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STEREOSPECIFIC SYNTHESIS OF CHIRAL BENZYLIC CENTERS FROM D-*erythro*-PENTULOSE DERIVATIVES*†

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ABSTRACT

Stereospecific, Grignard addition reactions are described that afford *C*-phenyl branched-chain pentitols having either the D-*arabino* (**2**) or D-*ribo* (**19**) stereochemistry, according to the mode of substitution of the starting 2-pentulose. The reaction of 3,5-*O*-benzylidene-1-deoxy-D-*erythro*-2-pentulose (**1**) with phenylmagnesium bromide led stereospecifically to 3,5-*O*-benzylidene-1-deoxy-2-*C*-phenyl-D-arabinitol (**2**), the configuration of which was established by a nuclear Overhauser experiment with its 2,4:3,5-dibenzylidene acetal (**3**). Acid hydrolysis of **2** led to the novel, crystalline 1-deoxy-2-*C*-phenyl-D-arabinitol (**4**), further characterized as its triacetate **5**. In attempts to mask certain hydroxyl groups of **2** selectively, the 2,4-*O*-isopropylidene (**6**) and 2,4-*O*-carbonyl (**7**) derivatives, the 4-acetate **8**, the 4-(trimethylsilyl) and 4-(*tert*-butyldimethylsilyl) ethers (**10** and **17**), and the corresponding 2-phenylcarbamates **9** (from **8**) and **11** (from **10**) were prepared. Catalytic hydrogenolysis of the carbamates **9** and **11** resulted in deoxygenation of the benzylic center with inversion of configuration to give 2(*S*)-3,5-*O*-benzylidene-1,2-dideoxy-2-*C*-phenyl-D-*erythro*-pentitol (**12**; from **11**) and its 4-*O*-acetyl analog **13** (from **9**). Benzylation of the trimethylsilyl ether **10** afforded 2-*O*-benzyl-3,5-*O*-benzylidene-1-deoxy-2-*C*-phenyl-4-*O*-(trimethylsilyl)-D-arabinitol (**15**), together with the corresponding 2,4-dibenzyl ether **14**. Acid hydrolysis of **15** yielded the crystalline, branched-chain, benzyl ether **16**. The *tert*-butyldimethylsilyl ether of **1** reacted with phenylmagnesium bromide to give, exclusively, the *C*-phenyl branched-chain pentitol (**19**) having the D-*ribo* stereochemistry.

INTRODUCTION

Carbohydrates are able to serve[2–4] as readily available and conveniently functionalized sources of asymmetric centers of known, absolute configuration for

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the synthesis of other molecules of biological interest*. Equally important[2,5] is the potential role of carbohydrates in asymmetric syntheses that generally involve conversion of a trigonally hybridized carbon atom, as in a carbonyl[2,6,7], alkenic[8,9], or imino[10,11] group, into a new, asymmetric center. The well-defined and readily varied geometry of carbohydrates provides a useful, asymmetric framework that renders many of these reactions highly stereospecific. After establishing the configuration of the newly formed center by spectroscopic† or other appropriate techniques, it may then be detached from the carbohydrate matrix by suitable, chain-degradative means and then be incorporated into molecules of pharmacological significance.

In this paper, we describe the highly stereospecific, Grignard addition of phenylmagnesium bromide to derivatives of the readily available 1-deoxy-D-*erythro*-pentulose[13] to afford, according to the prior mode of substitution, *C*-phenyl branched-chain pentitols having, exclusively, either the D-*arabino* or the D-*ribo* stereochemistry. These Grignard addition-products having a chiral, benzylic center as part of the carbohydrate molecule could be of interest, after excision of the asymmetric centers not required, as precursors for optically pure atrolactic aldehydes which, condensed with a suitably functionalized glycerol derivative, would allow access to potential anticholinergic agents[2,14] of the dioxolane type. Furthermore, these products, as well as their deoxygenated analogs, also reported herein, could be useful as sources of the chiral center for the synthesis of such biologically significant molecules as hormones and drugs related to[15] epinephrine (adrenaline) and[16] atropine that contain asymmetric, benzylic carbon atoms and whose pharmacological potency depends[17] critically on optical purity and on the configuration of the chiral center.

RESULTS AND DISCUSSION

When 3,5-*O*-benzylidene-1-deoxy-D-*erythro*-2-pentulose[13] (**1**) was treated with phenylmagnesium bromide in ether at 0°, a single, crystalline product, formulated as 3,5-*O*-benzylidene-1-deoxy-2-*C*-phenyl-D-arabinitol (**2**), was obtained in 77% yield after recrystallization. Thorough examination of the mother liquor by t.l.c. and by p.m.r. spectroscopy verified that none of the 2-epimer of **2** had been formed. About 5% of the starting ketone **1** remained unchanged, however, and was recovered by column chromatography, together with a second crop (3%) of **2**.

The configurational assignment of such asymmetric, tertiary alcohols as **2** generally poses considerable difficulties[12], but stereochemical characterization of **2** was convincingly achieved by a nuclear Overhauser experiment[18] with the 2,4:3,5-dibenzylidene acetal **3**. Saturation of the methyl signal at δ 1.80 caused a 30% enhancement of the signal area for the benzylidene proton resonating at δ 6.10. This

*See ref. 4 for two recent examples of syntheses, based on carbohydrate precursors, that lead to prostaglandins and thromboxanes.

†For a simple method of determining the configurations of tertiary alcoholic centers in carbohydrate derivatives, see ref. 12.

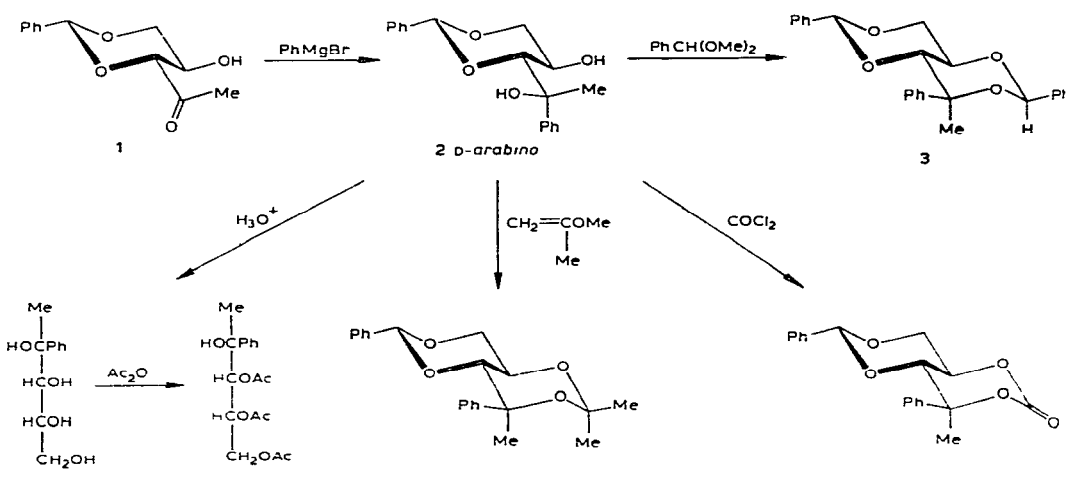
result established unequivocally that the methyl group is in close proximity to the acetal proton, and is entirely consistent with the 1,3-antiparallel disposition of these two groups anticipated for the product having the D-*arabino* configuration.

Compound **2** was unusually resistant to acid hydrolysis, and its conversion into 1-deoxy-2-*C*-phenyl-D-arabinitol (**4**) necessitated the use of 0.5M hydrochloric acid during an extended time at elevated temperature. A crystal-structure determination conducted on **4** confirmed[19] the D-*arabino* stereochemistry, and verified the configurational assignment for the newly formed, benzylic center earlier deduced from p.m.r. data.

