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PREPARATION OF 4,6-*O*-BENZYLIDENE-3-DEOXY-3-C-NITRO-D-GLUCAL AND -D-ALLAL AND 1,5-ANHYDRO-4,6-*O*-BENZYLIDENE-2,3-DIDEOXY-3-C-NITRO-D-*threo*-HEX-2-ENITOL

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ABSTRACT

Oxidation of 1,5-anhydro-D-mannitol with sodium metaperiodate, followed by nitromethane cyclization and benzylidenation afforded 1,5-anhydro-3-nitrohexitol derivatives having the D-*gluco*, D-*manno*, and D-*galacto* configurations. Conversion of the nitro alcohols into the nitro alkenes was accompanied by double-bond migration of the nitro 2,3-alkenes to give the 1,2-unsaturated derivatives.

INTRODUCTION

It is well known that α-nitro alkenes are generally more stable than the corresponding β-nitro alkenes because of conjugation of the nitro group with the carbon–carbon double bond[1]. Cyclohexylidenenitromethane, however, is converted into 1-nitromethylcyclohexene under basic conditions[2], indicating that the instability of an exo double bond in the cyclohexane ring is more serious than the loss of conjugation. Recently we found that the double bond of 1,5-anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-D-*erythro*-hex-2-enitol (**7**) migrated to the 1,2-position, yielding compound[3] **8**[†]. In contrast to **7**, double-bond migration of the corresponding methyl α- and β-D-glycosides and of 1-*O*-acetyl-α- and -β-D-glucopyranose was not observed; this is reasonable as double-bond migration in these compounds leads to the unfavorable ketene acetal derivative. One driving force for the double-bond migration observed in **7** should be the conjugation of the ring oxygen atom with the newly formed double bond (vinyl ether). Relief of $A^{(1,2)}$ strain[5*] between the nitro group and the oxygen atom at C-4 also seems to be responsible for the phenomenon. Therefore, we have synthesized 1,5-anhydro-4,6-*O*-benzylidene-2,3-

[§]Deceased.

[†]This compound was independently prepared from methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside with lithium dimethylcuprate[4].

*The importance of this strain in the realm of nitroalkenic sugars has been discussed extensively by Baer and his co-workers[6].

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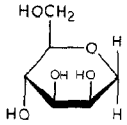
dideoxy-3-nitro-D-*threo*-hex-2-enitol (**14**), which has no such strain, and have treated it with triethylamine. In this paper, we report several methods for the preparation of **7**, a detailed study of the double-bond migration of **7**, and synthesis of **14** and its reaction with triethylamine.

RESULTS AND DISCUSSION

Oxidation of 1,5-anhydro-D-mannitol[7] (**1**) with sodium metaperiodate, followed by nitromethane cyclization in the presence of a catalytic amount of sodium



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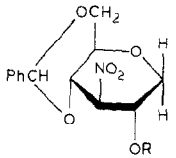

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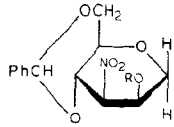
9: R = Ms



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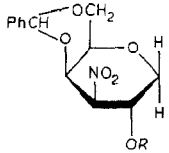
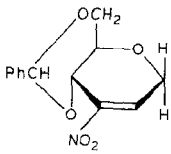


4: R = H
13: R = Ms



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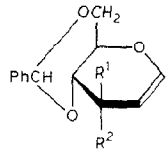
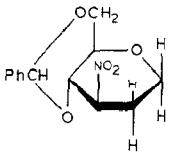


8: R^1 = NO_2, R^2 = H
10: R^1 = H, R^2 = NO_2



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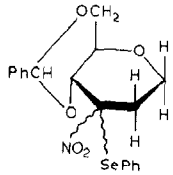

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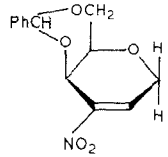

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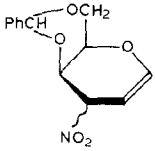

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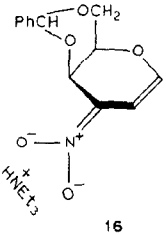

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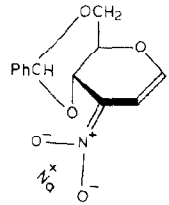

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methoxide, afforded a syrup, benzylidenation of which afforded 1,5-anhydro-4,6-*O*-benzylidene-3-deoxy-3-nitro-D-glucitol (**2**), -D-mannitol (**3**), and -D-galactitol (**4**) after separation by column chromatography. As expected[8], the yields of the last two compounds were improved by use of an equimolar amount of sodium methoxide.

