H, C_6H_5), 5.80 (s, 1 H, H-3), 5.41 (d, $J_{9a,9b}$ 4.2 Hz, 1 H, H-9a), 5.37 (s, 1 H, H-6), 4.97 (m, 1 H, H-4), 4.53 (d, $J_{2,2'}$ 12.8 Hz, 1 H, H-2), 4.35–4.22 (m, 3 H, H-8a, H-2′, H-8), 3.85 (dd, $J_{4b,8a}$ 9.8, $J_{4b,4a}$ 5.9 Hz, 1 H, H-4b), 3.35 (s, 3 H, OCH_3), 3.50–3.48 (m, 1 H, H-8′), 3.40–3.28 (m, 2 H, H-4a, H-9b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8 (C-2a), 144.7–126.4 (C_6H_5), 125.1 (C-3), 102.4 (C-6), 95.2 (C-9a), 84.2 (C-4), 77.7 (C-4b), 70.6 (C-8), 63.6 (C-8a), 62.7 (C-2), 59.5 (OCH_3), 53.3 (C-9b), 39.8 (C-4a); EIMS: *m/z* 180 (29), 149 (25), 109 (64), 107 47), 105 (66), 91 (94), 79 (100). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.45; H, 6.24.

Reduction of compound **8** *in methylene chloride*.—Following the method in Section 3.2 in CH_2Cl_2 at −40 °C, **8** (92 mg, 0.22 mmol) was treated with DIBALH (0.66 mL, 3.0 equiv, 1.0 M in toluene). After 4 h, more DIBALH (0.44 mL, 2.0 equiv) were added. After usual work-up and flash chromatography of the crude reaction mixture (7:3 hexane–EtOAc) we isolated compounds (2a*R*,6a*S*,6b*R*,7*S*,9a*S*)-7-[(1,1-dimethylethyl)dimethylsilyloxy]-1,2a,3,5,6a,6b,7,9a-octahydro-5-phenyl-4,6-dioxacyclohexa[e]cyclopenta[c]pyran-9-methanol (**10**) (73 mg, 79%) and **11** (7.4 mg, 8%), characterized as its diacetate {(3*R*,4*S*,4a*R*,5*S*,7a*S*)-3-acetyloxymethyl - 5 - [(1,1 - dimethylethyl)dimethylsilyloxy] - 4 - (phenylmethoxy) - 1,3,4,4a,5,7a-hexahydro - cyclopenta[c]pyran - 7 - methanol acetate} (**13**). Compound **10**: mp 81–84 °C; $[\alpha]_D^{25}$ +144° (*c* 0.20, $CHCl_3$); IR (KBr) *v* 3437, 1115, 1077, 1048, 837, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.54–7.34 (m, 5 H, C_6H_5), 5.86 (br s, 1 H, H-8), 5.58 (s, 1 H, H-5), 4.82 (dd, $J_{7,6b}$ 6.1, $J_{7,8}$ 2.2 Hz, 1 H, H-7), 4.33 (dd, $J_{3',3}$ 10.0, $J_{3',2a}$ 5.0 Hz, 1 H, H-3′), 4.24 (td, $J_{2a,6a} = J_{2a,3}$ 10.0, $J_{2a,3'}$ 5.0 Hz, 1 H, H-2a), 4.20 (br s, 2 H, 2 H-9′), 4.14 (dd, $J_{1',1}$ 11.0, $J_{1',9a}$ 6.1 Hz, 1 H, H-1′), 3.96 (dd, $J_{6a,2a}$ 10.0, $J_{6a,6b}$ 6.1 Hz, 1 H, H-6a), 3.59 (t, $J_{3,3'} = J_{3,2a}$ 10.0 Hz, 1 H, H-3), 3.56 (t, $J_{1,1'} = J_{1,9a}$ 11.0 Hz, 1 H, H-1), 2.91 (dt, $J_{9a,1}$ 11.0, $J_{9a,1'} = J_{9a,6b}$ 6.1 Hz, 1 H, H-9a), 2.56 (q, $J_{6b,7} = J_{6b,6a} = J_{6b,9a}$ 