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SYNTHESIS AND PHOTOLYSIS OF SOME CARBOHYDRATE 1,6-DIENES*

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ABSTRACT

Several attempts to abbreviate our earlier syntheses of the prostaglandin intermediates **4** and **5** by photocyclisation of carbohydrate-based 1,6-dienes (**15–18, 20, 22**) did not yield the required bicyclo[3.2.0]heptane derivatives. Photolysis of 7-*O*-*tert*-butyldimethylsilyl-1,3,4,5,8,9-hexadeoxy-6-*O*-methoxymethyl-D-*threo*-non-3,8-dien-2-ulose (**20**) and ethyl 6-*O*-*tert*-butyldimethylsilyl-2,3,4,7,8-pentadeoxy-5-*O*-methoxymethyl-D-*threo*-oct-2,7-dienonate (**22**) caused migration of the conjugated alkene bond.

INTRODUCTION

A recent interest in our laboratory has been the use of readily available carbohydrate compounds in the development of routes to optically pure prostaglandin intermediates that can be used in the preparation of the natural products and a wide range of their analogues[2]. One strategy involved the synthesis of the non-3,8-dienulose derivative **2** from the enal **1** and its photoisomerisation into the bicyclo[3.2.0]heptane derivative **3**, which was subsequently converted into the intermediates **4**[3] and **5**[4,5] from which prostaglandins have been obtained[6–9]. Although the reported methods represent formal syntheses of the intermediates **4** and **5** in their required enantiomeric forms, and although **1** is readily available from D-glucose, the procedures are lengthy and we have emphasised this in using racemic **5**, rather than the more inaccessible and expensive, enantiomerically pure form which is available from D-glucose[4], for the development of a route to carbacyclin[5].

To abbreviate the conversion of such carbohydrate-based 1,6-dienes as **2** into prostaglandins by way of compounds related to **5**, three aspects of the published route[4,5] require attention: (*a*) the removal of the oxygen function at the allylic centre carrying the tosyloxy group in **2**, (*b*) the specific conversion of the remaining substituted α-diol into the required epoxide, and (*c*) a more direct production of the cyclobutanone ring than by way of the acetyl-substituted system in **3**. We therefore planned a route which involved, as starting material, a sugar derivative having

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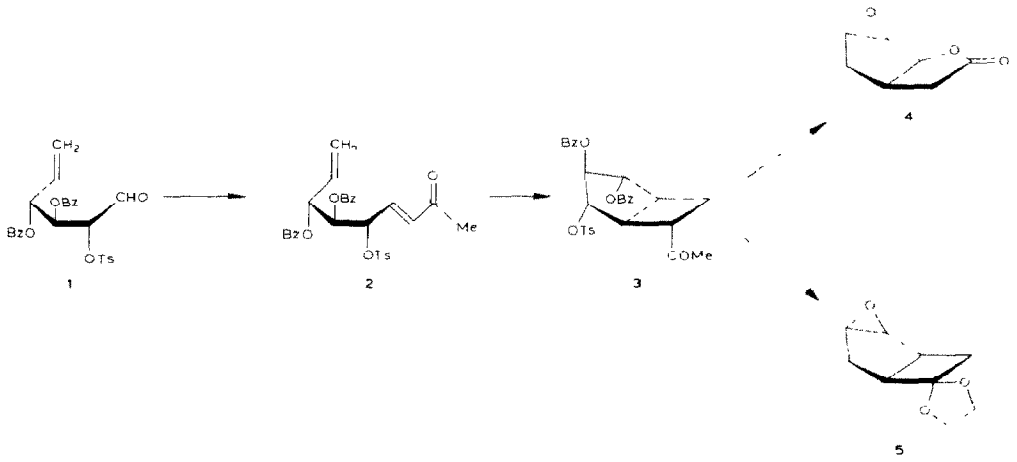
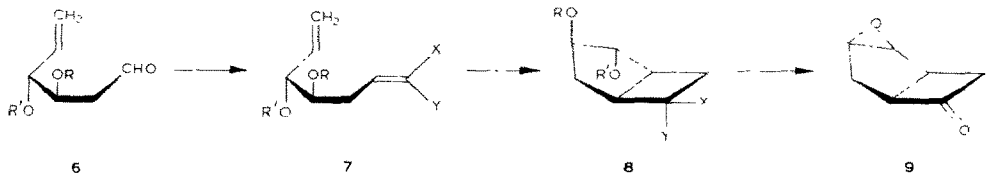


a deoxy group in the place of the tosyloxy group and with a differently substituted D-*threo*-diol such that the higher numbered hydroxyl group could be specifically made the leaving group for the production of the epoxide ring. Thirdly, we hoped to produce a hept-1,6-dienose derivative disubstituted at C-1 in such a way that, after photochemical ring-closure, the substituents could be removed simply to give a bicyclo[3.2.0]heptanone directly. We now report the synthesis of the enal **6**, which meets the first two requirements, and the synthesis of several 1,1-disubstituted hept-1,6-dienoses (**7**) which, in principle, could give the bicyclic products **8** by photochemical [2 + 2]cycloaddition and hence the cyclobutanone **9**, and thus the required acetal **5**.