In a first attempt to liberate the asymmetric, benzylic center from the carbohydrate framework, for subsequent utilization in the synthesis of compounds having biological interest, the branched-chain *C*-phenylpentitol **4** was subjected to periodate oxidation. However — and in contrast to a similar degradation described by Inch *et al.*[20] — the oxidation could not be arrested after scission of the C-3–C-4 bond to provide the desired, optically pure aldehyde, even when a deficiency of the oxidizing agent was used. The only product obtained in appreciable yield was acetophenone.

In order to prevent overoxidation and to retain the benzylic center, it was obvious that the tertiary alcoholic function had first to be masked by a suitable, temporary protecting group before degradation of the carbon chain by glycol cleavage could be contemplated. In pursuit of this goal, 1-deoxy-2-*C*-phenyl-D-arabinitol (**4**) was converted into the crystalline triacetate **5** which, however, utterly failed to react either with phenyl isocyanate in pyridine, or with[21] diazomethane in dichloromethane in the presence of boron trifluoride etherate: in both instances, the starting triacetate **5** was recovered quantitatively.

In another attempt, the benzylidene acetal **2** was treated with isopropenyl



Scheme 1

TABLE I

100-MHz ^{1}H-N.M.R. SPECTRAL DATA

Compound[a]	*Chemical shifts* (δ)[b] (*first-order couplings, Hz, in parentheses*)									
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5'}$)	*H-5* ($J_{4,5}$)	*H-5'* ($J_{5,5'}$)	*Aryl*	*PhC-H*	*4-OR* ($J_{4,OH}$)	*Others*[c]
2[d]	1.64s	—	3.57d (8.6)	3.94m (9.5)	4.19dd (5.2)	3.50t (9.5)	7.65–7.14m	5.27s	4.89d (2.5)	5.41s (2-OH)
3	1.80s	—	← 4.45–4.02 and 3.88–3.60m →				7.75–7.15m	5.48s	—	6.10s (PhC-H)
4[e]	1.52s	—	← 3.75–3.25m →				7.56–7.15m	—	4.62d (6.0)	5.49s 4.91d 4.39t (2,3,5-OH)
5	1.45s	—	5.54d (5.0)	5.10m (7.0)	4.48dd (2.8)	4.16dd (12.4)	7.60–7.18m	—	1.95s	2.85s (2-OH) 2.16s 1.66s (3,5-Ac)
6	1.60s	—	← 4.34–3.26m →				7.70–7.10m	5.48s	—	1.50s 1.29s (CMe_2)
7	1.73s	—	← 4.58–4.30 and 4.10–3.56m →				7.60–7.20m	5.51s	—	
8	1.18s	—	4.04d (9.2)	5.18m$_6$ (9.8)	4.22dd (5.6)	3.43t (10.7)	7.60–7.10m	5.57s	1.57s	2.74s (2-OH)
9[f]	1.48s	—	4.54d (9.0)	5.22m$_6$ (10.0)	4.13dd (5.8)	3.45t (10.8)	7.80–6.84m	5.59s	2.12s	10.71s (NH)
11	2.13s	—	← 4.50–3.43m →				7.60–6.85m	5.42s		6.71s (NH)

TABLE I (*continued*)

Compound[a]	*Chemical shifts* (δ)[b] (*first-order couplings, Hz, in parentheses*)									
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5'}$)	*H-5* ($J_{4,5}$)	*H-5'* ($J_{5,5'}$)	*Aryl*	*PhC-H*	*4-OR* ($J_{4,OH}$)	*Others*[c]
12[f]	1.41d (7.0)	~3.55m (3.0)	3.84dd (9.0)	3.80–3.55m	4.19dd (4.0)	3.80–3.55m (9.8)	7.68–7.04m	5.55s	6.54s (W_h 10)	
13	1.39d (7.0)	3.14dq (3.2)	3.93dd (9.8)	4.33m$_6$ (10.0)	4.59dd (5.0)	3.46t (10.0)	7.54–7.13m	5.45s	1.89s	
14	1.72s	—	4.03d (8.5)	3.73m$_6$ (9.0)	4.17dd (4.0)	3.51t (9.8)	7.60–6.90m	5.34s		4.59m$_4$ 4.25m$_3$ ($PhCH_2$)
15	1.63s	—	←———	4.16–3.49m	——→	3.41t (9.5)	7.56–6.78m	5.50s		~4.0m ($PhCH_2$)
16[f]	1.76s	—	4.25d (5.0)	3.60m (4.8)	←———	4.03dd ——→ (11.5)	7.76–7.06m	—		6.25 (~60 Hz wide) (3,4,5-OH) 4.35m$_4$ ($PhCH_2$)
17	1.59s	—	←———	4.22–3.28m	———	——→	7.64–7.00m	5.21s	0.82s (*t*-butyl)	3.88s (2-OH)
18	2.17s	—	←———	4.28–3.40m	———	——→	7.55–7.20m	5.44s	0.83s (*t*-butyl)	3.94m$_4$ ($PhCH_2$)
19	1.54s	—	←———	4.24–3.40m	———	——→	7.76–7.14m	5.47s	0.83s (*t*-butyl)	

[a]In chloroform-*d*, unless otherwise stated. [b]Signal multiplicities (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; m$_x$, sextet, septet, etc. [c]Assignments in parentheses. [d]In 3:1 chloroform-*d*–dimethyl sulfoxide-d_6. [e]In 9:1 dimethyl sulfoxide-d_6–chloroform-*d*; $J_{3,OH}$ 2.8 Hz; $J_{5,OH} = J_{5',OH}$ 5.5 Hz. [f]In pyridine-d_5.

methyl ether[22] in anticipation of obtaining a mixed acetal involving the 4-hydroxyl group. However, the syrupy product, obtained in essentially theoretical yield, proved to be the cyclic isopropylidene acetal **6**, as evidenced by p.m.r. (see Table I) and i.r. (no OH absorption band) spectroscopic data, as well as by mass spectrometry (*m/e* 340, $M^{+\cdot}$; 325, M−Me·; 267, M−Me·−acetone; 43, Ac^+) and elemental composition.

The facility whereby compound **2** tends to undergo cyclization to afford a *trans*-decalin type of system was further manifested by the formation of the cyclic carbonate **7**.

Introduction of a protecting group at the tertiary hydroxyl group was finally accomplished by treating the crystalline 4-acetate **8** with phenyl isocyanate under forcing conditions. However, the phenylcarbamate **9**, isolated crystalline in high yield, resisted all attempts at selective removal of the *O*-benzylidene group by acid, even under a variety of conditions examined. Instead, mixtures of **2**, **4**, and **8**, and other (unidentified) side-products were obtained. Therefore, catalytic hydrogenolysis of the benzylidene acetal **9** was investigated. After 24 h under atmospheric pressure in the presence of 5% palladium-on-charcoal, small proportions of a new compound (**13**) were detected by t.l.c. By applying more-vigorous conditions (6 $kg.cm^{-2}$ pressure of hydrogen), the reaction was complete after 48 h. The i.r. spectrum of the crystalline product (**13**) showed no hydroxyl absorption band, and the well-resolved p.m.r. spectrum (see Fig. 1 and Table I) revealed that the benzylidene group was still present (one-proton singlet at δ 5.45). A doublet (δ 1.38), instead of a singlet, accounted for the methyl group (C-1) and was shown by double-irradiation experi-