6.1 Hz, 1 H, H-6b), 1.59 (br s, 1 H, OH), 0.89 [s, 9 H, $Si(CH_3)_2C(CH_3)_3$], 0.04, 0.03 [s, s, 2 × 3 H, $Si(CH_3)_2C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1 (C-9), 137.8–126.4 (C_6H_5), 129.7 (C-8), 102.6 (C-5), 80.1 (C-6a), 75.1 (C-7), 71.7 (C-1), 70.3 (C-3), 68.8 (C-2a), 61.1 (C-9′), 45.3 (C-9a), *43.9 (C-6b), *25.9 [$Si(CH_3)_2C(CH_3)_3$], 17.9 [$Si(CH_3)_2C(CH_3)_3$], −4.5, −4.8 [2 C, $Si(CH_3)_2C(CH_3)_3$]; EIMS: *m/z* 269 (36), 251 (30), 133 (30), 129 (27), 105 (50), 75(100). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 65.99; H, 8.19. Found: C, 66.15; H, 8.48. Compound **13** [obtained from **11** (7.4 mg, 0.018 mmol) following the method in Section 3.3 after flash chromatography (4:1 hexane–EtOAc): **13** (7.2 mg, 81%)]: oil; $[\alpha]_D^{25}$ +162° (*c* 0.36, $CHCl_3$); IR (KBr) *v* 1742, 1455, 1367, 1246, 1104, 1075, 1042, 880, 837, 776 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.35–7.26 (m, 5 H, C_6H_5), 5.84 (br s, 1 H, H-6), 4.77 (dd, $J_{5,4a}$ 6.0, $J_{5,6}$ 2.4 Hz, 1 H, H-6), 4.63 (d, $J_{7'A,7'B}$ 13.9 Hz, 1 H, H-7′A), 4.63 (d, *J* 11.7 Hz, 1 H, $OCH_2C_6H_5$), 4.56 (d, $J_{7'A,7'B}$ 13.9 Hz, 1 H, H-7′B), 4.51 (d, *J* 11.7 Hz, 1 H, $OCH_2C_6H_5$), 4.34 (dm, $J_{3a',3a}$ 9.7 Hz, 1 H, H-3a′), 4.19–4.13 (m, 2 H, H-3, H-3a), 4.10 (dd, $J_{1',1}$ 11.2, $J_{1',7a}$ 6.0 Hz, 1 H, H-1′), 3.69 (dd, $J_{4,3}$ 9.8, $J_{4,4a}$ 6.0 Hz, 1 H, H-4), 3.49 (t, $J_{1,1'} = J_{1,7a}$ 11.2 Hz, 1 H, H-1), 2.73 (dt, $J_{7a,1}$ 11.2, $J_{7a,1'} = J_{7a,4a}$ 6.0 Hz, 1 H, H-7a), 2.55 (q, $J_{4a,5} = J_{4a,4} = J_{4a,7a}$ 6.0 Hz, 1 H, H-4a), 2.05, 2.01 (s, s, 2 × 3 H, 2 $OCOCH_3$), 0.83 [s, 9 H, $Si(CH_3)_2C(CH_3)_3$], 0.05, −0.016 [s, s, 2 × 3 H, $Si(CH_3)_2C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0 ($OCOCH_3$), 170.5 ($OCOCH_3$), 144.5 (C-7), 138.2–127.7 (C_6H_5),

131.8 (C-6), 75.8 (C-5), 75.4 (C-3), 73.5 (C-4), 71.6 (2 C, C-1, $OCH_2C_6H_5$), 64.2 (C-3a), 62.1 (C-7′), 45.0 (C-7a), 43.2 (C-4a), 25.8 [$Si(CH_3)_2C(CH_3)_3$], 20.9, 20.8 (2 $OCOCH_3$), 17.9 [$Si(CH_3)_2C(CH_3)_3$], −4.6, −5.0 [2 C, $Si(CH_3)_2C(CH_3)_3$]; EIMS: *m*/*z* 339 (25), 297 (37), 295 (42), 235 (29), 145 (24), 117 (38), 92 (26), 91 (100). Anal. Calcd for $C_{27}H_{40}O_7Si$: C, 64.26; H, 7.99. Found: C, 64.18; H, 7.65.