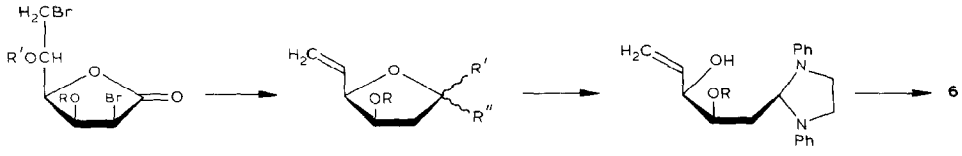


R = $MeOCH_2$, R′ = $Si(Me)_2{}^tBu$

RESULTS AND DISCUSSION

2,6-Dibromo-2,6-dideoxy-D-mannono-1,4-lactone (**10**), which is readily available from D-glucono-1,5-lactone or calcium D-gluconate[10], was readily converted into the 5-benzoate by selective esterification and thence into the crystalline 3-methoxymethyl ether **11** by treatment with dimethoxymethane in the presence of phosphorus pentaoxide[11]. The coupling pattern of the specifically deshielded proton *H*COBz of the 5-benzoate readily allowed the assignment of position of the ester group and hence the structure of **11**. Since Br-2 of **10** can be removed specifically by reduction[12], and since treatment with zinc would be expected to produce an

alkene from a bromide having a vicinal ester group[13], **11** was treated with a zinc–silver couple[14] in aqueous ethanol, and it gave the unsaturated lactone **12** in high yield. Reduction of **12** with di-isobutylaluminium hydride gave the hex-5-enofuranose derivative **13**, which was converted into the fully substituted *aldehydo*-sugar derivative **6** by way of the *N,N*-diphenylimidazolidine derivative[15] **14**.

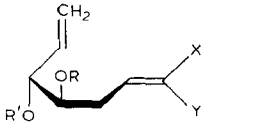


	R	R'
10	H	H
11	$MeOCH_2$	Bz

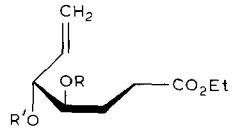
	R	R'	R''
12	$MeOCH_2$	O	O
13	$MeOCH_2$	H	OH

14 R = $MeOCH_2$

Four compounds with the general structure **7** were then synthesised from **6** as possible sources of bicyclic compounds **8** and hence the cyclobutanone **9**. These were the dichloride **15** (obtained by use of the ylid derived from diethyl trichloromethylphosphonate[16]), the analogous dibromide **16** (obtained by use of triphenylphosphine and carbon tetrabromide[17]), the dithiolane **17** (obtained by way of the phosphonate procedure[18]), and the α-aminonitrile **18** (synthesised by the use of the anion of diethylaminoacetonitrile[19]). In the last reaction, the first products were the corresponding stereoisomeric secondary alcohols which, on methanesulphonylation and then treatment with base, gave the two geometrically isomeric alkenes **18**.



	R	R'	X	Y
15	$MeOCH_2$	$Si(Me)_2{}^tBu$	Cl	Cl
16	$MeOCH_2$	$Si(Me)_2{}^tBu$	Br	Br
17	$MeOCH_2$	$Si(Me)_2{}^tBu$	S⌒S	
18	$MeOCH_2$	$Si(Me)_2{}^tBu$	CN	NEt_2



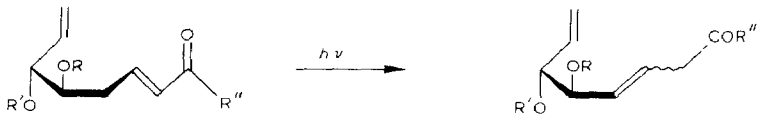
19 R = $MeOCH_2$
R' = $Si(Me)_2{}^tBu$

In our hands, the halides **15** and **16** proved to be unsuitable as precursors of bicyclo[3.2.0]heptane systems; irradiation of solutions of these compounds in benzene or ether at 254 or 350 nm in the presence of benzophenone as sensitisor, and at 20° or −78°, yielded nonspecific products which, in t.l.c., migrated as relatively slow-running streaks or else were so polar that they failed to migrate. Acid was produced during these photolyses but the addition of *N,N*-dimethylaniline did not prevent decomposition. Similarly, the dichloride **15**, on treatment with mercury(II) acetate in various solvents or with the mercury(II) trifluoromethanesulphonate–

N,N-dimethylaniline complex, which can cause transannular cyclisations[20], failed to give discrete products. In analogous fashion, the dithiolane **17** could not be cyclised photochemically to give the desired bicyclic product.

