Carbohydrate Research, 205 (1990) 283–291
Elsevier Science Publishers B.V., Amsterdam

Hexa-*O*-benzyl-5-hydroxy-pseudo-α-D-glucopyranose and its C-5 epimer*†

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(Received February 2nd, 1990; accepted for publication, March 17th, 1990)

ABSTRACT

(2*S*)-(2,4,5/3)-2,3,4-Tribenzyloxy-5-(tetrahydropyran-2-yloxy)cyclohexanone (**9**), when treated with vinylmagnesium bromide and trimethylsilylmethylmagnesium chloride, gave (1*S*)-(1O,2,4,5/1C,3)-2,3,4-tribenzyloxy-5-(tetrahydropyran-2-yloxy)-1-vinylcyclohexanol (**10**) and (1*R*)-(1O,2,4,5/1C,3)-2,3,4-tribenzyloxy-1-(trimethylsilylmethyl)cyclohexane-1,5-diol (**16**), respectively, with the *S* configuration at C-1 exclusively. Following oxidative cleavage of the double bond, **10** was converted into (1*S*)-(1O,2,4,5/1C,3)-1,2,3,4,5-pentabenzyloxy-1-(benzyloxymethyl)cyclohexane (**14**), the C-5 epimer **19** of which was obtained from the trimethylsilylmethyl-substituted adduct following hydroxylation of the double bond of the derived (2*R*)-(2,4,5/3)-2,3,4-tribenzyloxy-5-hydroxy-1-methylenecyclohexane (**17**). (2*S*)-(2,4,5/3)-2,3,4-Tribenzyloxy-5-hydroxycyclohexanone (**7**) was converted into its enantiomer **26** and into (1*S*)-(1O,2,4,5O/1C,5C)-2,3,4-tribenzyloxy-5-(trimethylsilyl)methyl-1-vinylcyclohexane-1,5-diol (**28**).

INTRODUCTION

The chemistry of the pseudo-pyranoses, *i.e.*, analogues of the pyranoid sugars that have a methylene group instead of the ring oxygen atom, has been well developed, notably by S. Ogawa and his co-workers, who mainly used racemic compounds derived by Diels–Alder procedures[1]. Because of the biological significance of these compounds, however, pure enantiomers are of particular interest, and appreciable effort has been expended on procedures to make them and their derivatives available from naturally occurring, inexpensive sugars[2–4]. The occurrence of valienamine (**1**) in acarbose and related inhibitors of alpha-amylase[5], the inhibitory activity[6] of **1**, and the occurrence of **1**, validamine (**2**), and hydroxyvalidamine (**3**) in validamycin A[7], B, and G[8], respectively, have called attention to the potential importance of pseudo-sugar derivatives. Validamycins B and G also contain the tertiary alcohol valiolamine (**4**), the first naturally occurring pseudo-sugar with a 5-hydroxy-pseudo-hexopyranose structure to be recognised[9]. The relatively strong α-D-glucosidase inhibitory activity[10] of **4** is of particular significance.

* Dedicated to Professor Leslie Hough in the year of his 65th birthday.
† Functionalised Carbocycles from Carbohydrates, Part 12. For Part 11, see R. J. Ferrier and A. E. Stütz, Carbohydr. Res., 1990, 200 (1990) 237–245.
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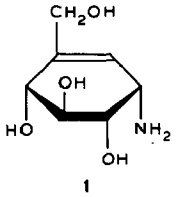
0008-6215/90/$ 03.50

Our interests in pseudo-pyranoses arose from the convenient route of synthesis to 2-deoxyinosose derivatives from substituted 6-deoxyhex-5-enopyranoses[11], which has been exploited[3,4,12–15] to obtain a range of pseudo-sugar derivatives. During studies related to the conversion of **5** into pseudo-pyranose derivatives, it was found that, with diazomethane, **5** gave mainly[16] the bicyclic tertiary alcohol **6**, and Köhn and Schmidt[13] observed the analogous formation, from **7**, of the tribenzyl derivative **8**. These results prompted a consideration of routes of synthesis of compounds of the valiolamine type and their tertiary-centre epimers.