*(2a*R,*6a*S,*6b*R,*7*S,*9a*S*) - 7 - [(1,1 - Dimethylethyl)dimethylsilyloxy] - 1,2a,3,5,6a,6b,7,9a - octahydro - 5 - phenyl - 4,6 - dioxacyclohexa[e]cyclopenta[c]pyran - 9 - methanol acetate* (**12**).—Following the method in Section 3.3: from compound **10** (17 mg, 0.041 mmol), product **12** (18.5 mg, 99%) was isolated after flash chromatography (9:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +140° (*c* 0.27, $CHCl_3$); IR (KBr) *ν* 1739, 1381, 1241, 1114, 1083, 1062, 832, 779, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.53–7.34 (m, 5 H, C_6H_5), 5.90 (br s, 1 H, H-8), 5.57 (s, 1 H, H-5), 4.80 (dd, $J_{7,6b}$ 6.4, $J_{7,8}$ 2.3 Hz, 1 H, H-7), 4.68 (d, $J_{9'A,9'B}$ 13.5 Hz, 1 H, H-9′A), 4.59 (d, $J_{9'A,9'B}$ 13.5 Hz, 1 H, H-9′B), 4.32 (dd, $J_{3',3}$ 10.0, $J_{3',2a}$ 5.0, 1 H, H-3′), 4.22 (td, $J_{2a,6a} = J_{2a,3} = 10.0$, $J_{2a,3'}$ 5.0 Hz, 1 H, H-2a), 4.13 (dd, $J_{1',1}$ 11.0, $J_{1',9a}$ 6.4 Hz, 1 H, H-1′), 3.94 (dd, $J_{6a,2a}$ 10.0, $J_{6a,6b}$ 6.4 Hz, 1 H, H-6a), 3.58 (t, $J_{3,3'} = J_{3,2a}$ 10.0 Hz, 1 H, H-3), 3.55 (t, $J_{1,1'} = J_{1,9a}$ 11.0 Hz, 1 H, H-1), 2.88 (dt, $J_{9a,1}$ 11.0, $J_{9a,1'} = J_{9a,6b}$ 6.4 Hz, 1 H, H-9a), 2.56 (q, $J_{6b,7} = J_{6b,6a} = J_{6b,9a}$ 6.4 Hz, 1 H, H-6b), 2.10 (s, 3 H, $OCOCH_3$), 0.88 [s, 9 H, $Si(CH_3)_2C(CH_3)_3$], 0.08, 0.015 [s, s, 2 × 3 H, $Si(CH_3)_2C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.5 ($OCOCH_3$), 143.9 (C-9), 137.8–126.4 (C_6H_5), 132.6 (C-8), 102.6 (C-5), 80.0 (C-6a), 75.1 (C-7), 71.5 (C-1), *70.3 (C-3), *68.8 (C-2a), 62.0 (C-9′), 45.6 (C-9a), 43.9 (C-6b), 25.9 [$Si(CH_3)_2C(CH_3)_3$], 20.8 ($OCOCH_3$), 17.9 [$Si(CH_3)_2C(CH_3)_3$], −4.5, −4.8 [2 C, $Si(CH_3)_2C(CH_3)_3$]; EIMS: *m*/*z* 219 (25), 207 (56), 193 (25), 117 (64), 105 (36), 91 (100). Anal. Calcd for $C_{25}H_{36}O_6Si$: C, 65.19; H, 7.88. Found: C, 65.02; H, 7.46.