Radiation of a solution of the nitrile **18** in benzene at 350 nm gave mainly the initial aldehyde **6**. It was suspected that moisture was present in the system since the addition of water to **18** could give a β-hydroxynitrile which could afford **6** by a reversal of the initial addition step. When the reaction was repeated under anhydrous conditions, only a trace of **6** was formed and a product with a mobility similar to that of **18** preponderated. Remarkably, this product was the ester **19**, which was readily characterised by n.m.r. and i.r. spectroscopy, but it is not clear how it was derived. It may be noted that a diradical, formed by excitation of the conjugated double-bond of **18**, has one centre stabilised by the substituents in the captodative manner[21]. Were this species to react with oxygen and a hydrogen atom acquired at the other centre to give a methylene group, it seems possible that the peroxy product could collapse to give **19**.

The failure to obtain cyclic products of the type **7** from **15–18** led to an investigation of the photolysis of the methyl ketone **20**, which is akin to the initial dienone **2** that underwent ring closure[4]. Irradiation of a solution of **20** in dichloromethane at 350 nm gave a single product with a chromatographic mobility similar to that of **20**, but which was distinguishable by its inability to quench the phosphor on silica gel plates. ^{1}H-N.m.r. spectroscopy indicated this product to be isomeric with **20** and that five vinylic protons were present, showing that cycloaddition had not occurred. Major changes had occurred in the resonances of the protons of the non-terminal double-bond. Initially, they resonated at δ 6.03 and 6.81, as is consistent with the conjugated nature of the bond, and finally they resonated near δ 4.7 and 5.6 which revealed that the double bond of the product was no longer conjugated with the carbonyl group. In complementary fashion, H-6 resonated at δ 3.55 in **20** and at δ 4.0 in the product, consistent with its having become allylic, from which it is assumed that the product has structure **21**. Double signals in the spectrum of **21** showed that the isomerisation had occurred to give mixed geometric isomers. Such isomerisations are well recognised for conjugated unsaturated ketones and are initiated by hydrogen abstraction, by the oxygen atoms of the excited carbonyl groups, from the γ-positions[22].



	R	R′	R″
20	$MeOCH_2$	$Si(Me)_2{}^tBu$	Me
22	$MeOCH_2$	$Si(Me)_2{}^tBu$	OEt

	R	R′	R″
21	$MeOCH_2$	$Si(Me)_2{}^tBu$	Me
23	$MeOCH_2$	$Si(Me)_2{}^tBu$	OEt

In analogous fashion, the conjugated ester **22** underwent deconjugation to give the isomeric compounds **23** on photolysis of a solution in ether at 254 nm. Analogous shifts occurred to the n.m.r. signals of the alkene protons, which moved from δ 5.8 and 7.0 to δ 4.6 and 5.7; the signal for H-5 moved downfield by 0.5 p.p.m.

Thus, it is clear that the substituents on 1,6-dienes play a major role in determining whether they readily take part in photochemical cycloaddition processes, and that, for such dienones as **2** and **20**, the presence of an oxygenated function at C-5 is important.

EXPERIMENTAL

N.m.r. spectra were recorded for solutions in $CDCl_3$ using a Varian FT80A instrument. Optical rotations were measured for solutions (*c* 1–2) in chloroform.

*5-O-Benzoyl-2,6-dibromo-2,6-dideoxy-3-O-methoxymethyl-*D*-mannono-1,4-lactone* (**11**). — Benzoyl chloride (11 mL) was added dropwise with stirring to a solution of 2,6-dibromo-2,6-deoxy-D-mannono-1,4-lactone[10] (**10**, 25 g) in pyridine (100 mL) at −30°, and the stirring was continued for 1 h as the temperature rose to −10°. The mixture was poured into water (1 L) and thrice extracted with chloroform, and the combined extracts were washed with dilute hydrochloric acid and aqueous sodium hydrogencarbonate. After drying, the chloroform was removed to give a dark-yellow syrup which, after purification by flash chromatography[23], gave the 5-benzoate (21.6 g, 65%), $[\alpha]_D$ −2°. ^{1}H-N.m.r. data: δ 3.77 (dd, 1 H, $J_{5,6}$ 4.1, $J_{6,6'}$ 11.8 Hz, H-6), 3.96 (dd, 1 H, $J_{5,6'}$ 3.1 Hz, H-6'), 4.54 (dd, 1 H, $J_{2,3}$ 4.2, $J_{3,4}$ 2.7 Hz, H-3), 4.78 (dd, 1 H, $J_{4,5}$ 8.6 Hz, H-4), 4.81 (d, 1 H, H-2), 5.51 (ddd, 1 H, H-5), and 7.2–8.1 (2 m, 5 H, Ph).

