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Note

Inversion of configuration at the propargylic alcohol center in sugar acetylenes

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Sugar propargylic alcohols, readily availbable from sugar aldehydes and acetylene[1], are usually obtained as separable mixtures of diastereoisomers. In attempts to exploit these valuable compounds for the synthesis of higher sugars, we became interested in inversion of configuration at the propargylic alcohol center. Although many reactions of propargylic alcohols and their derivatives have been described in the literature[2,3], very little is known about this elementary transformation. Godman and Horton[4] described the displacement reaction of 1-hexyn-3-yl-*p*-toluenesulfonate with sodium benzoate leading to 3-(benzoyloxy)-1-hexyne in 56% yield. However, because the substrate was racemic, nothing could be inferred about the stereochemical outcome of the reaction. Attempts at replacement of the propargylic hydroxyl group in **1** and **5** by nitrogen-carrying nucleophiles were unsuccessful[5].

For the present study, three pairs of diastereoisomeric propargylic alcohols were selected: 7,7,8,8-tetradehydro-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D- and β-L-*glycero*-D-*galacto*-octopyranose (**1** and **5**), methyl 2,3,4-tri-*O*-benzyl-7,7,8,8-tetradehydro-7,8-dideoxy-α-D- and β-L-*glycero*-D-*gluco*-octopyranoside (**9** and **12**) and 6,6,7,7-tetradehydro-6,7-dideoxy-α-D-*gluco*- and -β-L-*ido*-heptofuranose (**16** and **19**). From all of these as substrates, the corresponding *p*-toluenesulfonic and benzoic esters were prepared in high yield by using the standard methods.

Tosylates **2**, **6**, **10**, **13**, **17**, and **20** reacted readily with sodium benzoate in *N,N*-dimethylformamide solution at 120–130°, furnishing one or more reaction products that could be compared (t.l.c.) with the benzoates prepared. The inverted benzoates expected were obtained in low to moderate yields from tosylates **6**, **10**, and **13** (see Table I, entries 2–4). Substantial proportions of allenic benzoates **23** and **24** were also obtained. These products, originating from the well-known, 1,3-substitution of propargylic alcohol derivatives[2,3], were obtained as non-separable mixtures of diastereoisomers. Their gross structure could be readily determined from their ^{1}H-n.m.r. spectra, as well as from the hydrolytic conversion of allene **24** into the α,β-unsaturated aldehyde **26**.

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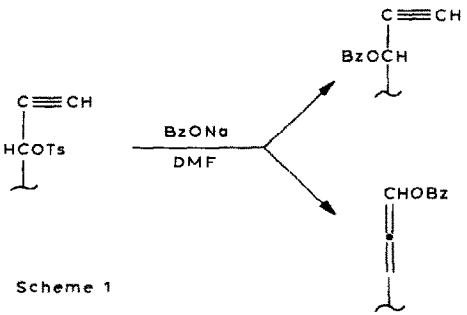
TABLE I

RESULTS OF INVERSION REACTION AT PROPARGYLIC ALCOHOL CENTER

Entry No.	*Substrate No.*	*Reaction conditions*	*Products*			
			Acetylenic ester No.	*Yield (%)*	*Allenic benzoate[a] No.*	*Yield (%)*
1	**2**	DMF, 120–130°, 3 h	—	—	**23**	37
2	**6**		**3**[b]	14	**23**	58
3	**10**		**14**[b]	38	**24**	22
4	**13**		**11**[b]	39	**24**	17
5	**17**		—	—	**25**	33
6	**20**		—	—	**25**	37
7	**1**	1,4-dioxane, reflux, 1 h	**8**[c]	90[d]	—	—
8	**5**		**4**[c]	66[d]	—	—
9	**9**	oxolane, r.t., 12 h	**15**[c]	69	—	—
10	**12**		**11**[b]	76	—	—
11	**16**	1,4-dioxane, reflux, 1 h	**22**[c]	67	—	—
12	**19**	oxolane, r.t., 12 h	**18**[b]	70	—	—

[a]Mixture of diastereoisomers. [b]Benzoate. [c]*p*-Nitrobenzoate. [d]Only a 50% yield after refluxing for 24 h in oxolane.