*(2a*R,*6a*S,*6b*R,*7*S,*9a*S*) - 7 - [(1,1 - Dimethylethyl)dimethylsilyloxy] - 1,2a,3,5,6a,7,9a - octahydro - 5 - phenyl - 4,6 - dioxacyclohexa[e]cyclopenta[c]pyran - 9 - carbaldehyde* (**14**).—To a solution of alcohol **10** (73 mg, 0.17 mmol) in dry CH_2Cl_2 (2 mL, 0.087 M), AcONa (4.3 mg, 0.35 mmol, 0.3 equiv), powdered molecular sieves 4 Å (55 mg) and PCC (75 mg, 0.35 mmol, 2 equiv) were added. The mixture was stirred at rt for 5 h. Filtration over Celite, evaporation and flash chromatography (19:1 hexane–EtOAc) afforded aldehyde **14** (59 mg, 82%): oil; $[\alpha]_D^{25}$ +141° (*c* 0.54, $CHCl_3$); IR (KBr) *ν* 1685, 1471, 1383, 1255, 1158, 1114, 1084, 1003, 837, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 9.82 (s, 1 H, CHO), 7.54–7.34 (m, 5 H, C_6H_5), 6.87 (d, $J_{8,7}$ 2.6 Hz, 1 H, H-8), 5.60 (s, 1 H, H-5), 5.01 (dd, $J_{7,6b}$ 6.2, $J_{7,8}$ 2.6 Hz, 1 H, H-7), 4.34 (dd, $J_{3',3}$ 9.9, $J_{3',2a}$ 5.0 Hz, 1 H, H-3′), 4.28 (dd, $J_{1',1}$ 11.4, $J_{1',9a}$ 6.2 Hz, 1 H, H-1′), 4.16 (td, $J_{2a,6a} = J_{2a,3}$ 9.9, $J_{2a,6a'}$ 5.0 Hz, 1 H, H-2a), 4.01 (dd, $J_{6a,2a}$ 9.9, $J_{6a,6b}$ 6.2 Hz, 1 H, H-6a), 3.61 (t, $J_{3,3'} = J_{3,2a}$ 9.9 Hz, 1 H, H-3), 3.41 (t, $J_{1,1'} = J_{1,9a}$ 11.4 Hz, 1 H, H-1), 3.29 (dt, $J_{9a,1}$ 11.4, $J_{9a,1'} = J_{9a,6b}$ 6.2 Hz, 1 H, H-9a), 2.59 (q, $J_{6b,7} = J_{6b,6a} = J_{6b,9a}$ 6.2 Hz, 1 H, H-6b), 0.89 [s, 9 H, $Si(CH_3)_2C(CH_3)_3$], 0.061, 0.059 [s, s, 2 × 3 H, $Si(CH_3)_2C(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 190.0 (CHO), 151.2 (C-8), 149.3 (C-9); 137.6–126.3 (C_6H_5), 102.5 (C-5), 79.5 (C-6a), 75.0 (C-7), 70.7 (C-1), 70.2 (C-3), 68.9 (C-2a), 43.1 (C-9a), 42.3 (C-6b), 25.8 [$Si(CH_3)_2C(CH_3)_3$], 17.9 [$Si(CH_3)_2C(CH_3)_3$], −4.6, −4.9 [2 C, $Si(CH_3)_2C(CH_3)_3$]; EIMS: *m*/*z* 359 (76), 267 (38), 253 (51), 181 (43), 129 (35), 105 (66), 75 (100). Anal. Calcd for $C_{23}H_{32}O_5Si$: C, 66.31; H, 7.74. Found: C, 66.16; H, 7.52.