A solution of the 5-benzoate (7.0 g) in dichloromethane–dimethoxymethane (150 mL, 1:2) was stirred for 15 min with phosphorus pentaoxide (10.0 g) and then decanted. The residue was washed with dichloromethane, and the combined organic phases were washed with water and aqueous sodium hydrogencarbonate. After drying, the solvent was removed to give **11** (7.01 g, 90%). After recrystallisation from ethyl acetate–light petroleum, the product had m.p. 152–154°, $[\alpha]_D$ −49°. ^{1}H-N.m.r. data: δ 3.22 (s, 3 H, OMe), 3.82 (dd, 1 H, $J_{5,6}$ 3.4, $J_{6,6'}$ 11.9 Hz, H-6), 4.09 (dd, 1 H, $J_{5,6'}$ 2.9 Hz, H-6'), 4.55–5.0 (m, 5 H, H-2,3,4, OCH_2O), 5.49 (ddd, 1 H, $J_{4,5}$ 8.1 Hz, H-5), and 7.3–8.1 (2 m, 5 H, Ph).

Anal. Calc. for $C_{15}H_{16}Br_2O_6$: C, 39.8; H, 3.5; Br, 35.3. Found: C, 39.7; H, 3.4; Br, 35.3.

*2,5,6-Trideoxy-3-O-methoxymethyl-*D*-*threo*-hex-5-enono-1,4-lactone* (**12**). — The dibromolactone **11** (3.0 g) was dissolved in refluxing aqueous ethanol (100 mL), zinc–silver couple[14] (15 g) was added with stirring, and the mixture was further stirred for 8 h at 20°. The solids were removed with the aid of Celite, and the solvent was distilled off to give an oil which was purified by flash chromatography to give **12** (1.01 g, 87%), $[\alpha]_D$ +24°. N.m.r. data: ^{1}H, δ 2.55 (dd, 1 H, $J_{2,2'}$

16, $J_{2,3}$ 3.4 Hz, H-2), 2.80 (dd, 1 H, $J_{2',3}$ 4.8 Hz, H-2'), 3.35 (s, 1 H, OMe), 4.45 (dt, 1 H, $J_{3,4}$ 4.7 Hz, H-3), 4.63 (s, 2 H, OCH_2O), 4.91 (dd, 1 H, $J_{4,5}$ 5.7 Hz, H-4), 5.39 (dd, 1 H, $J_{5,6}$ 11.8, $J_{6,6'}$ 0.7 Hz, H-6), 5.45 (dd, 1 H, $J_{5,6'}$ 15.4 Hz, H-6'), and 6.05 (ddd, 1 H, H-5); ^{13}C, δ 36.3 (C-2), 55.8 (OMe), 74.3 (C-3), 83.9 (C-4), 95.8 (OCH_2O), 119.9 (C-6), 131.3 (C-5), and 174.5 (C-1).

Anal. Calc. for $C_8H_{12}O_4$: C, 55.8; H, 7.0. Found: C, 55.6; H, 7.1.

2,5,6-Trideoxy-3-O-methoxymethyl-D-threo-*hex-5-enofuranose* (**13**). — A solution of di-isobutylaluminium hydride (1.02 mol) in dichloromethane (5 mL) was added with stirring under nitrogen to a solution of **12** (0.88 g) in dichloromethane (20 mL) at −78°. Stirring was continued at this temperature for 20 min, and the mixture was then quenched with water (2 mL), warmed to 20°, and filtered with the aid of Celite. The organic phase was separated and dried, the solvent was removed, and the residue was purified by flash chromatography to give **13** (0.72 g, 81%), $[\alpha]_D$ −7.5° N.m.r. data: ^1H, δ 2.2 (m, 2 H, H-2,2'), 3.33, 3.35 (2 s, 3 H, OMe), 3.4–3.9 (bs, 1 H, OH), 4.2–4.5 (m, 1 H, H-3), 4.6–4.65 (m, 2 H, OCH_2O), and 5.1–6.2 (m, 4 H, H-4,5,6,6'): ^{13}C, δ 40.6, 41.0 (C-2), 55.5, 55.7 (OMe), 77.4, 78.0 (C-2), 81.6, 84.4 (C-4), 95.6 (OCH_2O), 97.6, 98.7 (C-1), 118.0 (C-6), 133.9, and 134.8 (C-5).

Anal. Calc. for $C_8H_{14}O_4$: C, 55.1; H, 8.1. Found: C, 54.6; H, 8.0.