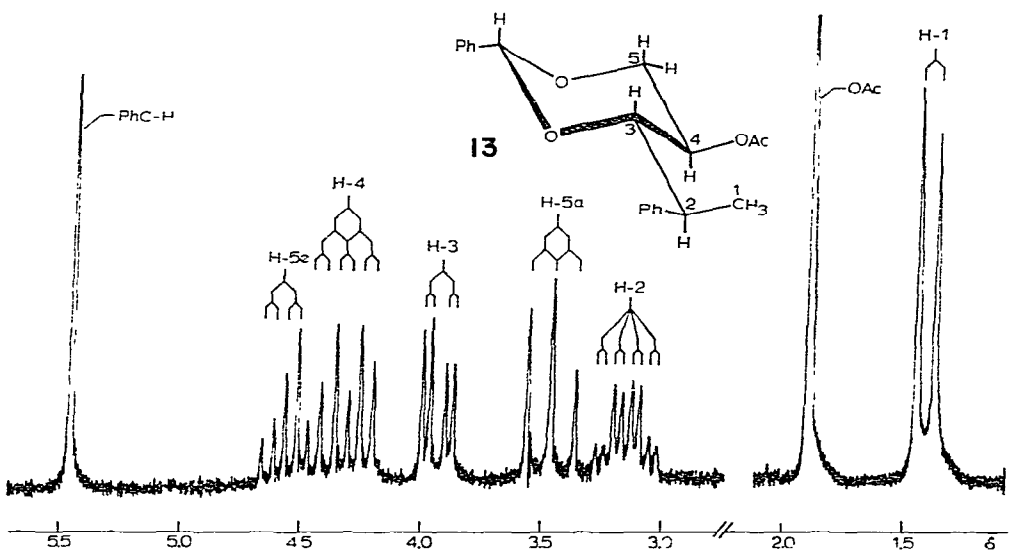
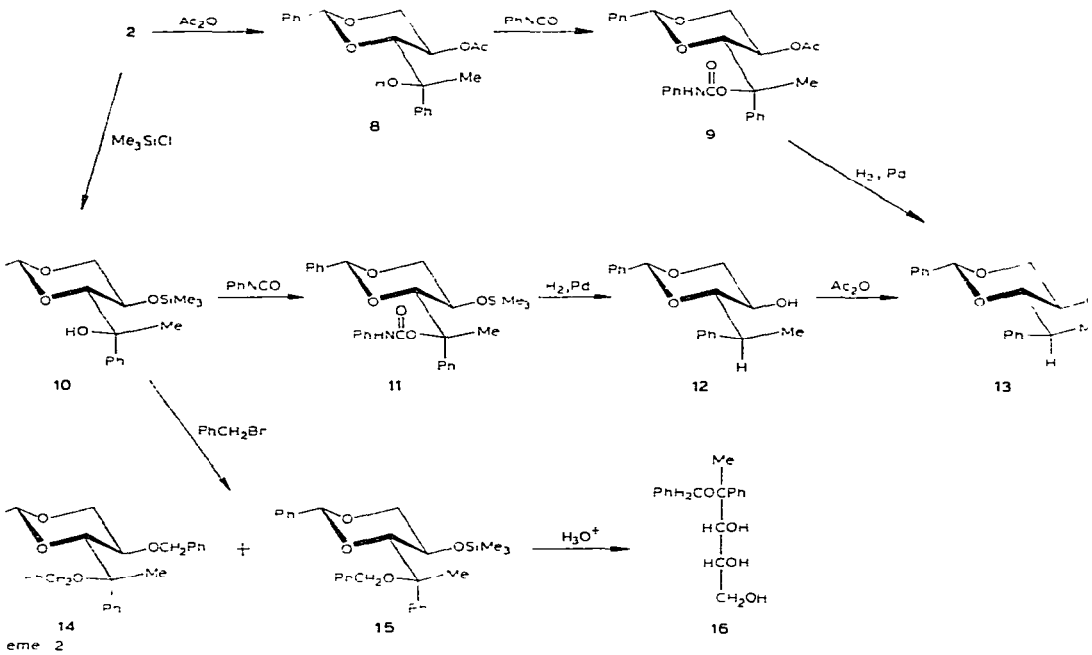


Fig. 1. Partial, 100-MHz, ^{1}H-n.m.r. spectrum of 2(*S*)-4-*O*-acetyl-3,5-*O*-benzylidene-1,2-dideoxy-2-*C*-phenyl-D-*erythro*-pentitol (**13**) in chloroform-*d*.

ments to be coupled to the one-proton, 8-line signal at high field (H-2, δ 3.14). This information, together with the complete assignment of the remaining signals (verified by decoupling experiments) and the i.r. spectrum [no NH or C=O (carbamate) absorption bands], suggested that deoxygenation at C-2 had taken place to yield 2(*S*)-4-*O*-acetyl-3,5-*O*-benzylidene-1,2-dideoxy-2-*C*-phenyl-D-*erythro*-pentitol (**13**).

The deoxygenated *C*-phenylpentitol **13** was also obtained by an alternative sequence. The trimethylsilyl ether **10**, prepared from **2** in almost theoretical yield, was converted into the carbamate **11**. The lower yield (41%) of **11**, as compared with the near-quantitative conversion of the 4-acetyl analog **8** into **9**, is undoubtedly due to the lability of the silyl ether group towards the alumina used for isolation. As with its 4-acetyl analog **9**, the 4-(trimethylsilyl)ated carbamate **11** withstood all attempts to remove the benzylidene acetal group selectively, but catalytic hydrogenolysis of it afforded the deoxygenated product **12**. The structure assigned to **12** was fully supported by i.r. and p.m.r. (Table I) spectral data and by mass spectrometry (see Experimental section). Its 4-*O*-acetyl derivative (**13**) was indistinguishable (by physical and spectroscopic data, and X-ray powder pattern) from the product already obtained from **9**.



The catalytic hydrogenolysis of the chiral carbamates **9** and **11**, in addition to being highly stereospecific, is considered to proceed with inversion of configuration. This conclusion is based on analysis of p.m.r. data of **13** and its hydroxyl analog **8**, employing arguments similar to those used[2,20] in the configurational elucidation of

5,6-dideoxy-5-*C*-phenyl-α-D-*xylo*-hexofuranose derivatives. However, it must be emphasized that the configurational assignment (*S*) for the benzylic center at C-2 in **12** and **13** should be considered tentative and awaits final confirmation by X-ray crystal-structure determination.

This remarkable reaction, which may prove extremely useful in asymmetric syntheses, is somewhat reminiscent of the palladium-catalyzed hydrogenolysis of phenylurethans to give arenes[23], and[24] the catalytic hydrogenolysis of benzyl derivatives; the scope and limitations of this reaction are now being evaluated.