After the structure of valiolamine, especially the configuration at the tertiary centre, had been elucidated[10], several studies were devoted to the 5-hydroxy-pseudo-hexopyranoses; in particular, racemic 5-hydroxy-α- and -β-pseudo-gluco- and -ido-pyranose have been prepared[17]. We now describe stereospecific routes to the compounds with the α-D-*gluco* and β-L-*ido* configurations by modifications of the published procedures. Paulsen and his colleagues[12] developed a non-stereospecific route to valiolamine and several closely related derivatives by initial reaction of a modified 1,3-dithianyl anion at the carbonyl centre of the enone readily obtainable from **7**, and Köhn and Schmidt[13] used the 1,3-dithianyl anion together with **7** (with some of the secondary alcohol epimer) to synthesise 5-hydroxy-pseudo-α- and -β-D-glucose stereospecifically. The entering carbanions attacked the carbonyl groups from the equatorial direction preferentially[18] (in the latter reaction, exclusively), as expected.



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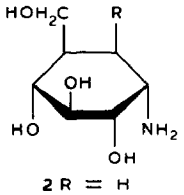

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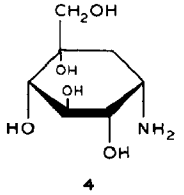
3 R = OH



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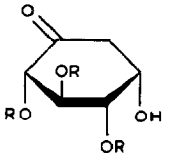

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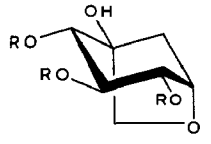
7 R = Bn

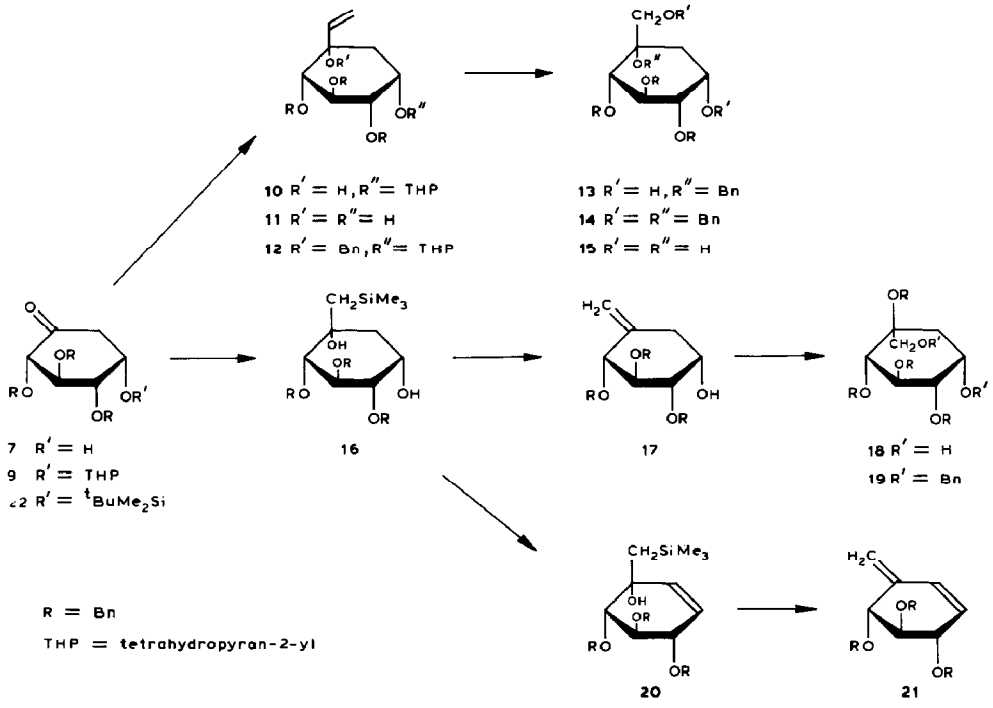


6 R = Bz
8 R = Bn

RESULTS AND DISCUSSION

The first procedure, applied to the tetrahydropyran-2-yl derivative **9** of the tri-*O*-benzyl derivative **7**, involved stereospecific equatorial attack at the carbonyl

group by vinylmagnesium chloride to give the tertiary alcohol **10**, from which the diol **11** was prepared. Benzylation of **10** gave the fully substituted compound **12**, the double bond of which was cleaved with sodium periodate–osmium tetraoxide[19]. Reduction of the resulting aldehyde with sodium borohydride and acid-catalysed removal of the acetal gave the diol **13**, from which the fully benzylated 5-hydroxy-pseudo-α-D-glucopyranose (**14**) was obtained. The hexa-*O*-benzyl product, obtained by benzylation of the 2,3,4-tri-*O*-benzyl derivative **15**, described by Köhn and Schmidt[13], and **14**, gave identical ^{1}H- and ^{13}C-n.m.r. spectra.