4-O-tert-Butyldimethylsilyl-2,5,6-trideoxy-3-O-methoxymethyl-D-threo-aldehydo-*hex-5-enose* (**6**). — Treatment of a solution of **13** (0.53 g) in methanol (25 mL) with 1,2-bis(phenylamino)ethane (1.4 g) under reflux for 5 h gave a chromatographically more-mobile product. The solvent was removed, the residue was dissolved in *N,N*-dimethylformamide (10 mL), imidazole (0.62 g) and *tert*-butyldimethylsilyl chloride (0.92 g) were added, and the solution was kept at 0° for 3 h and 20° for 15 h. Ether was added, the mixture was washed with dilute aqueous hydrochloric acid, and the organic phase was then stirred with aqueous 5% hydrochloric acid for 0.5 h. The ether layer was separated, washed with aqueous sodium hydrogencarbonate and water, and dried, and the solvent was removed. Flash chromatography of the residue gave **6** (0.49 g, 55%), $[\alpha]_D$ +57°. N.m.r. data: ^1H, δ 0.01, 0.03 (2 s, 6 H, $SiMe_2$), 0.83 (s, 9 H, CMe_3), 2.35 (ddd, 1 H, $J_{1,2}$ 2.5, $J_{2,2'}$ 16.2, $J_{2,3}$ 7.5 Hz, H-2), 2.62 (ddd, 1 H, $J_{1,2'}$ 1.8, $J_{2',3}$ 4.4 Hz, H-2'), 3.29 (s, 3 H, OMe), 4.02 (dt, 1 H, $J_{3,4}$ 4.5 Hz, H-3), 4.30 (tt, 1 H, $J_{4,5}$ 4.5, $J_{4,6} = J_{4,6'} = 1.5$ Hz, H-4), 4.65 (s, 2 H, OCH_2O), 5.17 (dt, 1 H, $J_{5,6}$ 10.0, $J_{6,6'}$ 1.5 Hz, H-6), 5.29 (dt, 1 H, $J_{5,6'}$ 17.4 Hz, H-6'), 5.87 (ddd, 1 H, H-5), and 9.66 (dd, 1 H, H-1); ^{13}C, δ −4.9, −4.6 ($SiMe_2$), 18.2 (CMe_3), 25.9 (CMe_3), 44.6 (C-2), 55.7 (OMe), 73.8, 76.5 (C-3,4), 97.2 (OCH_2O), 116.6 (C-6), 136.4 (C-5), and 200.0 (C-1).

Anal. Calc. for $C_{14}H_{28}O_4Si$: C, 58.4; H, 9.8. Found: C, 58.6; H, 9.7.

5-O-tert-Butyldimethylsilyl-1,1-dichloro-1,2,3,6,7-pentadeoxy-4-O-methoxymethyl-D-threo-*hept-1,6-dienose* (**15**). — A solution of butyl-lithium (1.2 mol) in hexane was added dropwise to a solution of diethyl trichloromethylphosphonate (0.2 g) in ether–tetrahydrofuran (5 mL, 6:4) at −100° and the mixture was stirred for 5 min prior to the slow addition of a solution of **6** (0.2 g) in the same solvent

(1 mL). Stirring was continued as the solution warmed to 20° during 3 h. Ether was added, the mixture was washed with water and dried, and the solvent was removed. The syrupy residue was purified by flash chromatography to give **15** (0.18 g, 73%), $[\alpha]_D$ +58°; $\lambda_{max}^{Et_2O}$ 208 nm (ε 6800). N.m.r. data: ^1H, δ 0.01, 0.03 (2 s, 6 H, $SiMe_2$), 0.85 (s, 9 H, CMe_3), 2.15 (ddd, 1 H, $J_{2,3}$ 7.3, $J_{3,4}$ 8, $J_{3,3'}$ 16 Hz, H-3), 2.45 (ddd, 1 H, $J_{2,3'}$ 7.3, $J_{3',4}$ 4.4 Hz, H-3'), 3.32 (s, 3 H, OMe), 3.50 (m, 1 H, H-4), 4.19 (tt, 1 H, $J_{4,5} = J_{5,6} = 5.2$, $J_{5,7} = J_{5,7'} = 1.5$ Hz, H-5), 4.58, 4.66 (2 d, 2 H, J 10.8 Hz, OCH_2O), 5.16 (ddd, 1 H, $J_{6,7}$ 10, $J_{7,7'}$ 2.4 Hz, H-7), 5.22 (ddd, 1 H, $J_{6,7'}$ 17.3 Hz, H-7'), 5.86 (ddd, 1 H, H-6), and 5.92 (t, 1 H, H-2); ^{13}C, δ −4.9, −4.6 ($SiMe_2$), 18.2 (CMe_3), 25.9 (CMe_3), 30.8 (C-3), 55.6 (OCH_3), 74.6, 79.9 (C-4,5), 97.1 (OCH_2O), 116.3 (C-7), 120.5 (C-1), 127.3 (C-2), and 136.7 (C-6).

Anal. Calc. for $C_{15}H_{28}Cl_2O_3Si$: C, 50.7; H, 8.0. Found: C, 50.6; H, 8.2.