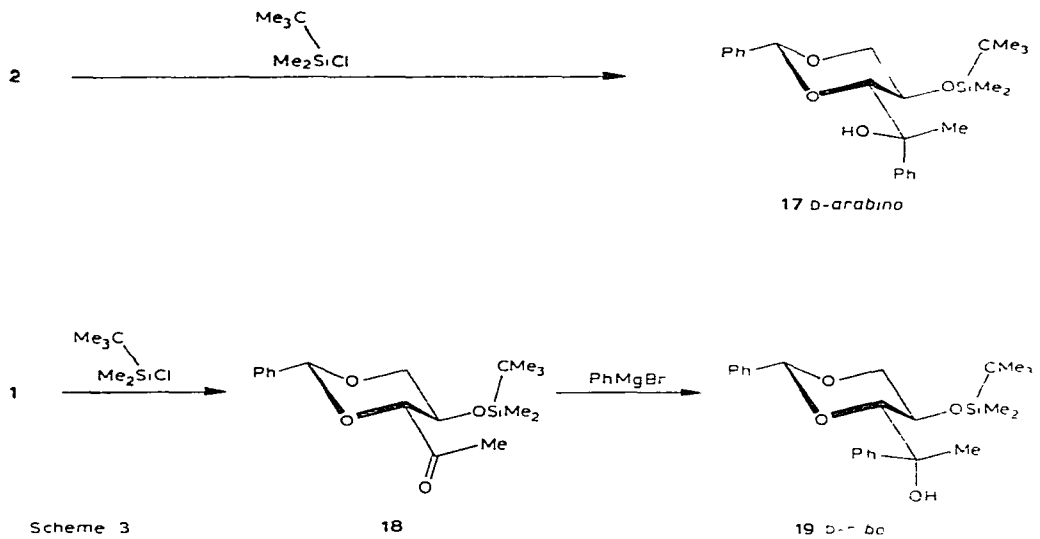
Because the carbamoyl substituent was too susceptible to solvolysis under the conditions required for deprotection of the hydroxyl groups at C-3, C-4, and C-5, the benzyl group was envisaged as a protecting group for the tertiary alcoholic function, with subsequent chain-degradation by glycol cleavage in view. Rather unexpectedly, the trimethylsilyl ether group in **10** survived to a considerable extent the vigorous benzylation conditions, and the desired benzyl ether **15** was, after separation by column chromatography from the 2,4-dibenzyl ether **14** (30%), isolated as a syrup in 47% yield. Compound **15** was subjected to mild, acid hydrolysis, to afford crystalline 2-*O*-benzyl-1-deoxy-2-*C*-phenyl-D-arabinitol (**16**), a compound that may be considered a "storage form" of (*S*)-2-(benzyloxy)-2-phenylpropanal, the enantiomer of which has been prepared[20] by Inch and his co-workers.

In order to increase the yield of the desired product (**15**), and quench dibenzylation (leading to **14**) in the benzylation reaction, it was proposed to replace the trimethylsilyl substituent in **10** by the *tert*-butyldimethylsilyl group, a protecting substituent that is known[25] to combine stability under a wide range of conditions with susceptibility to facile removal.

Preliminary benzylation experiments with the *tert*-butyldimethylsilyl derivative **17** proved to be exceedingly effective, and, therefore, more of this product (**17**) was needed. As well as following the sequence already outlined (**1**→**2**→**17**), the reverse approach, involving initial silylation and subsequent Grignard addition was also examined, as *tert*-butyldimethylsilyl ethers are considered[25] to be compatible with the conditions of the Grignard reaction. Although the benzylidenepentulose **1** had failed to react with chlorotriphenylmethane, it gave >90% of the syrupy silyl ether **18** when treated with *tert*-butylchlorodimethylsilane in *N*,*N*-dimethylformamide, with imidazole as the catalyst. On treatment of **18** with phenylmagnesium bromide under the conditions used for the preparation of **2**, a syrupy product (**19**) was obtained in high yield. It had a chromatographic mobility similar to, and an elemental composition identical with, that of compound **17**, and it gave the same mass spectrum (see Experimental section), except for the intensities of certain fragment-ions. However, i.r. and p.m.r. (see Table I) spectral comparison of **17** and **19** (although the p.m.r. spectra were essentially second-order) displayed distinctive differences, and this observation was further substantiated by the values of the specific rotations of **17** (−57°) and **19** (+42°) in chloroform. As the D-*arabino* stereochemistry had been unequivocally established for **17**, compound **19** must, therefore, be the D-*ribo* isomer.

Although it is well known[2] that the stereoselectivity of reactions of Grignard

reagents with carbonyl-sugar derivatives may be considerably *modified* by change of the reaction conditions or change of a substituent, we consider that this reaction of phenylmagnesium bromide with 3,5-*O*-benzylidene-1-deoxy-D-*erythro*-2-pentulose (**1**) and its 4-(*tert*-butyldimethylsilyl) ether **18** may constitute the first reported example wherein the mode of addition of the reagent can be completely reversed within a given carbohydrate framework, and lead exclusively to either the D-*arabino* (**2**) or the D-*ribo* isomer (**19**), in high yields.



Scheme 3 18 19 D-*ribo*

The stereospecific synthesis of chiral benzylic centers by utilizing a carbohydrate precursor, as described in this paper, combines the desirable features of optically pure products, convenience of operation, high yields, and, with the option to generate deoxygenated benzylic centers, a versatile basis of access to chiral hydrocarbons.

EXPERIMENTAL

General methods. — Evaporations were performed under diminished pressure at a bath temperature below 50°. Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. A Perkin–Elmer Model 141 polarimeter and 1-dm tubes were used for measurement of specific rotations in chloroform, unless otherwise stated. I.r. spectra were recorded with a Perkin–Elmer Model 457 grating i.r. spectrometer, with solids dispersed in potassium bromide, and syrups as films on sodium chloride discs. ^{1}H-N.m.r. spectra were recorded at 100 MHz with a Varian HA-100 spectrometer; chemical shifts refer to an internal standard of tetramethylsilane ($\delta = 0.00$), and are listed, together with first-order, spin-coupling values (Hz) in Table I. The assignments were in most instances confirmed by decoupling experi-

ments. The nuclear Overhauser effects were measured at 100 MHz for a degassed solution of **3** in chloroform-*d* (10% w/v), with tetramethylsilane for field-frequency locking; the spectra were recorded in the manner described by Bell and Saunders[26], and integrated by use of a planimeter. T.l.c. was performed on precoated plates of Silica Gel 60 (E. Merck, Darmstadt); zones were detected by u.v. light, and by spraying with sulfuric acid and subsequently heating. Solvent volumes are v/v; petroleum ether refers to the fraction boiling at 65–110°. Column chromatography was performed with silica gel (Merck No. 7734; 63–200 μm) or with neutral alumina (Fisher Scientific Company; Brockman activity 1; 80–200 mesh). Microanalyses were performed by W. N. Rond. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-9 double-focusing, high-resolution spectrometer operating at an ionizing potential of 70 eV and an accelerating potential of 8 kV; the source temperature (direct-inlet system) was 120°. The spectra of all benzylidene acetals described here displayed intense peaks for ions (*m/e* 107, 106, 105, 91, 79, and 77) from the aryl group; the notations *f* and *h* in the assignments refer to ring-rupture processes typical[27] of 1,3,6,8-tetraoxabicyclo[4.4.0]decane systems. For pairs of clearly related ions having *m/e* values *a* and *b* and relative intensities *x* and *y*, that arise by loss of fragments *p* and *q* from M, the following type of abbreviated notation is used: *m/e a/b* (*x/y*, M−*p/q*). X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. The camera diameter was 114.59 mm. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

*3,5-O-Benzylidene-1-deoxy-2-C-phenyl-*D*-arabinitol* (**2**). — To a cold (−5°) solution of phenylmagnesium bromide [prepared from magnesium turnings (23 g, 950 mmol) and bromobenzene (120 g, 760 mmol)] in dry ether (500 ml) was added dropwise a solution of 3,5-*O*-benzylidene-1-deoxy-D-*erythro*-pentulose[13] (**1**, 41.6 g, 187 mmol) in dry ether (500 ml) during 2 h with continuous stirring. After a further 2 h at −5° and 15 h at 25°, water (20 ml) was carefully added, and the mixture was filtered with the aid of Celite (~30 g). The filter cake was thoroughly washed with tetrahydrofuran, and the combined filtrates were evaporated. A solution of the resulting, white solid in chloroform (400 ml) was washed with cold, aqueous ammonium chloride, dried (sodium sulfate), and evaporated, to afford crude **2** (53 g, 94%), which was recrystallized from hot chloroform (80 ml) by adding ether (250 ml) to give an analytically pure product; yield 43.4 g (77%). Evaporation of the mother liquor afforded an oil (~10 g) that was shown by t.l.c. (3:2 ether–petroleum ether) to contain substantial proportions of **2** and the starting ketone **1**, together with several, unidentified side-products. Column chromatography on silica gel with the t.l.c. solvent as the eluant furnished small amounts of **1** (2 g) and an additional crop of **2** (1.7 g, after recrystallization from ethyl acetate–hexane); total yield of **2**, 45.1 g (80%), m.p. 165–166°, $[\alpha]_D^{20}$ −54° (*c* 3); R_F 0.48 (3:2 ether–petroleum ether); ν_{max}^{KBr} 3400 cm^{-1} (OH); *m/e* (rel. intensity): 300 (0.8, M^+), 283 (0.7, M−·OH), 196 (0.8, M−PhCHO), 179 [28, M−PhC(OH)CH_3], 162 (44, 179−·OH), 149 (3, *h* ion), 121 [100, PhC(OH)CH_3^+], and 43 (52, Ac^+); X-ray powder diffraction data: 8.93 m.