Synthesis of the 5-epimer of **14**, *i.e.*, the *β*-L-*ido* derivative, was accomplished by Peterson methylenation[20] (trimethylsilylmethylmagnesium chloride, followed by treatment with acid) of **9** and afforded the alkene **17** by way of the diol **16**. Hydroxylation of the double bond of **17** with *N*-morpholine *N*-oxide and osmium tetraoxide[21] occurred from the equatorial side exclusively to give the tri-*O*-benzyl derivative **18**, benzylation of which gave the fully substituted *β-ido* product **19**, which was readily distinguishable from the isomer **14** by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

Selective triflation at the secondary site of the diol **16** and base-catalysed removal of triflic acid gave the ene **20**, from which the known[15] diene **21** was obtained on treatment with acid. Racemic compounds related to **20** and **21** have been encountered in synthesis studies related to the validamycins[22].

The enantiomeric reversibility of compounds of the readily accessible 2-deoxy-inosose series, and, thus, their extended versatility, was demonstrated by the transfor-

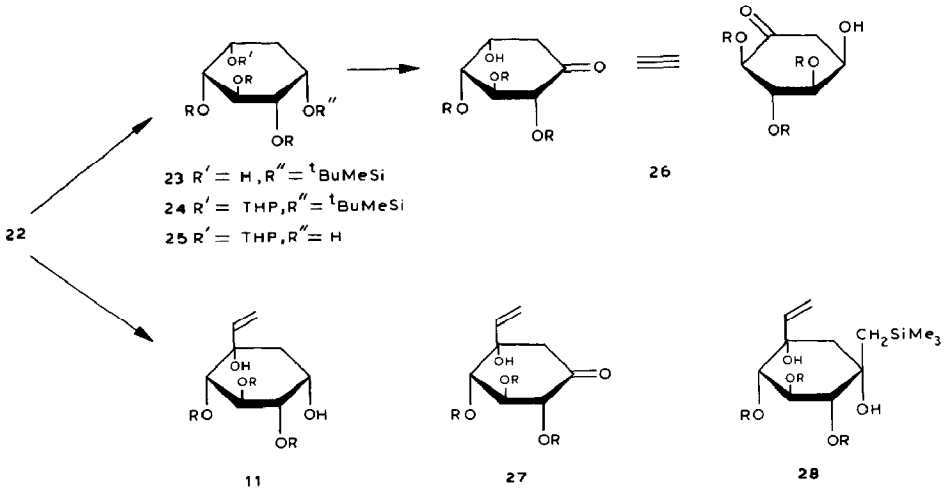


TABLE I

300-MHz ^{1}H-n.m.r. data for solutions in $CDCl_3$

Compound	*Chemical shifts (δ)*						
	H-2	*H-3*	*H-4*	*H-5*	*H-6*	*H-6′*	*Others*
11	3.39	4.11	3.46	4.15	2.07	1.55	H-1′ 5.79, H-1″ 5.42, H-1″ 5.20, Bn
13	3.50	4.25	3.40	4.08	2.20	1.44	H-1′ 3.72, H-1′ 3.62, Bn
14	3.66	4.51	3.48	3.92	2.34	1.61	H-1′ 3.72, H-1′ 3.46, Bn
18	3.62	3.91	3.57	4.09	2.08	1.64	H-1′ 4.13, H-1′ 3.61, Bn
19	3.91	4.14	3.66	4.04	3.15	1.45	H-1′ 4.30, H-1′ 4.19, Bn
22	4.02	4.10	3.69	4.29	2.50	2.42	Bn, Me
23	3.36	4.16	3.30	4.10	2.14	1.44	H-1 4.27, Bn, Me
27	3.84	4.08	4.22		2.61	2.53	H-1′ 6.00, H-1″ 5.48, H-1″ 5.30, Bn
28	3.43	4.09	3.26		2.05	1.50	H-1′ 5.78, H-1″ 5.46, H-1″ 5.20, H-5′ 1.41, H-5′ 0.54, Bn, Me