*1,1-Dibromo-5-*O*-*tert*-butyldimethylsilyl-1,2,3,6,7-pentadeoxy-4-*O*-methoxymethyl-*D*-*threo*-hept-1,6-dienose* (**16**). — To a solution of triphenylphosphine (0.5 g) and carbon tetrabromide (0.35 g) in dichloromethane (5 mL) at 0° was added a solution of **6** (0.1 g) in dichloromethane (1 mL). The mixture was stirred for 15 min at this temperature, washed with water, dried, filtered through silica gel, and concentrated to dryness. Preparative t.l.c. of the residue gave **16** (0.13 g, 85%), $[\alpha]_D$ +45°; $\lambda_{max}^{Et_2O}$ 210 nm. N.m.r. data: ^1H, δ 0.04, 0.06 (2 s, 6 H, $SiMe_2$), 0.89 (s, 9 H, CMe_3), 1.95–2.50 (m, 2 H, H-3,3'), 3.37 (s, 3 H, OMe), 3.60 (m, 1 H, H-4), 4.22 (tt, 1 H, $J_{4,5} = J_{5,6} = 5.1$, $J_{5,7} = J_{5,7'} = 1$ Hz, H-5), 4.66 (2 d, 2 H, J 10.7 Hz, OCH_2O), 5.21 (ddd, 1 H, $J_{6,7}$ 10, $J_{7,7'}$ 2 Hz, H-7), 5.26 (ddd, 1 H, $J_{6,7'}$ 18.2 Hz, H-7'), 5.80 (ddd, 1 H, H-6), and 6.51 (t, 1 H, $J_{2,3} = J_{2,3'} = 7.1$ Hz, H-2); ^{13}C, δ −4.9, −4.6 ($SiMe_2$), 18.2 (CMe_3), 25.9 (CMe_3), 34.1 (C-3), 55.7 (OMe), 74.7, 79.6 (C-4,5), 89.4 (C-1), 97.1 (OCH_2O), 116.4 (C-7), 136.1, and 136.7 (C-2,6).

Anal. Calc. for $C_{15}H_{28}Br_2O_3Si$: C, 40.6; H, 6.4; Br, 36.0. Found: C, 41.0; H, 6.6; Br, 35.0.

*5-*O*-tert-Butyldimethylsilyl-2,3,6,7-tetradeoxy-4-*O*-methoxymethyl-*D*-threo-hept-1,6-dienose trimethylene dithioacetal* (**17**). — 1.4M Butyl-lithium in light petroleum (0.48 mL) was added with stirring at −10° under nitrogen to a solution of diethyl 1,3-dithian-2-ylphosphonate (0.17 g) in tetrahydrofuran. After the solution had been kept for 30 min at this temperature, a solution of **6** (0.15 g) in tetrahydrofuran (1 mL) was added and stirring was continued for 30 min. Ether was then added, the solution was washed with water and dried, and the solvent was removed. The residue was purified by flash chromatography to give **17** (0.16 g, 81%), $[\alpha]_D$ +40°; $\lambda_{max}^{Et_2O}$ 257 nm (ε 6030). N.m.r. data: ^1H, δ 0.03, 0.05 (2 s, 6 H, $SiMe_2$), 0.89 (s, 9 H, CMe_3), 2.0–2.5 (m, 4 H, H-3,3', $CH_2CH_2CH_2$), 2.82 (t, 4 H, J 5.7 Hz, CH_2S), 3.35 (s, 3 H, OMe), 3.50 (m, 1 H, H-4), 4.20 (tt, 1 H, $J_{4,5} = J_{5,6} = 5.2$, $J_{5,7} = J_{5,7'} = 1.3$ Hz, H-5), 4.61, 4.70 (2 d, 2 H, J 10.2 Hz, OCH_2O), 5.18 (ddd, 1 H, $J_{6,7}$ 9.9, $J_{7,7'}$ 2.5 Hz, H-7), 5.24 (ddd, 1 H, $J_{6,7'}$ 17.3 Hz, H-7'), 5.90 (ddd, 1 H, H-6), and 6.00 (t, 1 H, $J_{2,3} = J_{2,3'} = 7.3$ Hz, H-2); ^{13}C, δ −4.9, −4.7 ($SiMe_2$), 18.2 (CMe_3), 25.3 ($CH_2CH_2CH_2$), 25.9 (CMe_3), 29.5, 30.2, 30.4 (C-3, SCH_2), 55.5

(OMe), 74.9, 80.6 (C-4,5), 96.9 (OCH_2O), 115.9 (C-7), 127.3 (C-1), 130.6 (C-2), and 137.2 (C-6).

Anal. Calc. for $C_{18}H_{34}O_3S_2Si$: C, 55.4; H, 8.8. Found: C, 55.5; H, 8.9.