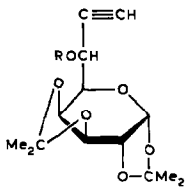


Scheme 1

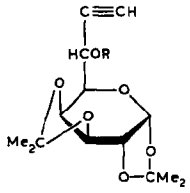
In the remaining three reactions, with tosylates **2**, **17**, and **20** only moderate yields of the corresponding 1,3-substitution products were obtained (see Table I, entries 1, 5, and 6).

The displacement reaction of a mesyloxy group by cesium propanoate has recently been claimed as an efficient inversion method for alcohols[6]. Reaction of the mesylate prepared from **1** with cesium propanoate in *N,N*-dimethylformamide during 12 h at 70° gave 66% of a mixture of diastereoisomeric allenic propanoates (**27**). The mesylate prepared from **5** remained unchanged after heating with cesium propanoate for 12 h at 110° in DMF solution.

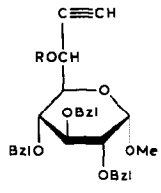
The Mitsunobu inversion reaction[7], *i.e.*, reaction of alcohols with triphenyl-



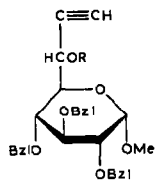
1 R = H
2 R = Ts
3 R = Bz
4 R = $COC_6H_4NO_2$-*p*



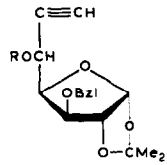
5 R = H
6 R = Ts
7 R = Bz
8 R = $COC_6H_4NO_2$-*p*



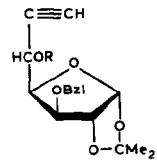
9 R = H
10 R = Ts
11 R = Bz



12 R = H
13 R = Ts
14 R = Bz
15 R = $COC_6H_4NO_2$-*p*

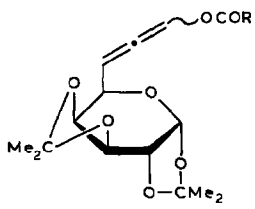


16 R = H
17 R = Ts
18 R = Bz

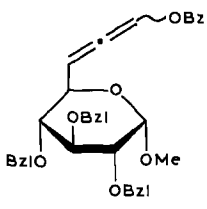


19 R = H
20 R = Ts
21 R = Bz
22 R = $COC_6H_4NO_2$-*p*

phosphine–diethyl azodicarboxylate (TPP-DEAD) betaine and benzoic acid, is characterized by mild, essentially neutral, reaction conditions, and affords inverted benzoates in good yield. Propargylic alcohols **12** and **19** were treated with an excess of TPP-DEAD betaine and benzoic acid, to give the inverted benzoates **11** and **18** as single products in good yield (see Table I, entries 10 and 12). In the remaining four reactions, with alcohols **1**, **5**, **9**, and **16**, no formation of the benzoates could be observed, even after prolonged reaction (3 days). When benzoic acid was replaced by the (more acidic) *p*-nitrobenzoic acid, alcohol **9** gave the inverted *p*-nitrobenzoate (**15**) in 69% yield. Also, after refluxing in 1,4-dioxane solution alcohols **1**, **5**, and **16** reacted with TPP-DEAD betaine and *p*-nitrobenzoic acid, to give the respective, inverted *p*-nitrobenzoates in good yield (see Table I, entries 7, 8, and 11). The identification of the reaction products was based on direct comparison of the products



23 R = Ph
27 R = Et



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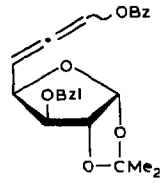

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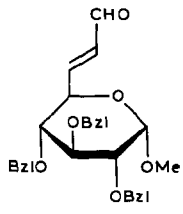

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of hydrolysis with the parent acetylenic alcohols.

Although the Mitsunobu substitution-reaction is known to be very sensitive to steric hindrance[7], its low tendency to rearrangement reactions, and its compatibility with various reagents and conditions, make it the reaction of choice for inversion of configuration in sugar propargylic alcohols.