7.59 m, 6.94 vw, 6.39 vw, 5.74 vs (1), 5.38 vw, 5.02 vw, 4.64 vs (2), 4.35 m, 4.08 m, 3.74 vs (3), and 3.42 m.

Anal. Calc. for $C_{18}H_{20}O_4$ (300.34): C, 71.98; H, 6.71. Found: C, 72.00; H, 6.70.

*2,4:3,5-Di-O-benzylidene-1-deoxy-2-C-phenyl-*D*-arabinitol* (**3**). — A mixture of the branched-chain pentitol **2** (2 g, 6.66 mmol), α,α-dimethoxytoluene (2.5 g, 16.4 mmol), and *p*-toluenesulfonic acid monohydrate (50 mg) in dry *N*,*N*-dimethylformamide (50 ml) was heated for 3 h at ~70° under evacuation (water aspirator). The solution was then poured into ice–water (250 ml) containing sodium hydrogencarbonate (12.5 g), and the mixture was extracted with dichloromethane (three 40-ml portions). The combined extract was washed with water, dried (magnesium sulfate), and evaporated. 2-Propanol (to remove residual *N*,*N*-dimethylformamide; two 30-ml portions) and ether (30 ml) were successively added to and evaporated from the residue, to afford analytically pure **3** (2.4 g, 93%) as a foam that, after being kept for several days, proved to be crystalline (X-ray powder diffraction pattern). This product could be recrystallized from ethanol, but with poor recovery; m.p. 132–133°, $[\alpha]_D^{21}$ −72.3° (*c* 1); *m/e* (rel. intensity): 388 (0.02, M^+), 389/387 (0.01/0.05, M ± 1), 282 (0.25, M − PhCHO), 268 (3.8, M − PhCO· − Me·), 252/162 (0.04/44, *f* ions), and 239/149 (0.2/8, *h* ions); X-ray powder diffraction data: 13.69 vw, 10.64 m, 9.40 m, 8.46 m, 6.60 m, 5.32 m, 5.11 m, 4.98 w, 4.61 vs (1), 4.24 s (2), 3.86 s (3), and 3.77 m.

Anal. Calc. for $C_{25}H_{24}O_4$ (388.47): C, 77.30; H, 6.23. Found: C, 77.03; H, 5.95.

*1-Deoxy-2-C-phenyl-*D*-arabinitol* (**4**). — A suspension of the benzylidene acetal **2** (6.96 g, 23.1 mmol) in a mixture of tetrahydrofuran (40 ml), ethanol (80 ml), water (32 ml), and ~10M hydrochloric acid (8 ml) was kept for 16 h at 25° and then for 3 h at 70°. After neutralization of the acid with barium carbonate, and filtration (Celite), the filtrate was evaporated to a syrup that was dissolved in tetrahydrofuran. The turbid solution was filtered, and the filtrate was evaporated to afford a gum (5 g) that was purified by column chromatography on silica gel with 19:1 ether–methanol as the eluant. Evaporation of the effluent gave pure, crystalline **4**: yield 3 g (60%); R_F 0.42. Recrystallization was effected from 1:7 methanol–ether; m.p. 132–133°, $[\alpha]_D^{17}$ +31.2° (*c* 2.4, tetrahydrofuran); ν_{max}^{KBr} 3600 and 3350 (OH), 1625, 1505, 865, 780, and 710 cm^{-1} (aryl); *m/e* (rel. intensity): 197/194 (0.5/0.8, M − Me·/H_2O), 179/163 (0.4/0.7, 194 − Me·/·CH_2OH), 121 [100, $PhC(OH)CH_3^+$], 105 (6, $PhCO^+$), 91 [1.2, $CH_2(OH)CH(OH)CH(OH)^+$], 77 (6, Ph^+), and 43 (62, Ac^+); X-ray powder diffraction data: 8.15 s, 6.58 s, 5.17 vs (1), 4.75 m, 4.55 vs (2), 4.20 w, 4.05 w, 3.80 w, 3.64 vs (3), 3.47 m, 3.16 w, and 3.05 w.

Anal. Calc. for $C_{11}H_{16}O_4$ (212.24): C, 62.25; H, 7.60. Found: C, 62.15; H, 7.59.

*3,4,5-Tri-O-acetyl-1-deoxy-2-C-phenyl-*D*-arabinitol* (**5**). — The arabinitol derivative **4** (1.6 g, 7.5 mmol) was treated with 1:2 acetic anhydride–pyridine (15 ml) for 18 h at 25°. Conventional processing of the mixture afforded a colorless solid that was recrystallized from 9:1 water–ethanol; yield 2.44 g (95%), m.p. 117–118°, $[\alpha]_D^{16}$ −19.6° (*c* 2.3); R_F 0.22 (1:1 ether–petroleum ether); ν_{max}^{KBr} 3580 (OH), 1740 (C=O), 1500, 880, 762, and 705 cm^{-1} (aryl); *m/e* (rel. intensity): 321 (0.8, M − ·OH), 278 (1, M − AcOH), 263 (0.7, 278 − Me·), 163 (9), 158 (10), 145 [2.3, $CH_2(OAc)CHOAc^+$],

121 [86, $PhC(OH)CH_3^+$], 116 (10), 115 (15), 105 (6.5, $PhCO^+$), 77 (3.3, Ph^+), 60 (2, $AcOH^{+\cdot}$), and 43 (100, Ac^+); X-ray powder diffraction data: 9.40 w, 8.15 w, 7.10 vs (1), 6.50 m, 5.26 w, 4.63 s (2), 4.44 m, 4.20 s (3), 3.87 vw, and 3.67 vw.

Anal. Calc. for $C_{17}H_{22}O_7$ (338.35): C, 60.34; H, 6.55. Found: C, 60.32; H, 6.33.

*3,5-O-Benzylidene-1-deoxy-2,4-O-isopropylidene-2-C-phenyl-*D*-arabinitol* (**6**). — A mixture of the benzylidene acetal **2** (2 g, 6.6 mmol), isopropenyl methyl ether (4 ml), *p*-toluenesulfonic acid monohydrate (20 mg), and Drierite (~1 g) in *N,N*-dimethylformamide (30 ml) was stirred for 6 h at 25°, and then an aqueous solution of potassium hydrogencarbonate (5%, 200 ml) was added. Extraction with chloroform, and evaporation of the extract, afforded compound **6** as a colorless gum; yield 2.2 g (95%). For analytical purposes, a sample was chromatographed on silica gel with 1:19 ether–petroleum ether (R_F 0.35); $[\alpha]_D^{26}$ −113.3° (*c* 3.3); ν_{max}^{film} 1385 (CMe_2), 1600, 1500, 850, 765, 750, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 340 (0.8, $M^{+\cdot}$), 325 (8.9, $M-Me\cdot$), 282 (0.7, $M-Me_2CO$), 267 (36, $325-Me_2CO$), 220 (11.8, $M-PhCOCH_3$), 205 (12, $220-Me\cdot$), 191/149 (1/23, *h* ions), 162 (62, *f* ion), and 43 (21, Ac^+).