Compound	*Coupling constants (Hz)*					
	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
11	9.3	9.7	3.1	3.0	3.1	15.4
13	9.9	9.6	3.4	3.0	3.1	15.3
14	9.7	9.5	3.5	3.1	3.3	15.6
18	9.0	8.7	3.4	4.3	3.2	14.7
19	9.1	9.4	3.3	4.0		14.4
22	9.2	9.0	2.0	4.4	2.5	14.4
23	9.4	9.4	2.6	3.3		15.0
27	8.9	9.6				14.4
28	9.5	9.5				15.1

mation of the hydroxyketone **7** into its enantiomer. *tert*-Butyldimethylsilylation of **7** gave the ether **22**, reduction of which with sodium borohydride led to the axial alcohol **23** (ref. 23). Tetrahydropyranylation of **23** gave **24**, and fluoride-catalysed desilylation then gave **25** which was oxidised to the ketone, acid-catalysed removal of the acetal protecting group of which gave the enantiomer (**26**) of **7**. These enantiomers represent selectively oxidised symmetrical pentahydroxycyclohexane derivatives akin to the selectively substituted symmetrical pentahydroxycyclohexane derivatives recently reported[23].

Oxidation of the secondary hydroxyl group of the diol **11** and reaction of the resulting ketone **27** with (trimethylsilyl)methylmagnesium chloride gave a product with $[\alpha]_D$ −28° (dichloromethane) and ^{1}H- and ^{13}C-n.m.r. data consistent with its being the doubly branched compound **28**. Deoxyinositol derivatives having various branch points in the 1,3-relationship are clearly available from **28**, the configuration at C-5 of which is assessed to be as shown, *i.e.*, it is the product of equatorial attack at the carbonyl group as occurred above (**9**→**10**; **9**→**16**).

The ^{1}H- and ^{13}C-n.m.r. spectra of **11**, **13**, **14**, **18**, **19**, **22**, **23**, **27**, and **28** are recorded in Tables I and II, respectively. Compounds **27** and **28** had $[\alpha]_D$ −5.2 and −28.0°, respectively. Correct elemental analyses (C,H) were obtained after the manuscript was submitted.

TABLE II

^{13}C-N.m.r. chemical shifts for solutions in $CDCl_3$

Compound	*Chemical shifts (δ)*[a]			
	C-1–C-4	*C-5*	*C-6*	*Others*
11	85.1, 83.0, 80.8, 77.1	67.7	36.8	142.4, 114.8 (vinyl) 76.2, 76.0, 73.8, 72.4 (CH_2Ph)
13	83.7, 83.65, 82.0, 80.4	67.0[b]	33.8	63.7 (CH_2OH) 76.1, 72.4, 67.5[b] (CH_2Ph)
14	83.5, 83.3, 80.4, 79.4	71.6[b]	30.8	65.9 (CH_2OBn) 75.9, 75.7, 73.7, 73.6, 72.9, 72.2[b] (CH_2Ph)
18	87.5, 82.4, 80.4, 76.5[b]	68.1	36.7	66.0 (CH_2OH) 75.8[b], 74.6, 73.2 (CH_2Ph)
19	86.7, 82.3, 81.1, 75.9[b]		29.3	65.9 (CH_2OBn) 75.7[b], 73.5, 73.45, 72.3, 71.5 (CH_2Ph)
22	203.7 (C-1), 86.0, 82.5, 82.0	68.1	45.3	75.8, 73.6, 73.3 (CH_2Ph), 25.9 (^{t}Bu), −4.34, −4.83 (2 Me)
23	71.9, 83.4, 82.8, 79.3,	68.8	33.6	76.0, 74.0, 72.5 (CH_2Ph), 26.0 (^{t}Bu), −4.2, −5.2 (2 Me)
27	202.8 (C-1), 85.8, 84.3, 83.5	73.8	47.8	115.3, 141.4 (vinyl) 76.3, 76.1, 75.4 (CH_2Ph)
28	87.3, 85.5, 82.7, 76.6[b]	76.5[b]	43.8	142.6, 114.5 (vinyl) 29.0 (CH_2Si) 76.4[b], 76.1, 75.9 (CH_2Ph), 0.8 (CH_3Si)

[a] Appropriate resonances were observed for the benzyl group aromatic carbon atoms. [b] May be interchanged.

EXPERIMENTAL

General procedures. — The ^1H- and ^{13}C-n.m.r. spectra were recorded for solutions in $CDCl_3$ (unless otherwise indicated) with a Bruker MSL 300 or FT80A spectrometer. Optical rotations were determined for 0.5–1% solutions in chloroform (unless otherwise indicated), using a 1-dm cell and a Perkin–Elmer 241 or a Jasco DP Digital polarimeter. Column chromatography was performed on silica gel (Riedel de Haen S, 0.063–0.2 mm).