EXPERIMENTAL

General. — Melting points were determined with a Kofler apparatus and are not corrected. Optical rotations were measured with a Perkin–Elmer 141 spectropolarimeter, for solutions in chloroform at 20 ± 2°. ^{1}H-N.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). I.r. spectra were recorded with a Beckman IR 4240 spectrophotometer. Column chromatography was performed on silica gel (230–400 mesh; Merck). Extracts were dried with anhydrous magnesium sulfate.

Compounds **1**, **2**, **5**, and **6** were prepared according to ref. 8; compounds **16**, **18**, **19**, and **21**, according to ref. 9.

Methyl 2,3,4-tri-O-benzyl-7,7,8,8-tetradehydro-7,8-dideoxy-α-D- and β-L-glycero-D-gluco-octopyranoside (**9** *and* **12**). — A solution of methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside[10] (4.0 g, 8.6 mmol) in oxolane (50 mL) was added dropwise at room temperature, to a stirred solution of bromomagnesium acetylide (generated from 20 mmol of ethylmagnesium bromide and acetylene in 100 mL of oxolane[8]). The mixture was now stirred for 30 min at room temperature, and the excess of the Grignard reagent was decomposed by careful addition of saturated, aq. ammonium chloride. The organic layer was separated and the aqueous phase was extracted with ether. The layer and extracts were combined and evaporated and the residue was chromatographed with 4:1 light petroleum–ethyl acetate, affording **9** and **12**.

Alcohol **9**, 2.80 g (5.74 mmol, 66.7%), m.p. 75–76°, $[\alpha]_D$ +11° (*c* 2); ^{1}H-n.m.r. data: *inter alia*, δ 7.23 (15 H, aromatic H), 3.39 (s, 3 H, OCH_3), and 2.38 (d, 1 H, $J_{8,6}$ 2.0 Hz, H-8).

Anal. Calc. for $C_{30}H_{32}O_6 \cdot 0.5\ H_2O$: C, 72.4; H, 6.9. Found: C, 72.9; H, 6.6.

The configuration of **9** was recently established[11] as D-*glycero*-D-*gluco*.

Alcohol **12**, 910 mg (1.86 mmol, 21.6%), m.p. 90–91°, $[\alpha]_D$ +39° (*c* 1.5); ^{1}H-n.m.r. data: *inter alia*, δ 7.25 (15 H, aromatic H), 3.36 (s, 3 H, OCH_3), and 2.46 (d, 1 H, $J_{8,6}$ 2.0 Hz, H-8).

Anal. Calc. for $C_{30}H_{32}O_6 \cdot 0.5\ H_2O$: C, 72.4; H, 6.9. Found: C, 72.8; H, 6.6.

Propargylic tosylates. — These derivatives were prepared under standard conditios (*p*-toluenesulfonyl chloride and pyridine), and were purified by column chromatography with 4:1 light petroleum–ether.

6,6,7,7-Tetradehydro-6,7-dideoxy-1,2-O-isopropylidene-5-O-p-tolylsulfonyl-α-D-gluco-heptofuranose (**17**), yield: 85%; m.p. 151–152°, $[\alpha]_D$ +35° (*c* 1.5); ^{1}H-n.m.r. data: *inter alia*, δ 7.25 (2 H and 7 H, aromatic H), 5.85 (d, 1 H, $J_{1,2}$ 3.5 Hz,

H-1), 5.40 (dd, 1 H, $J_{5,7}$ 2.0, $J_{5,4}$ 6.0 Hz, H-5), 2.40 (d, 1 H, H-7), 2.35 (s, 3 H, $-SO_2C_6H_4CH_3$), and 1.45 and 1.30 [$C(CH_3)_2$].

Anal. Calc. for $C_{24}H_{26}O_7S$: C, 62.9; H, 5.7. Found: C, 63.1; H, 5.6.