Anal. Calc. for $C_{21}H_{24}O_4$ (340.40): C, 74.09; H, 7.11. Found: C, 74.34; H, 7.15.

*3,5-O-Benzylidene-2,4-O-carbonyl-1-deoxy-2-C-phenyl-*D*-arabinitol* (**7**). — To a cooled (0°) solution of compound **2** (1.5 g, 5 mmol) in dry pyridine (30 ml) was added a solution of phosgene in benzene (12.5% w/v; 6 ml, 7.5 mmol). After 6 h at 25°, the excess of phosgene was decomposed by adding a saturated, aqueous solution of potassium hydrogencarbonate (200 ml), and the mixture was extracted with chloroform. Evaporation of the dried (sodium sulfate) extract gave a syrup that was freed from residual pyridine by evaporating small portions of toluene from it. Subsequent decolorization (chloroform solution, activated charcoal) afforded analytically pure **7** as an amorphous foam; yield 1.5 g (92%), $[\alpha]_D^{25}$ −106.6° (*c* 3); R_F 0.55 (1:1 ether–petroleum ether); ν_{max}^{film} 1765 (C=O), 1600, 1500, 775, 750, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 326 (20, $M^{+\cdot}$), 221/220 (2/20, $M-PhCO\cdot/PhCHO$), 206 (18, $M-PhCOCH_3$), 162 (3.1, *f* ion), 149 (16.5, *h* ion), 145 (17), 120 (16, $PhCOCH_3^{+\cdot}$), and 43 (14, Ac^+).

Anal. Calc. for $C_{19}H_{18}O_5$ (326.33): C, 69.92; H, 5.56. Found: C, 70.17; H, 5.84.

*4-O-Acetyl-3,5-O-benzylidene-1-deoxy-2-C-phenyl-*D*-arabinitol* (**8**). — The benzylidene acetal **2** (6 g, 20 mmol) was treated with 1:4 acetic anhydride–pyridine for 18 h at 25°. Conventional processing afforded crude, crystalline **8** (6.8 g) that was recrystallized from cyclohexane; yield 6.5 g (94%), m.p. 118–119°, $[\alpha]_D^{26}$ −16.7° (*c* 4.5); R_F 0.44 (3:7 ether–petroleum ether); ν_{max}^{KBr} 3470 (OH), 1725 (C=O), 1385 and 1375 (CH_3), 1600, 1495, 775, and 708 cm^{-1} (aryl); *m/e* (rel. intensity): 342 (0.7, $M^{+\cdot}$), 325/282 (0.7/0.8, $M-\cdot OH/AcOH$), 222 (7.2, $M-PhCOCH_3$), 179/162 (2/27, $222-Ac\cdot/AcOH$), 149 (10, *h* ion), 121 [57, $PhC(OH)CH_3^+$], 116 (8, $222-PhCHO$), 115 [65, $M-PhC(OH)CH_3-PhCO\cdot$], and 43 (100, Ac^+); X-ray powder diffraction data: 9.45 m, 7.78 m, 7.10 s, 6.70 vs (1), 5.63 s, 5.46 w, 5.18 vs (3), 4.63 vs (2), 4.13 m, 3.92 w, 3.81 w, and 3.71 m.

Anal. Calc. for $C_{20}H_{22}O_5$ (342.38): C, 70.16; H, 6.48. Found: C, 70.22; H, 6.55.

4-O-Acetyl-3,5-O-benzylidene-1-deoxy-2-C-phenyl-2-O-(phenylcarbamoyl)-D-arabinitol (**9**). — A mixture of the arabinitol derivative **8** (15 g, 43 mmol) and phenyl isocyanate (6 ml, 55.4 mmol) in dry pyridine (60 ml) was heated at 100° with the exclusion of moisture. After 6 h, more phenyl isocyanate (8 ml, 73.9 mmol) was added, and heating was continued for an additional 16 h. Evaporation of the solvent furnished a yellow solid that was dissolved in benzene (~60 ml), and the solution was placed on a column (35 × 600 mm) that had been packed with a slurry of neutral alumina in 1:1 ether–petroleum ether. Less-polar impurities were first eluted with 1:1 ether–petroleum ether (1000 ml) and then ether (2000 ml), and the product (**9**) was eluted with 3:2 ether–ethyl acetate. Evaporation of the solvent afforded the carbamate **9** as a white solid, in essentially theoretical yield (20 g), that was sufficiently pure for most purposes. Analytically pure **9** was obtained by recrystallization from 1:19 water–ethanol: yield 16.34 g (81%), m.p. 171–172°, $[\alpha]_D^{26}$ −36° (*c* 4, tetrahydrofuran): R_F 0.35 (3:7 ether–petroleum ether); ν_{max}^{KBr} 3340 (NH), 1740 (C=O, carbamate), 1720 (C=O, acetate), 1600, 1525, 1495, 775, 769, 758, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 461 (0.8, $M^{\mp}$), 418/341 (0.7/0.8, M − Ac·/PhNHCO·), 325 (3.6, M − $PhNHCO_2$·), 265/219 (0.8/3.1, 325 − AcOH/PhCHO), 221 (2.2, 341 − $PhCOCH_3$), 204 (7, 219 − Me·) 162/115 (14/35, 221 − Ac·/PhCHO), 149 (12, *h* ion), 121 (30, $PhC(OH)CH_3^+$ or $PhNHCOH^+$), 93 (12, $PhNH_2^+$), and 43 (100, Ac^+); X-ray powder diffraction data: 15.22 w, 11.85 s, 7.92 m, 5.88 vs (1), 5.62 s, 5.32 m, 4.96 vs (3), 4.51 w, 4.31 vs (2), 3.88 m, and 3.51 m.

Anal. Calc. for $C_{27}H_{27}NO_6$ (461.49): C, 70.27; H, 5.90; N, 3.04. Found: C, 70.54; H, 6.07; N, 2.92.

3,5-O-Benzylidene-1-deoxy-2-C-phenyl-4-O-(trimethylsilyl)-D-arabinitol (**10**). — To a cooled (0°) solution of the arabinitol derivative **2** (11 g, 36.6 mmol) in dry dichloromethane (150 ml) were successively added hexamethyldisilazane (12 ml, 57.6 mmol), chlorotrimethylsilane (6 ml, 47.3 mmol), and pyridine (1 ml). After 2.5 h at 25°, the excess of silylating reagents was decomposed by adding methanol (20 ml) to the cooled solution. The precipitate (ammonium chloride) was filtered off, and the filtrate evaporated. Toluene (three 20-ml portions) was added to and evaporated from the residue, to remove the last traces of pyridine, affording the title compound **10** as a syrup; yield 13.5 g (100%); ν_{max}^{film} 3500 (OH), 1390 (CH_3), 1600, 1500, 760, and 700 cm^{-1} (aryl). Although **10** was chromatographically homogeneous (R_F 0.73 in 3:7 ether–petroleum ether), an elemental analysis within acceptable limits was not obtained.