(1S)-(1O,2,4,5/1C,3)-2,3,4-Tribenzyloxy-1-vinylcyclohexane-1,5-diol (**11**). — The ketone **7** (refs. 13, 24) (4.5 g) in dichloromethane (200 mL) was treated with 3,4-dihydro-2*H*-pyran (4 mL) and pyridinium tosylate (0.5 g) for 15 h at 20°. The solution was washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. Column chromatography (hexane–ethyl acetate, 4:1) of the residue gave a 1.5:1 mixture (4.7 g, 94%) of the tetrahydropyran-2-yl ethers **9**, which were identified by ^{13}C-n.m.r. spectroscopy. A solution of **9** (1.8 g) in tetrahydrofuran (10 mL) was added at −78° to vinylmagnesium bromide (4.3 mol. equiv. in this solvent, 30 mL), and the mixture was stirred for 1 h, then allowed to warm to 20°. Dichloromethane (150 mL) was added, and the organic phase was washed with dilute HCl, aqueous $NaHCO_3$, and water, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate, 5:1) gave **10** (1.65 g, 87%) as a mixture of epimers at the acetal centre. A solution of **10** (1.5 g) in methanol–dichloromethane (100 mL, 1:1) containing *p*-toluenesulphonic acid (0.1 g) was kept for 4 h at 20°. Dichloromethane (150 mL) was added, the solution was washed with aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate, 3:1) of the residue gave **11** as a slightly yellow syrup (1.05 g, 83%), $[\alpha]_D$ −40°.

Anal. Calc. for $C_{29}H_{32}O_5$: C, 75.6; H, 7.0. Found: C, 75.5; H, 7.1.

(1S)-(1O,2,4,5/1C,3)-1,2,3,4-Tetrabenzyloxy-5-(tetrahydropyran-2-yloxy)-1-vinylcyclohexane (**12**). — Oil-free potassium hydride (0.25 g) followed by benzyl bromide (0.72 g) were added to a solution of **10** (0.35 g) in tetrahydrofuran (15 mL) and *N,N*-dimethylformamide (5 mL) at 20° and the brown mixture was stirred for 1 h. Methanol (5 mL) was added slowly, the solution was partitioned between dichloromethane (100 mL) and water, and the organic phase was dried (Na_2SO_4) and concentrated. Column chromatography (hexane–ethyl acetate, 6:1–3:1) of the syrupy residue gave **12** (0.36 g, 88%).

Anal. Calc. for $C_{41}H_{46}O_6$: C, 77.6; H, 7.3. Found: C, 77.2; H, 7.0.

(1S)-(1O,2,4,5/1C,3)-1,2,3,4-Tetrabenzyloxy-5-hydroxy-1-(hydroxymethyl)cyclohexane (**13**). — A saturated aqueous solution of sodium metaperiodate (20 mL) containing osmium tetraoxide (0.01 g) was added to a solution of **12** (0.45 g) in ether (20 mL), and the mixture was stirred vigorously for 12 h at 20°. Ether (70 mL) and water (50 mL) were added, the organic phase was dried (Na_2SO_4), concentrated to 10 mL, and added to a solution of sodium borohydride (0.6 g) in methanol (30 mL) at 0°. After 0.5 h, ethyl acetate was added, the mixture was partitioned between dichloromethane and aqueous 5% HCl, and the organic phase was washed with aqueous $NaHCO_3$, dried

(Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate, 5:1) of the residue gave the hydroxymethyl analogue of the vinyl starting material (0.34 g, 75%).

This product (0.076 g) was treated with *p*-toluenesulphonic acid (0.02 g) in methanol (15 mL) and dichloromethane (15 mL) for 5 h at 20°. The usual processing and column chromatography (hexane–ethyl acetate, 3:1–1:1) gave **13** (0.06 g, 91%), $[\alpha]_D$ −20°.

Anal. Calc. for $C_{35}H_{38}O_6$: C, 75.8; H, 6.9. Found: C, 75.8; H, 7.0.