*3-O-Benzyl-6,6,7,7-tetradehydro-6,7-dideoxy-1,2,-O-isopropylidene-5-O-p-tolylsulfonyl-β-*L*-ido-heptofuranose* (**20**), yield: 93%, oil, $[\alpha]_D$ +10° (*c* 1.6); ^{1}H-n.m.r. data: *inter alia*, δ 7.52 and 7.23 (2 H and 7 H, aromatic H), 5.75 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.23 (dd, 1 H, $J_{5,4}$ 9.0, $J_{5,7}$ 2.25 Hz, H-5), 2.44 (4 H, H-7 and $-SO_2C_6H_4CH_3$), and 1.48 and 1.29 [$C(CH_3)_2$].

Anal. Calc. for $C_{24}H_{26}O_7S$: C, 62.9; H, 5.7. Found: C, 63.2; H, 5.8.

*Methyl 2,3,4-tri-O-benzyl-7,7,8,8-tetradehydro-7,8-dideoxy-6-O-p-tolylsulfonyl-α-*D*-glycero-*D*-gluco-octopyranoside* (**10**), yield: 80%, $[\alpha]_D$ +10° (*c* 2); ^{1}H-n.m.r. data: *inter alia*, δ 7.78 and 7.40 (2 H and 17 H, aromatic H), 5.61 (bs, 1 H, H-6), 3.38 (s, 3 H, OCH_3), and 2.40 (4 H, H-8 and $-SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{37}H_{38}O_8S$: C, 69.1; H, 6.0. Found: C, 69.5; H, 6.2.

*Methyl 2,3,4-tri-O-benzyl-7,7,8,8-tetradehydro-7,8-dideoxy-6-O-p-tolylsulfonyl-β-*L*-glycero-*D*-gluco-octopyranoside* (**13**), yield: 75%, $[\alpha]_D$ +24° (*c* 2); ^{1}H-n.m.r. data: *inter alia*, δ 7.73 and 7.35 (2 H and 17 H, aromatic H), 5.40 (t, 1 H, $J_{6,5}$ 2.0 Hz, H-6), 3.36 (s, 3 H, OCH_3), and 2.48 (4 H, H-8 and $-SO_2C_6H_4CH_3$).

Anal. Calc. for $C_{37}H_{38}O_8S$: C, 69.1; H, 6.0. Found: C, 69.0; H, 6.3.

Propargylic benzoates. — These derivatives were prepared using benzoyl chloride and pyridine, and were purified by column chromatography, with 9:1 light petroleum–ethyl acetate.

*6-O-Benzoyl-7,7,8,8-tetradehydro-7,8-dideoxy-1,2,3,4-di-O-isopropylidene-α-*D*-glycero-*D*-galacto-octopyranoside* (**3**), yield: 75%, m.p. 170–171°, $[\alpha]_D$ −96° (*c* 1.0); ^{1}H-n.m.r. data: *inter alia*, δ 7.93 and 7.38 (2 H and 3 H, aromatic H), 5.68 (dd, 1 H, $J_{6,8}$ 2.0, $J_{6,5}$ 9.0 Hz, H-6), 5.60 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 2.51 (d, 1 H, H-8), and 1.59, 1.43, 1.35, and 1.26 [4 s, 12 H, 2 $C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{24}O_7$: C, 64.9; H, 6.2. Found: C, 64.9; H, 6.3.

*7,7,8,8-Tetradehydro-7,8-dideoxy-1,2,3,4-di-O-isopropylidene-β-*L*-glycero-*D*-galacto-octopyranoside* (**7**), yield: 88%, m.p. 93–94°, $[\alpha]_D$ −45° (*c* 1.9); ^{1}H-n.m.r. data: *inter alia*, δ 8.03 and 7.44 (2 H and 3 H, aromatic H), 5.78 (dd, 1 H, $J_{6,8}$ 2.0, $J_{6,5}$ 9.8 Hz, H-6), 5.53 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 2.47 (d, 1 H, H-8), and 1.50, 1.35, and 1.22 [3 s, 12 H, 2 $C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{24}O_7$: C, 64.9; H, 6.2. Found: C, 65.0; H, 6.1.