3,5-O-Benzylidene-1-deoxy-2-C-phenyl-2-O-(phenylcarbamoyl)-4-O-(trimethylsilyl)-D-arabinitol (**11**). — A mixture of the trimethylsilyl ether **10** (13.5 g, 36.2 mmol) and phenyl isocyanate (5 ml, 46.2 mmol) with dry pyridine (60 ml) was heated for 16 h at 60° and, after addition of more phenyl isocyanate (6 ml, 55.4 mmol), for a further 6 h at 100°. The mixture was then processed as described for the carbamate **9**. The crude product was freed from impurities by chromatography on a column (35 × 600 mm) of neutral alumina, elution being performed with ether–petroleum ether [1:4 (1000 ml), 3:7 (1000 ml), and 1:1 (1500 ml)], and finally ether to recover the product.

Evaporation of the solvent afforded the pure carbamate **11** as a thick gum; yield 7.5 g (42%), $[\alpha]_D^{26}$ −7.2° (*c* 3); ν_{max}^{film} 3350 (NH), 1730 (C=O), 1605, 1525, 1500, 880, 850, 760, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 491 (1, M^+), 371/355 (0.8/2.2, M − PhNHCO·/$PhNHCO_2$·), 251 [43, M − $PhNHCO_2\dot{C}(CH_3)Ph$], 149 (2.5, *h* ion), 146/145 (16/28, 251 − PhCO·/PhCHO), 121 [50. $PhC(OH)CH_3^+$ or $PhNHCOH^+$], 93 (12, $PhNH_2^+$), and 73 (100, Me_3Si^+).

Anal. Calc. for $C_{28}H_{33}NO_5Si$ (491.57): C, 68.41; H, 6.77. Found: C, 68.85; H, 6.84.

2(S)-*3,5*-O-*Benzylidene-1,2-dideoxy-2*-C-*phenyl*-D-erythro-*pentitol* (**12**). — A solution of the phenylcarbamate **11** (7 g, 14 mmol) in aqueous methanol (80%; 100 ml) was boiled for 90 min under reflux, and the solvent was then evaporated off. The residue was dissolved in ethanol (50 ml) and hydrogenated under pressure (6 $kg.cm^{-2}$) for 20 h in the presence of 5% palladium-on-charcoal (600 mg). The catalyst was filtered off, and the filtrate evaporated to afford an oil (5.12 g) that was placed on a column (35 × 500 mm) of alumina. Elution with ether (1500 ml) and then ether–ethyl acetate (9:1, 4:1, 7:3, and 3:2; a 500-ml portion of each), and evaporation of the solvent furnished pure compound **12** as a syrup; yield 3 g (71%), $[\alpha]_D^{26}$ +75° (*c* 1.6); R_F 0.50 (3:2 ether–petroleum ether); ν_{max}^{film} 3450 (OH), 1600, 1500, 765, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 284 (0.4, M^+), 179 (86, M − PhCO·/$Ph\dot{C}HCH_3$), 107 (100, $PhCHOH^+$; m* at 64.0, calc. for 179→ 107: 63.96), and 105 [36, $PhCO^+$ or $PhCHCH_3^+$].

Anal. Calc. for $C_{18}H_{20}O_3$ (284.34): C, 76.03; H, 7.09. Found: C, 76.43; H, 7.54.

2(S)-*4*-O-*Acetyl-3,5*-O-*benzylidene-1,2-dideoxy-2*-C-*phenyl*-D-erythro-*pentitol* (**13**). — *A. From 4*-O-*acetyl-3,5*-O-*benzylidene-1-deoxy-2*-C-*phenyl-2*-O-(*phenylcarbamoyl*)-D-*arabinitol* (**9**) *by catalytic hydrogenation.* The phenylcarbamate **9** (4.76 g, 10.3 mmol) in tetrahydrofuran (20 ml) and ethanol (80 ml) was hydrogenated under pressure (6 $kg.cm^{-2}$) for 48 h in the presence of 5% palladium-on-charcoal (600 mg). T.l.c. (3:7 ether–petroleum ether) then revealed that all of the starting material (R_F 0.35) had been converted into a single, new product (R_F 0.63). The mixture was treated with Dowex-50 X8 (H^+) cation-exchange resin (20 ml) and then evaporated to a syrup (3.17 g) that was placed on a column (30 × 600 mm) of silica gel which was eluted with 1:4 ether–petroleum ether. Evaporation of the solvent gave **13** as a crystalline solid (2.8 g, 85%) that was recrystallized from ethanol–water; yield 2.64 g (80%), m.p. 78–79°, $[\alpha]_D^{26}$ +31° (*c* 2.7); ν_{max}^{KBr} 1740 (C=O), 1600, 1500, 770, and 705 cm^{-1} (aryl); *m/e* (rel. intensity): 326 (0.8, M^+), 266 (1, M − AcOH), 221 (29, M − PhCO·/$Ph\dot{C}HCH_3$), 115 (100, 221 − PhCHO), 105 (10, $PhCO^+$ or $Ph\dot{C}HCH_3$), and 43 (29, Ac^+); X-ray powder diffraction data: 14.84 w, 9.15 vs (2,2), 7.04 s, 5.86 s, 5.25 s, 4.88 m, 4.39 vs (1), 3.96 vs (2,2), 3.65 s, 3.45 m, 3.22 m, and 3.05 m.

Anal. Calc. for $C_{20}H_{22}O_4$ (326.38): C, 73.60; H, 6.79. Found: C, 73.63; H, 7.04.

B. From 2(S)-*3,5*-O-*benzylidene-1,2-dideoxy-2*-C-*phenyl*-D-erythro-*pentitol* (**12**) *by acetylation.* The dideoxypentitol **12** (2.84 g, 10 mmol) was treated with 1:4 acetic anhydride–pyridine (25 ml) for 18 h at 25°. Conventional processing furnished

crystals that were recrystallized from ethanol–water to give pure **13**; yield 3 g (92%), indistinguishable (by mixed m.p., optical rotation, X-ray powder pattern, and spectroscopic data) from the sample prepared by route A.

Reaction of 3,5-O-benzylidene-1-deoxy-2-C-phenyl-4-O-(trimethylsilyl)-D-arabinitol (**10**) *with α-bromotoluene.* — A suspension of the trimethylsilyl ether **10** (5 g, 13.4 mmol) and sodium hydride (1.61 g, 70 mmol) in dry *N,N*-dimethylformamide (40 ml) was stirred for 3 h at 25°. α-Bromotoluene (14.3 g, 84 mmol) was then added dropwise to the cooled (0°) mixture during 1 h. After 18 h at 25°, methanol (20 ml) was carefully added, and the resulting solution was poured into ice–water (300 ml). Extraction with chloroform, and evaporation of the dried (sodium sulfate) extract, furnished a syrup that contained (t.l.c., 1:9 ether–petroleum ether) two major components (R_F 0.60 and 0.40). These were fractionated by chromatography on a column (40 × 860 mm) of silica gel with ether–petroleum ether [1:19 (1000 ml) and then 1:9] as the eluant.

The fastest-moving component (R_F 0.60) was obtained as a syrup, identified as *2-O-benzyl-3,5-O-benzylidene-1-deoxy-2-C-phenyl-4-O-(trimethylsilyl)-D-arabinitol* (**15**); yield 3 g (47%), $[\alpha]_D^{26}$ +11.3° (*c* 2.7); ν_{max}^{film} 1395, 1375 (CH_3), 1600, 1500, 760, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 462 (0.2, M^+), 447/371 (0.5/0.5, M − Me·/$PhCH_2$·), 193 [100, M − Me_3Si· − $PhC(CH_3)OCH_2Ph$], 120 (2.2, $PhCOCH_3^+$), and 73 (23, Me_3Si^+).

Anal. Calc. for $C_{28}H_{34}O_4Si$ (462.63): C, 72.70; H, 7.51. Found: C, 72.82; H, 7.51.