*6-O-tert-Butyldimethylsilyl-2,3,4,7,8-pentadeoxy-2-diethylamino-5-O-methoxymethyl-*D-threo-*oct-2,7-dienononitrile* (**18**). — 1.4M Butyl-lithium in hexane (1.4 mL) was added at −20° and under nitrogen to a solution of di-isopropylamine (0.27 mL) in tetrahydrofuran (5 mL), and the mixture was stirred for 15 min. Hexamethylphosphoric triamide (0.34 mL) was added and the temperature was taken to −78° before the addition of a solution of diethylaminoacetonitrile (0.22 g) in tetrahydrofuran (1 mL). After 10 min, a solution of **6** (0.43 g) in tetrahydrofuran (1 mL) was added and the mixture was stirred at −78° for 30 min. T.l.c. then revealed two less-mobile products which were derivatised by treatment with triethylamine (0.42 mL) followed by methanesulphonyl chloride (0.23 mL). ^{1}H-N.m.r. spectroscopy indicated that the product, obtained in a separate preparation, was a mixture of the diastereoisomeric mesylates of alcohols produced by addition to **6**. ^{1}H-N.m.r. data: δ 0.06, 0.09 (2 s, 6 H, $SiMe_2$), 0.90 (s, 9 H, CMe_3), 1.06 (t, 6 H, 2 CH_2CH_3), 1.6–1.8 (m, 2 H, H-4,4′), 2.45–2.7 (m, 4 H, 2 CH_2CH_3), 3.18 (s, 3 H, OMs), 3.39 (s, 3 H, OMe), 3.7 (m, 1 H, H-2), 4.3–4.9 (m, 3 H, H-3,5,6), 5.1–5.4 (m, 2 H, H-8,8′), and 5.9 (m, 1 H, H-7).

The solution was allowed to warm to 20°, 1,5-diazabicyclo[5.4.0]undec-5-ene (0.67 mL) was added, and the mixture was stirred for 3 h. Ether was added and the solution was washed with aqueous sodium chloride, dilute hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and water, and then dried, and the solvent was removed. The resultant isomeric products were separated by preparative t.l.c. The more-mobile alkene **18** (60 mg, 10%) had $[\alpha]_D$ +50°. ^{1}H-N.m.r. data: δ 0.01, 0.02 (2 s, 6 H, $SiMe_2$), 0.86 (s, 9 H, CMe_3), 0.96 (t, 6 H, 2 CH_2CH_3), 2.1–2.7 (m, 2 H, H-4,4′), 2.65 (q, 4 H, 2 CH_2CH_3), 3.33 (s, 3 H, OMe), 3.4 (m, 1 H, H-5), 4.21 (tt, 1 H, $J_{5,6} = J_{6,7} = 4.9$, $J_{6,8} = J_{6,8'} = 1.4$ Hz, H-6), 4.58, 4.66 (2 d, 2 H, J 11 Hz, OCH_2O), 5.15 (ddd, 1 H, $J_{7,8}$ 9.9, $J_{8,8}$ 2.1 Hz, H-8), 5.20 (ddd, 1 H, $J_{7,8'}$ 17.4 Hz, H-8′), 5.86 (ddd, 1 H, H-7), and 6.19 (t, 1 H, $J_{3,4} = J_{3,4'} = 7.1$ Hz, H-3).

Anal. Calc. for $C_{20}H_{38}N_2O_3Si$: C, 62.8; H, 10.0. Found: C, 62.9; H, 10.2.

The less-mobile isomer (70 mg, 12%), $[\alpha]_D$ +50°, had a ^{1}H-n.m.r. spectrum similar to that noted above but the methylene protons of the ethyl groups resonated at δ 3.1 and H-3 at δ 5.3.

*7-O-tert-Butyldimethylsilyl-1,3,4,5,8,9-hexadeoxy-6-O-methoxymethyl-*D-threo-*non-3,8-dien-2-ulose* (**20**). — A solution of **13** (0.2 g) in 1,4-dioxane (5 mL) was heated with acetylmethylenetriphenylphosphorane (0.55 g) under reflux for 3 h. The solvent was removed, and the residue was purified by flash chromatography to give the unstable hydroxydienone (0.24 g, 96%), which was immediately dissolved in *N,N*-dimethylformamide (3 mL) and treated with imidazole (0.15 g) and *tert*-butyldimethylsilyl chloride (0.25 g). The mixture was stirred at 20° for 3 h and then partitioned between dichloromethane and water. The organic phase was