*Methyl-6-O-benzoyl-2,3,4-tri-O-benzyl-7,7,8,8-tetradehydro-7,8-dideoxy-α-*D*-glycero-*D*-gluco-octopyranoside* (**11**), yield: 80%, m.p. 132–133°, $[\alpha]_D$ +30° (*c* 1.8); ^{1}H-n.m.r. data: *inter alia*, δ 8.10 and 7.33 (2 H and 3 H, aromatic H), 6.03 (bs, 1 H, H-6), 3,50 (s, 3 H, OCH_3), and 2.48 (d, 1 H, $J_{6,8}$ 2.0 Hz, H-8).

Anal. Calc. for $C_{37}H_{36}O_7$: C, 75.0; H, 6.1. Found: C, 74.7; H, 6.2.

*Methyl 6-O-benzoyl-2,3,4-tri-O-benzyl-7,7,8,8-tetradehydro-7,8-dideoxy-β-*L*-glycero-*D*-gluco-octopyranoside* (**14**), yield: 75%, syrup, $[\alpha]_D$ +21° (*c* 1.0); ^{1}H-n.m.r. data: *inter alia*, δ 8.01 and 7.30 (2 H and 3 H, aromatic H), 6.00 (t, 1 H, $J_{6,5} \approx J_{6,8} \approx$ 2.0 Hz, H-6), 3.35 (s, 3 H, OCH_3), and 2.48 (d, 1 H, H-8).

Anal. Calc. for $C_{37}H_{36}O_7$: C, 75.0; H, 6.1. Found: C, 74.9; H, 6.0.

Nucleophilic displacement of tosyloxy group in sugar acetylenic tosylates with sodium benzoate. — Propargylic tosylates **2**, **6**, **10**, **13**, **17**, and **20** (~500 mg each) were separately dissolved in *N,N*-dimethylfomamide (10 mL), and sodium benzoate (~3 mol. equiv.) was added. The heterogeneous mixture was stirred for 3 h at 120–130°, cooled to room temperature, and extracted thrice with ether. The respective crude products were separated by column chromatography with 4:1 light petroleum–ether. The yields of products are recorded in Table I.

8-O-Benzoyl-6,7-dideoxy-1,2:3,4-di-O-isopropylidene-α,β-D-galacto-oct-6,7-dienopyranose (**23**), a syrup; $[\alpha]_D$ +16° (*c* 1,1) (for the product obtained from **2**); $[\alpha]_D$ +14° (*c* 1.8) (from **6**); ν_{max} 1980 and 1735 cm^{-1}; ^{1}H-n.m.r. data: *inter alia*, δ 8.01 and 7.40 (2 H and 3 H, aromatic H), 7.71 (d, 1 H, $J_{8,6}$ 6.0 Hz, H-8), 6.03 (t, 1 H, $J_{6,5}$ 6.0 Hz, H-6), 5.53 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), and 1.53, 1.48, 1.36, and 1.34 [4 s, 12 H, 2 $C(CH_3)_2$].

Methyl 8-O-benzoyl-2,3,4-tri-O-benzyl-6,7-dideoxy-α,β-D-gluco-oct-6,7-dienopyranoside (**24**), syrup; $[\alpha]_D$ +78° (*c* 1.1) (from *10*), $[\alpha]_D$ +72° (*c* 0.8) (from *13*); ν_{max} 1985 and 1730 cm^{-1}; ^{1}H-n.m.r. (500 MHz) data: *inter alia*, δ 7.86 and 7.77 (2 d, 1 H, $J_{8,6}$ 6.0 Hz, H-8 of both diastereoisomers), 6.03 and 5.99 (2 t, 1 H, $J_{6,5}$ 6.0 Hz, H-6 of both diastereoisomers), and 3.42 (s, 3 H, OCH_3).

7-O-Benzoyl-3-O-benzyl-5,6-dideoxy-1,2-O-isopropylidene-α,β-D-gluco-hept-5,6-dienofuranose (**25**), syrup, $[\alpha]_D$ +10° (*c* 1.1) (from **17** and from **20**); ν_{max} 1980 and 1740 cm^{-1}; ^{1}H-n.m.r. data: *inter alia*, δ 8.02 and 7.40 (2 H and 8 H, aromatic H), 7.80 (d, 1 H, $J_{7,5}$ 5.5 Hz, H-7), 6.12 (dd, 1 H, $J_{5,4}$ 7.5 Hz, H-5), and 1.50 and 1.32 [2 s, 6 H, $C(CH_3)_2$].