(1S)-(1O,2,4,5/1C,3)-1,2,3,4,5-Pentabenzyloxy-1-(benzyloxymethyl)cyclohexane (**14**). — Oil-free potassium hydride (0.06 g) followed by benzyl bromide (0.015 g) were added to a solution of **13** (0.05 g) in tetrahydrofuran (12 mL) and *N,N*-dimethylformamide (4 mL), and the mixture was stirred for 2 h at 20°. Methanol (5 mL) was added, the suspension was partitioned between dichloromethane (50 mL) and dilute HCl (50 mL), and the organic phase was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate, 10:1–4:1) of the residue gave **14** (0.059 g, 89%), $[\alpha]_D$ +11°.

A sample (0.05 g) of the tri-*O*-benzyl derivative **15** (ref. 13) was benzylated and the product was isolated in similar manner, to give **14** with identical ^1H- and ^{13}C-n.m.r. spectra to the compound produced from **13**.

(2R)-(2,4,5/3)-2,3,4-Tribenzyloxy-5-hydroxy-1-methylenecyclohexane (**17**). — A solution of **9** (2.3 g) in tetrahydrofuran (25 mL) was added dropwise to a freshly prepared solution of (trimethylsilylmethyl)magnesium chloride (2.6 g, 4 mol. equiv.) in ether at −78°; the mixture was kept at −78° for 3 h and then allowed to warm to 20° during 16 h. Dichloromethane (200 mL) was added, the solution was extracted with cold dilute HCl, washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. The yellow syrupy residue was treated with *p*-toluenesulphonic acid (0.05 g) in methanol (50 mL) and dichloromethane (50 mL) for 15 h at 20°. The usual processing and column chromatography (hexane–ethyl acetate, 8:1–6:1) gave **16** (1.5 g, 65%) as a colourless syrup, $[\alpha]_D$ −12°.

A solution of **16** (0.70 g) in dichloromethane (40 mL) containing *p*-toluenesulphonic acid (0.20 g) was heated under reflux for 3 h, then washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate, 3:1) of the residue gave **17** (0.41 g, 71%) as a semi-solid mass, which could not be recrystallised, $[\alpha]_D$ −44°.

Anal. Calc. for $C_{28}H_{30}O_4$: C, 78.1; H, 7.0. Found: C, 77.7; H, 7.1.

(1R)-(1C,2,4,5/1O,3)-3,4-Tribenzyloxy-1-(hydroxymethyl)cyclohexane-1,5-diol (**18**). — *N*-Morpholine *N*-oxide monohydrate (0.30 g) followed by osmium tetraoxide (0.008 g) were added to a solution of **17** (0.085 g) in dichloromethane (40 mL), and the mixture was stirred at 20° for 4 h. Saturated aqueous sodium sulphide (5 mL) was added and stirring was continued for 15 min. The mixture was partitioned between water (60 mL) and dichloromethane (50 mL), and the organic phase was dried (Na_2SO_4) and concentrated. Column chromatography (hexane–ethyl acetate, 1:1–1:3) of the residue gave **18** (0.078 g, 85%) as an oil, $[\alpha]_D$ +3.2°.

Anal. Calc. for $C_{28}H_{32}O_6$: C, 72.4; H, 6.9. Found: C, 72.0; H, 7.0.

(1R)-(1C,2,4,5/1O,3)-1,2,3,4,5-Pentabenzyloxy-1-(benzyloxymethyl)cyclohexane (**19**). — A solution of **18** (0.045 g) in tetrahydrofuran (9 mL) and *N,N*-dimethylformamide (3 mL) was treated with oil-free potassium hydride (0.06 g) followed by benzyl bromide (0.21 g), and the mixture was stirred at 20° for 1.5 h. Methanol (5 mL) was added, the mixture was partitioned between dichloromethane (50 mL) and aqueous HCl (50 mL), and the organic phase was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate 10:1–4:1) of the residue gave **19** (0.062 g, 87%) as a colourless syrup, $[\alpha]_D$ +37°.

Anal. Calc. for $C_{49}H_{50}O_6$: C, 80.1; H, 6.9. Found: C, 79.8; H, 6.8.