washed with dilute hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and water, and then dried. Removal of the solvent and preparative t.l.c. of the residue gave **20** (0.22 g, 58% from the hemiacetal), $[\alpha]_D$ +50°; $\lambda_{max}^{Et_2O}$ 218 nm (ε 1.32 × 10^4). N.m.r. data: ^{1}H, δ 0.04, 0.08 (2 s, 6 H, $SiMe_2$), 0.87 (s, 9 H, CMe_3), 2.16 (s, 3 H, H-1), 2.1–2.4 (m, 2 H, H-5,5'), 3.30 (s, 3 H, OMe), 3.57 (m, 1 H, H-6), 4.22 (tt, 1 H, $J_{6,7} = J_{7,8} = 5.1$, $J_{7,9} = J_{7,9'} = 1.3$ Hz, H-7), 4.57, 4.67 (2 d, 2 H, J 11.7 Hz, OCH_2O), 5.11 (ddd, 1 H, $J_{8,9}$ 10.0, $J_{9,9'}$ 2.4 Hz, H-9), 5.21 (ddd, 1 H, $J_{8,9'}$ 17.4 Hz, H-9'), 5.87 (ddd, 1 H, H-8), 6.03 (dt, 1 H, $J_{3,4}$ 16, $J_{3,5} = J_{3,5'} = 1.2$ Hz, H-3), and 6.77 (dt, 1 H, $J_{4,5} = J_{4,5'} = 6.8$ Hz, H-4); ^{13}C, δ −4.9, −4.6 ($SiMe_2$), 18.2 (CMe_3), 25.9 (CMe_3), 26.8 (C-1), 33.5 (C-5), 55.7 (OMe), 74.6, 80.5 (C-6,7), 97.2 (OCH_2O), 116.4 (C-9), 133.0 (C-3), 136.8 (C-8), 145.4 (C-4), and 198.0 (C-2).

Anal. Calc. for $C_{17}H_{32}O_4Si$: C, 62.1; H, 9.8. Found: C, 61.9; H, 10.0.

*Ethyl 6-*O*-tert-Butyldimethylsilyl-2,3,4,7,8-pentadeoxy-5-*O*-methoxymethyl-*D-threo-*oct-2,7-dienonate* (**22**). — A solution of **13** (0.2 g) in tetrahydrofuran (12 mL) was heated under reflux with ethoxycarbonylmethylenetriphenylphosphorane (0.8 g) for 3 h. The solvent was removed, and the residue was treated with a solution of *tert*-butyldimethylsilyl chloride (0.4 g) and imidazole (0.4 g) in *N,N*-dimethylformamide (8 mL) for 4 h at 80°. Ether was then added, and the solution was washed with water, dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water, and dried. The solvent was removed, and the residue was purified by flash chromatography to give **22** (0.28 g, 69%), $[\alpha]_D$ +52°. N.m.r. data: ^{1}H, δ 0.05, 0.07 (2 s, 6 H, $SiMe_2$), 0.90 (s, 9 H, CMe_3), 1.27 (t, 3 H, J 7.1 Hz, CH_2CH_3), 2.1–2.4 (m, 2 H, H-4,4'), 3.36 (s, 3 H, OMe), 3.58 (m, 1 H, H-5), 4.15 (q, 2 H, CH_2CH_3), 4.25 (m, 1 H, H-6), 4.60, 4.70 (2 d, 2 H, J 11.7 Hz, OCH_2O), 5.17 (ddd, 1 H, $J_{7,8}$ 10.0, $J_{8,8'}$ 2.5, $J_{6,8}$ 1.3 Hz, H-8), 5.22 (ddd, 1 H, $J_{7,8'}$ 18.5, $J_{6,8'}$ 1.2 Hz, H-8'), 5.83 (d, 1 H, J 17.2 Hz, H-2), 5.90 (ddd, 1 H, $J_{6,7}$ 4.9 Hz, H-7), and 6.97 (dt, 1 H, $J_{3,4} = J_{3,4'} = 7$ Hz, H-3); ^{13}C, δ −4.9, −4.6 ($SiMe_2$), 14.3 (CH_2CH_3), 18.2 (CMe_3), 25.9 (CMe_3), 33.1 (C-4), 55.7 (OMe), 60.1 (CH_2CH_3), 74.5, 80.3 (C-5,6), 97.1 (OCH_2O), 116.3 (C-8), 123.2 (C-2), 136.8 (C-7), 146.3 (C-3), and 166.3 (C-1).

Anal. Calc. for $C_{18}H_{34}O_5Si$: C, 60.4; H, 9.5. Found: C, 60.5; H, 9.5.

Photolysis of **22**. — A solution of **22** (0.13 g) in dry ether (20 mL) was purged with nitrogen and photolysed in a quartz tube at 254 nm for 2 h. Two products with similar t.l.c mobilities were formed. Preparative t.l.c. gave **23** (94 mg, 72%). N.m.r. data: ^{1}H, δ 0.04 (bs, 6 H, $SiMe_2$), 0.89 (s, 9 H, CMe_3), 1.24 (t, 3 H, J 7 Hz, CH_2CH_3), 3.1 (m, 2 H, H-2), 3.35 (s, 3 H, OMe), 4.1 (m, 4 H, H-5,6, CH_2CH_3), 4.6 (m, 3 H, OCH_2O, H-3), and 5.0–6.0 (m, 4 H, H-4,7,8,8'); ^{13}C, δ *(inter alia)* 115.7, 115.8 (C-8), 126.2 (C-3 or 4), 129.3, 130.6 (C-4 or 3), 137.5, 137.6 (C-7), 171.2, and 175.6 (C-1).

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