Methyl 8-aldehydo-2,3,4-tri-O-benzyl-6,7-dideoxy-α-D-gluco-oct-6-enodialdo-1,5-pyranoside (**26**). — Allenic benzoate **24** (50 mg) was dissolved in methanol (1 mL), and potassium carbonate (100 mg) was added. After stirring for ~20 min at room temp., t.l.c. with 2:1 light petroleum–ethyl acetate indicated disappearance of the substrate, and formation of a new product. The mixture was diluted with ether (10 mL), and filtered, and the filtrate was washed with water, dried, and evaporated to dryness. The residue was chromatographed on a short column of silica gel with 5:1 light petroleum–ethyl acetate, to furnish **26**; 25 mg, ν_{max} 1690 and 1640 cm^{-1}. This product was identified by t.l.c. and i.r. comparison with synthetic aldehyde **26** prepared as follows. Methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside[10] (180 mg) and formylmethylene-triphenylphosphorane (150 mg) were dissolved in dry toluene, and the solution refluxed for 2 h. After evaporation, the residue was purified on a column of silica gel with 9:1 light petroleum–acetone, to yield aldehyde **26** (120 mg, 64%); syrup, $[\alpha]_D$ +92° (*c* 2.6); ν_{max} 1690 and 1640 cm^{-1}; *m/z* 488 (M^+), 457 ($M - OCH_3$), 456 ($M^+ - CH_3OH$), and 379 ($M^+ - C_7H_7$); ^{1}H-n.m.r. data: *inter alia*, δ 9.25 (d, 1 H, $J_{8,7}$ 7.5 Hz, H-8), 6.23 (ABq, 2 H, $J_{6,5}$ 3.5, $J_{6,7}$ 15.0 Hz, H-6,7), and 3.33 (s, 3 H, OCH_3).

Nucleophilic displacement of mesyloxy groups in sugar acetylenic mesylates with cesium propanoate. — Alcohols **1** and **5** were converted into 6-*O*-mesyl deriva-

tives under standard conditions (methanesulfonyl chloride and pyridine). Crude mesylates (300 mg each) were separately dissolved in dry *N,N*-dimethylformamide (10 mL), dry cesium propanoate (2 equiv.) was added and the mixture was stirred for 12 h at 70°. After cooling to room temperature water (30 mL) was added and the products were extracted with ether (2 × 50 mL).

The mesylate obtained from L-*glycero* alcohol **5** remained unchanged. The mesylate obtained from **1** was converted into 6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-8-*O*-propanoyl-α,β-D-*galacto*-oct-6,7-dienopyranose (**27**). Yield (after chromatography with 3:1 light petroleum–ether); 190 mg, syrup: ^{1}H-n.m.r. data: *inter alia*, δ 7.47 (d, 1 H, $J_{8,6}$ 5.6 Hz, H-8), 5.80 (dt, 1 H, $J_{6,5}$ 6.8 Hz, H-6), and 5.40 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1).

Mitsunobu inversion-reaction with sugar propargylic alcohols. — Alcohols **1**, **5**, **9**, **12**, **16**, and **19** (2 mmol each) were separately dissolved in dry oxolane (5 mL), and to the solution were added triphenylphosphine (2.63 g, 10 mmol), benzoic acid (1.22 g, 10 mmol) and diethyl azodicarboxylate (1.74 g, 1.6 mL, 10 mmol). Each mixture was stirred overnight at room temperature and then checked by t.l.c. with 3:2 light petroleum–ethyl acetate. Alcohols **1**, **5**, **9**, and **16** remained unchanged. Alcohols **12** and **19** were respectively converted into the benzoates **11** and **18**. These benzoates were isolated by flash chromatography with 9:1 and then 4:1 light petroleum–ethyl acetate, and identified by comparison (t.l.c. and i.r.) with original benzoates prepared directly from alcohols **9** and **16**.