(3S)-(3,5/4)-3,4,5-Tribenzoyloxy-6-methylenecyclohexene (**21**). — A solution of **16** (0.32 g) in dichloromethane (20 mL) was treated for 1 h at 20° with pyridine (1.5 mL) and trifluoromethanesulphonic anhydride (0.4 mL), each added as a solution in dichloromethane (15 mL). More dichloromethane (30 mL) was added, and the solution was extracted with aqueous $NaHCO_3$, and dried ($MgSO_4$). Treatment of the organic solution with 1,5-diazobicyclo[5.4.0]undec-5-ene (1 mL) yielded two alkenes when the mixture was kept overnight at 20°. The major product (0.11 g, 36% isolated) had $[\alpha]_D$ +50° and was the allyl alcohol **20**. The minor product (0.06 g, 20% isolated) was the vinyl ether (n.m.r. characterisation) formed by elimination of trifluoromethanesulphonic acid in the alternative direction. Pyridinium tosylate (0.002 g) was added to a solution of the major alkene (0.05 g) in methanol (1 mL) and dichloromethane (1 mL). Work-up after 15 min and column chromatography (hexane–ethyl acetate, 4:1) gave **21** (0.025 g, 60%), m.p. 50.5–53°, $[\alpha]_D$ +21°; lit.[15] m.p. 54–55°, $[\alpha]_D$ +28°.

*(2R)-(2,4,5/3)-2,3,4-Tribenzyloxy-5-*tert*-butyldimethylsilyloxycyclohexanone* (**22**). — *tert*-Butyldimethylsilyl chloride (0.3 g) and imidazole (0.5 g) were added to a solution of **7** (0.45 g) in *N,N*-dimethylformamide (0.35 mL), and the solution was kept at 20° for 3 h and then partioned between dichloromethane (70 mL) and aqueous 5% HCl (80 mL). The organic phase was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate, 5:1) of the residue gave **22** (0.49 g, 86%) as a pale-yellow syrup, $[\alpha]_D$ −14°.

Anal. Calc. for $C_{33}H_{42}O_5Si$: C, 72.5; H, 7.7. Found: C, 72.2; H, 7.9.

*(1R)-(1,2,4,5/3)-2,3,4-Tribenzyloxy-5-*tert*-butyldimethylsilyloxycyclohexanol* (**23**). — A solution of **22** (0.25 g) in methanol (10 mL) at 0° was added with stirring to a solution of sodium borohydride (0.15 g) in methanol (25 mL). After 0.5 h, the mixture was partitioned between dichloromethane (60 mL) and dilute HCl (50 mL), and the organic phase was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. Column chromatography (hexane–ethyl acetate, 3:1) of the residue gave **23** (0.135 g, 90%) as a white wax, $[\alpha]_D$ +5.2°.

Anal. Calc. for $C_{33}H_{44}O_5Si$: C, 72.3; H, 8.1. Found: C, 72.2; H, 8.1.

(2R)-(2,4,5/3)-2,3,4-Tribenzyloxy-5-hydroxycyclohexanone (**26**). — To a solution of **23** (0.12 g) in dichloromethane (35 mL) were added 3,4-dihydro-2*H*-pyran (0.5 mL) and pyridinium tosylate (0.1 g). The solution was kept at 20° for 3 h, then washed with aqueous $NaHCO_3$ dried (Na_2SO_4), and concentrated. To a solution of the residue

in tetrahydrofuran (25 mL) was added M tetrabutylammonium fluoride trihydrate in tetrahydrofuran (1.5 mL). After 10 h, the solvent was removed and the residue was purified by column chromatography (hexane–ethyl acetate, 3:1). A solution of the resulting oil in dichloromethane (15 mL) was stirred with pyridinum dichromate (0.35 g) for 8 h at 20° and the inorganic materials were removed by filtration through silica gel. Methanol (15 mL) and *p*-toluenesulphonic acid (0.05 g) were added, and the solution was kept at 3 h for 20° and then partitioned between dichloromethane (50 mL) and aqueous $NaHCO_3$ (50 mL). The organic phase was dried (Na_2SO_4) and concentrated. Column chromatography (hexane–ethyl acetate 3:2) of the residue gave **26** (0.054 g, 57%) as an oil, $[\alpha]_D$ +42°, the ^{1}H-and ^{13}C-n.m.r. spectra of which were identical to those of **7**; lit.[15] m.p. 113–114°, $[\alpha]_D$ −51°, for **7**.

Anal. Calc. for $C_{27}H_{28}O_5$: C, 75.0; H, 6.5. Found: C, 74.9; H, 6.6.

ACKNOWLEDGMENTS

We thank the New Zealand University Grants Committee for the award of a Postdoctoral Fellowship (to A.E.S.), FWF (Vienna) for an Erwin Schrödinger Stipendium, and the Wellington Medical Research Foundation for financial support.

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