Reduction of compound **9**.—Following the method in Section 3.2, **9**, in CH_2Cl_2 at −40 °C, (99 mg, 0.31 mmol), was treated with DIBALH (0.94 mL, 3.0 equiv). After 4 h, more DIBALH (0.6 mL, 2.0 equiv) and after 3 h further, DIBALH (0.3 mL, 1 equiv) was added. After usual work-up and flash chromatography of the crude reaction product (7:3 hexane–EtOAc) we isolated compounds *(2a*R*,6a*S*,6b*R*,7*S*,9a*S*)*-7-methoxy-1,2a,3,5,6a,6b,7,9a-octahydro-5-phenyl-4,6-dioxacyclohexa[e]cyclopenta[c]pyran-9-methanol (**15**) (32 mg, 32%) and (3*R*,4*S*,4a*R*,5*S*,7a*S*)-3-hydroxymethyl-1,3,4,4a,5,7a-hexahydro-5-methoxy-4-phenylmethoxy-cyclopenta[c]pyran-7-methanol (**16**) (34 mg, 34%). Compound **15**: mp 107–110 °C; $[\alpha]_D^{25}$ +159° (*c* 0,07, $CHCl_3$); IR (KBr) *ν* 3426, 1110, 1083, 1005 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.53–7.34 (m, 5

H, C_6H_5), 6.00 (d, $J_{8,7}$ 1.5 Hz, 1 H, H-8), 5.58 (s, 1 H, H-5), 4.30 (dd, $J_{3',3}$ 10.0, $J_{3',2a}$ 4.9 Hz, 1 H, H-3′), 4.29 (dd, $J_{7,6b}$ 6.2, $J_{7,8}$ 1.5 Hz, 1 H, H-7), 4.18 (br d, $J_{9',OH}$ 4.4 Hz, 2 H, 2 H-9′), 4.14 (dd, $J_{1',1}$ 11.2, $J_{1',9a}$ 6.2 Hz, 1 H, H-1′), 4.04 (td, $J_{2a,6a} = J_{2a,3}$ 10.0, $J_{2a,3'}$ 4.9 Hz, 1 H, H-2a), 3.95 (dd, $J_{6a,2a}$ 10.0, $J_{6a,6b}$ 6.2 Hz, 1 H, H-6a), 3.59 (t, $J_{3,3'} = J_{3,2a}$ 10.0 Hz, 1 H, H-3), 3.48 (s, 3 H, OCH_3), 3.47 (t, $J_{1,1'} = J_{1,9a}$ 11.2 Hz, 1 H, H-1), 2.90 (dt, $J_{9a,1}$ 11.2, $J_{9a,1'} = J_{9a,6b}$ 6.2 Hz, 1 H, H-9a), 2.59 (q, $J_{6b,7} = J_{6b,6a} = J_{6b,9a}$ 6.2 Hz, 1 H, H-6b), 1.69 (t, $J_{OH,9'}$ 4.4 Hz, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.6 (C-9), 137.8–126.3 (C_6H_5), 127.3 (C-8), 102.7 (C-5), 84.5 (C-7), 79.6 (C-6a), 71.9 (C-1), 70.3 (C-3), 69.1 (C-2a), 61.2 (C-9′), 58.8 (OCH_3), 45.2 (C-9a), 43.6 (C-6b); EIMS: m/z 270 (7), 164 (21), 135 (51), 105 (52), 91(76), 79 (100). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.96. Found: C, 67.96; H, 7.30. Compound **16**: oil; IR (KBr) ν 3436, 2239, 1453, 1077, 910, 734 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.26 (m, 5 H, C_6H_5), 6.03 (br d, $J_{6,5}$ 1.8 Hz, 1 H, H-6), 4.59 (s, 2 H, $OCH_2C_6H_5$), 4.46 (dm, $J_{5,4a}$ 6.5 Hz, 1 H, H-5), 4.17 (br s, 2 H, 2 H-7′), 4.11 (ddm, $J_{1',1}$ 11.0, $J_{1',7a}$ 6.4 Hz, 1 H, H-1′), 3.85 (dd, $J_{4,3}$ 9.8, $J_{4,4a}$ 7.5 Hz, 1 H, H-4), 3.80 (dm, $J_{3a',3a}$ 9.9, $J_{3a',3}$ 2.2 Hz, 1 H, H-3a′), 3.63 (ddd, $J_{3,4}$ 9.8, $J_{3,3a}$ 6.1, $J_{3,3a'}$ 2.2 Hz, 1 H, H-3), 3.56 (dd, $J_{3a,3a'}$ 9.9, $J_{3a,3}$ 6.1 Hz, 1 H, H-3a), 3.31 (t, $J_{1,1'} = J_{1,7a}$ 11.0 Hz, 1 H, H-1), 3.30 (s, 3 H, OCH_3), 3.04 (d, $J_{OH,3a}$ 10.9 Hz, 1 H, OH), 2.83–2.75 (m, 1 H, H-7a), 2.55 (q, $J_{4a,5} = J_{4a,4} = J_{4a,7a}$ 6.0 Hz, 1 H, H-4a), 1.68 (br d, $J_{OH,7'}$ 14.7 Hz, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5 (C-7), 138.1–127.5 (C_6H_5), 123.7 (C-6), 84.8 (C-5), 80.0 (C-3), 73.6 ($OCH_2C_6H_5$), 71.1 (C-1), *70.8 (C-3a), *67.5 (C-4), 61.2 (C-7′), 55.8 (OCH_3), 44.7 (C-7a), *43.8 (C-4a); *EIMS: m/z 288 (9), 107 (29), 91 (100). Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.32; H, 7.87.