Under analogous conditions, alcohol **9** reacted with TPP-DEAD betaine and *p*-nitrobenzoic acid, furnishing *p*-nitrobenzoate **15**. The remaining alcohols (**1**, **5**, and **16**) reacted with the same mixture of reagents in boiling 1,4-dioxane solution (1 h) to yield the respective inverted *p*-nitrobenzoates (see Table I, entries 7–9 and 11).

The *p*-nitrobenzoates were hydrolyzed in methanolic solution with potassium carbonate during ~20 min at room temperature and the free propargylic alcohols were directly identified (t.l.c. and i.r.) with original samples.

7,7,8,8-Tetradehydro-7,8-dideoxy-1,2:3,4-di-O-*isopropylidene-6*-O-(p-*nitrobenzoyl*)-α-D-glycero-D-galacto-*octopyranose* (**4**), a foam, m.p. 63.5–65°, $[\alpha]_D$ −82° (*c* 1.1); ^{1}H-n.m.r. data: *inter alia*, δ 8.37 (4 H, aromatic H), 5.81 (dd, 1 H, $J_{6,8}$ 1.8, $J_{6,5}$ 9.2 Hz, H-6), 5.68 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 2.63 (d, 1 H, H-8), and 1.63, 1.47, 1.40, and 1.32 [4 s, 12 H, 2 $C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{23}NO_9$: C, 58.2; H, 5.4; N, 3.2. Found: C, 57.9; H, 5.6; N, 3.0.

7,7,8,8-Tetradehydro-7,8-dideoxy-1,2:3,4-di-O-*isopropylidene-6*-O-(p-*nitrobenzoyl*)-β-L-glycero-D-galacto-*octopyranose* (**8**), m.p. 170–173°, $[\alpha]_D$ −56° (*c* 1.1); ^{1}H-n.m.r. data: *inter alia*, δ 8.40 (4 H, aromatic H), 5.92 (dd, 1 H, $J_{6,8}$ 2.0, $J_{6,5}$ 9.6 Hz, H-6), 5.62 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 2.73 (d, 1 H, H-8), and 1.67, 1.53, and 1.42 [3 s, 12 H, 2 $C(CH_3)_2$].

Anal. Calc. for $C_{21}H_{23}NO_9$: C, 58.2; H, 5.4; N, 3.2. Found: C, 58.2; H, 5.5; N, 2.8.

Methyl 2,3,4-tri-O-benzyl-7,7,8,8-tetradehydro-7,8-dideoxy-6-O-(p-*nitro*-

benzoyl)-β-L-glycero-D-gluco-*octopyranoside* (**15**), a foam, m.p. 50.–52°, $[\alpha]_D$ +7° (*c* 1.3); ^{1}H-n.m.r. data: *inter alia*, δ 8.18 and 7.30 (4 H and 15 H, aromatic H), 5.98 (t, 1 H, $J_{6,8} \approx J_{6,5}$ = 2.2 Hz, H-6), 3.30 (s, 3 H, OCH_3), and 2.50 (d, 1 H, H-8).

Anal. Calc. for $C_{37}H_{35}NO_9$: C, 69.7; H, 5.5; N, 2.2. Found: C, 69.7; H, 5.5; N, 2.0.

3-O-Benzyl-6,6,7,7-tetradehydro-6,7-dideoxy-1,2-O-isopropylidene-5-O-(p-nitrobenzoyl)-β-L-ido-*heptofuranose* (**22**), m.p. 138.–138.5°, $[\alpha]_D$ −31° (*c* 0.7); ^{1}H-n.m.r. data: *inter alia*, δ 8.27 and 7.38 (4 H and 5 H, aromatic H), 6.00 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.93 (dd, 1 H, $J_{5,4}$ 9.2, $J_{5,7}$ 2.0 Hz, H-5), 2.47 (d, 1 H, H-7), and 1.52, 1.30 [2 s, 6 H, $C(CH_3)_2$].

Anal. Calc. for $C_{24}H_{23}NO_8$: C, 63.6; H, 5.1; N, 3.1. Found: C, 63.6; H, 4.9; N, 2.9.

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