Evaporation of the fractions containing the product having R_F 0.40 gave syrupy *2,4-di-O-benzyl-3,5-O-benzylidene-1-deoxy-2-C-phenyl-D-arabinitol* (**14**); yield 2 g (30%), $[\alpha]_D^{26}$ −33° (*c* 3.5); ν_{max}^{film} 1605, 1590, 760, 740, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 480 (0.2, M^+), 269 [3.1, M − $PhC(CH_3)OCH_2Ph$], 237 (3.5, M − $PhCH_2O$· − PhCHO − CH_2O), 211 [30, $PhC(CH_3)OCH_2Ph^+$], and 91 (100, $PhCH_2^+$).

Anal. Calc. for $C_{32}H_{32}O_4$ (480.58): C, 79.97; H, 6.71. Found: C, 80.20; H, 6.88.

2-O-Benzyl-1-deoxy-2-C-phenyl-D-arabinitol (**16**). — A solution of the benzyl ether **15** (2.5 g, 5.4 mmol) in a mixture of tetrahydrofuran (15 ml), ethanol (10 ml), water (2 ml), and ~10M hydrochloric acid (3 ml) was kept for 20 h at 0°. After neutralization of the acid with barium carbonate, tetrahydrofuran (100 ml) was added, and the mixture was filtered. Evaporation of the filtrate afforded a syrup that was purified by column chromatography on silica gel with ether as the eluant, to give crystalline **16**; yield 650 mg (40%). After recrystallization from 9:1 isopropyl ether–petroleum ether, it had m.p. 62–63°, $[\alpha]_D^{26}$ −18° (*c* 2, ethanol); ν_{max}^{KBr} 3450, 3300 (OH), 1605, 1500, 765, 755, and 705 cm^{-1} (aryl); *m/e* (rel. intensity): 302 (0.3, M^+), 284 (0.1, M − H_2O), 253 (0.5, 284 − ·CH_2OH), 211 [2, M − $PhCH_2$· or $PhC(CH_3)OCH_2Ph^+$], 194 (3, M − $PhCH_2OH$), 133 [4.3, 194 − $CH_2(OH)CH(OH)$·], 121 [87, $PhC(OH)CH_3^+$], and 91 (100, $PhCH_2^+$ or $CH_2(OH)CH(OH)CH(OH)^+$]; X-ray powder diffraction data: 14.13 vs (1), 7.82 m, 7.10 w, 5.98 vs (3,3), 5.37 vs (3,3), 5.03 s, 4.40 s, 4.19 vs (2), 3.90 m, 3.51 w, 3.13 w, and 2.81 w.

Anal. Calc. for $C_{18}H_{22}O_4$ (302.36): C, 71.50; H, 7.33. Found: C, 71.30; H, 7.33.

3,5-O-Benzylidene-4-O-(tert-*butyldimethylsilyl*)*-1-deoxy-2-C-phenyl-*D-*arabinitol* (**17**). — A solution of the arabinitol derivative **2** (10.4 g, 34.6 mmol), imidazole (7.07 g, 104 mmol), and *tert*-butylchlorodimethylsilane (6.5 g, 42 mmol) in dry *N,N*-dimethylformamide (50 ml) was heated for 5 h at 75°, and then evaporated to a syrup. Chromatography on a column (40 × 800 mm) of silica gel with 1:19 ether–petroleum ether as the eluant afforded analytically pure 4-ether **17** as a syrup; yield 13.6 g (94%), $[\alpha]_D^{26}$ −57° (*c* 2.3); R_F 0.52 (1:9 ether–petroleum ether); ν_{max}^{film} 3510 (OH), 1395 and 1370 (CH_3), 1605, 1500, 785, 770, 760, and 705 cm^{-1} (aryl); *m/e* (rel. intensity): 414 (0.2, $M^{\ddagger}$), 397 (0.8, M − ·OH), 357 [8.5, M − $(CH_3)_3C$·], 293 [24, M − PhĊ$(CH_3)OCH_2Ph$], 251 (30, 357 − PhCHO), 233 (19, 251 − H_2O), 187 (14, 293 − PhCHO), 131 [21, 251 − $PhCOCH_3$ or $(CH_3)_3CSi(CH_3)_2O^+$], 121 [53, $PhC(OH)CH_3^+$], 117 (94), 115 [17, $(CH_3)_3CSi(CH_3)_2^+$], 75 (100), 73 (100), and 57 [11, $(CH_3)_3C^+$].

Anal. Calc. for $C_{24}H_{34}O_4Si$ (414.53): C, 69.53; H, 8.27. Found: C, 69.46; H, 8.14.

3,5-O-Benzylidene-4-O-(tert-*butyldimethylsilyl*)*-1-deoxy-*D-erythro-*2-pentulose* (**18**). — The *O*-benzylidenepentulose **1** (4.5 g, 20 mmol) in *N,N*-dimethylformamide (40 ml) was silylated with *tert*-butylchlorodimethylsilane (4.82 g, 32 mmol) and imidazole (4.3 g, 63 mmol), essentially as just described for **17**. The crude product was purified by column chromatography on silica gel with 19:1 benzene–ethyl acetate as the eluant, to afford pure **18** (R_F 0.73) as a syrup; yield 6.66 g (95%), $[\alpha]_D^{26}$ −1.3° (*c* 3.3); ν_{max}^{film} 1730 (C=O), 1605, 1500, and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 336 (0.1, $M^{\ddagger}$), 293 (2.1, M − Ac·), 279 [46, M − $(CH_3)_3C$·], 221 [0.6, M − $(CH_3)_3CSi(CH_3)_2$·], 173 (20, 279 − PhCHO), 145 (100, 173 − CO), 115 (5; m* at 91.2, calc. for 145 → 115: 91.21), 101 (68), 57 [4, $(CH_3)_3C^+$], and 43 (27, Ac^+).

Anal. Calc. for $C_{18}H_{28}O_4Si$ (336.42): C, 64.26; H, 8.39. Found: C, 64.11; H, 8.53.

3,5-O-Benzylidene-4-O-(tert-*butyldimethylsilyl*)*-1-deoxy-2-C-phenyl-*D-*ribitol* (**19**). — The Grignard reaction of the silylated ketone **18** (6.5 g, 20 mmol) with phenylmagnesium bromide [prepared from 2.43 g (100 mmol) of magnesium turnings and 12.5 g (80 mmol) of bromobenzene in dry ether (60 ml)] was performed as already described for **2**. The pure, syrupy product (**19**) was obtained by column chromatography on silica gel with 1:19 ether–petroleum ether as the eluant; yield 7.24 g (89%), $[\alpha]_D^{26}$ +42° (*c* 3); R_F 0.50 (1:9 ether–petroleum ether); ν_{max}^{film} 3510 (OH), 1390 (CH_3), 1605, 1500, 785, 770, and 755 cm^{-1} (aryl); *m/e* (rel. intensity): 414 (0.5, $M^{\ddagger}$), 357 [2.3, M − $(CH_3)_3C$·], 293 [6.4, M − PhĊ$(CH_3)OCH_2Ph$], 251 (5, 357 − PhCHO), 233 (5, 251 − H_2O), 223 (21), 187 (4.6, 293 − PhCHO), 131 [22, 251 − $PhCOCH_3$ or $(CH_3)_3CSi(CH_3)_2O^+$], 121 (63, $PhC(OH)CH_3^+$], 117 (100), 115 [19, $(CH_3)_3CSi(CH_3)_2^+$], 75 (75), 73 (92), and 57 [14, $(CH_3)_3C^+$)].

Anal. Calc. for $C_{24}H_{34}O_4Si$ (414.53): C, 69.53; H, 8.27. Found: C, 69.83; H, 8.39.

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