*(3*R,*4*S,*4a*R,*5*S,*7a*S)*-4-Acetyloxy-3-(phenylmethoxy)methyl - 1,3,4,4a,5,7a - hexahydro - 5-methoxy-cyclopenta[c]pyran-7-methanol acetate* (**17**).—Following the method in Section 3.3, compound **16** (15 mg, 0.047 mmol) afforded **17** (17 mg, 90%), after chromatography (7:3 hexane–EtOAc): oil; $[\alpha]_D^{25}$ + 169° (*c* 1.44, $CHCl_3$); IR (film) ν 2929, 2869, 1738, 1454, 1372, 1238, 1092, 1035, 924, 737, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.28 (m, 5 H, C_6H_5), 6.06 (br d, $J_{6,5}$ 1.2 Hz, 1 H, H-6), 5.13 (dd, $J_{4,3}$ 10.4, $J_{4,4a}$ 6.6 Hz, 1 H, H-4), 4.65 (d, $J_{7'A,7'B}$ 14.0 Hz, 1 H, H-7′A), 4.65 (d, *J* 12.2 Hz, 1 H, $OCH_2C_6H_5$), 4.57 (d, $J_{7'A,7'B}$ 14.0 Hz, 1 H, H-7′B), 4.47 (d, *J* 12.2 Hz, 1 H, $CH_2C_6H_5$), 4.16 (ddd, $J_{1,1'}$ 11.0, $J_{1',7a}$ 6.6, *J* 1.2 Hz, 1 H, H-1′), 4.07 (dd, $J_{5,4a}$ 6.6, *J* 2.3 Hz, 1 H, H-5), 4.01 (ddd, $J_{3,4}$ 10.4, $J_{3,3a}$ 5.0, $J_{3,3a'}$ 2.3 Hz, 1 H, H-3), 3.56 (dd, $J_{3a',3a}$ 10.5, $J_{3a',3}$ 2.3 Hz, 1 H, H-3a′), 3.47 (dd, $J_{3a,3a'}$ 10.5, $J_{3a,3}$ 5.0 Hz, 1 H, H-3a), 3.44 (t, $J_{1,1'} = J_{1,7a} = 11.0$ Hz, H-1), 3.13 (s, 3 H, OCH_3), 2.85 (dt, $J_{7a,1}$ 11.0, $J_{7a,1'} = J_{7a,4a}$ 6.6 Hz, 1 H, H-7a), 2.80 (q, $J_{4a,5} = J_{4a,4} = J_{4a,7a}$ 6.6 Hz, 1 H, H-4a), 2.07, 1.99 (s, s, 2 × 3 H, 2 $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.7 (2 $OCOCH_3$), 146.4 (C-7), 138.3–127.8 (C_6H_5), 129.0 (C-6), 84.5 (C-5), 75.9 (C-3), 73.7 ($OCH_2C_6H_5$), 71.6 (C-1), 69.4 (C-3a), 69.3 (C-4), 62.3 (C-7′), 57.8 (OCH_3), 45.2 (C-7a), 42.8 (C-4a), 21.2, 21.1 (2 $OCOCH_3$); EIMS: m/z 372 (4), 266 (11), 163 (35), 121 (26), 91 (100), 43 (57). Anal. Calcd for $C_{22}H_{28}O_7$: C, 65.33; H, 6.98. Found: C, 65.47; H, 6.77.

Acknowledgements

J.R.C. is a fellow of the Consejería de Educación y Cultura (CAM). The authors thank one of the referees for attracting our attention to some details of the mechanism of the DIBALH reduction process.

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