Acetylation of the glucitol **2** (1 mmol) and mannitol derivative **3** (1 mmol) with pyridine (0.6 mL) and acetic anhydride (0.74 mL) in dichloromethane (5 mL) afforded the acetates **5** and **6**, respectively, in excellent yields. Similar acetylation of the galactitol derivative **4**, however, was complicated, and the anticipated acetate could not be isolated. Furthermore, direct formation of the nitro alkene **14** by treatment of **4** with hot acetic anhydride in the presence of sodium acetate, as employed for the preparation of the corresponding methyl 3-nitro-D-*threo*-hex-2-enopyranosides[9], failed.

Treatment of the acetate **5** with sodium hydrogencarbonate in boiling benzene afforded the glucal derivative **8** in conjunction with the desired nitro alkene **7**, before completion of the reaction, as has already been reported[3].

The nitro alcohol **2** (1 mmol) was then treated with methanesulfonyl chloride (1.1 mmol) and triethylamine (2.2 mmol)[10], to give the nitro alkene **7** (44%) and the glucal **8** (12%), together with the unreacted alcohol **2** (29%). Although various reaction-conditions (ratios of reagents, reaction temperature, reaction time, and so on) were examined, the yield of **7** could not be improved, however, as partial migration occurred before the reaction was complete. The methanesulfonate **9** might be a more appropriate precursor for **7** than the acetate **5**, because elimination of a sulfonic acid should take place under milder conditions than that of acetic acid. Preparation of **9**, therefore, was attempted*. Treatment of **2** (1 mmol) with methanesulfonyl chloride (2.2 mmol) and triethylamine (1.1 mmol) in oxolane resulted in the recovery mostly of **2**, together with small amounts of the sulfonate **9**, as judged by t.l.c. Additional methanesulfonyl chloride (2.2 mmol) and triethylamine (1.1 mmol) were then added to the mixture, providing the sulfonate **9** in 33% yield, together with the alcohol **2** (56%). Treatment of **9** with sodium carbonate in oxolane for 66 h at room temperature yielded the nitro alkene **7** in 87% yield without contamination by the glucal derivative **8**.

When the acetate **5** was treated with 5 equiv. of triethylamine in dichloromethane for 70 min at room temperature, the allal derivative **10** (22%) was obtained, together with the glucal derivative **8** (76%). The structure of **10** was determined on the basis of elemental analysis, i.r. [1635 (C=C) and 1550 cm^{-1} (NO_2)], and n.m.r. spectroscopy (alkenic protons at δ 6.71 and 4.93). Treatment of the nitro alkene **7** with a catalytic amount of triethylamine in dichloromethane for 3 h at room temperature also afforded a mixture of **8** (65%) and **10** (24%).

*The 2-methanesulfonate of methyl 4,6-*O*-benzylidene-3-deoxy-3-nitro-α-D-glucopyranoside was isolated by treatment with methanesulfonyl chloride (1.1 equiv.) and triethylamine (1 equiv.); however, the nitro alkene was obtained by use of 2.1 equiv. of triethylamine[10b].

The nitro alkene **7** was isolated in 75% yield, together with the glucal derivative **8** (8%) and the acetate **5** (14%) by treatment of **5** with sodium carbonate in boiling oxolane for 13 h*.

In contrast to the case with the 2-*O*-acetylglucitol derivative **5**, the 2-*O*-acetylmannitol derivative **6** provided the nitro alkene **7** (76%) upon were stirring with sodium carbonate in oxolane for 48 h at room temperature.

These methods for the preparation of **7** still present some difficulties (availability of the starting material, yield, and/or separation). Therefore, we evaluated a new synthetic method for nitro alkenes from the corresponding nitro alkane[11] that involves the phenylselenylation of nitronates, followed by oxidative elimination of the seleno group. As oxidative elimination proceeds under neutral or weakly acidic conditions, this method might be applied to such a base-sensitive nitro alkene as **7**. The 2-deoxyalditol **11**, obtained in high yield by reduction of the acetate **5** with sodium borohydride in dimethyl sulfoxide, was treated with butyllithium, followed by the addition of phenylselenenyl bromide, giving the 3-nitro-3-phenylselenenyl derivative **12**. Without isolation of **12**, 35% aqueous hydrogen peroxide was added, providing the nitro alkene **7** in 72% yield without formation of the glucal derivative **8**.

After unsuccessful attempts to acetylate the galactitol derivative **4**, as already described, methanesulfonylation of **4** was performed. Treatment of **4** (1 mmol) with methanesulfonyl chloride (1.1 mmol) and triethylamine (2.02 mmol) in oxolane afforded the desired nitro alkene **14** (15%), together with the sulfonate **13** (15%), glycal **15** (3%), and alcohol **4** (31%). The nitro alkene and the glycal structures for **14** and **15**, respectively, were determined on the basis of elemental analyses, i.r. [1520 cm^{-1} (C=C-NO_2) for **14**, 1650 (C=C) and 1545 cm^{-1} (NO_2) for **15**] and n.m.r. spectra [alkenic proton at δ 7.49 for **14** and signals at δ 6.78 (H-1), 5.07 (H-2), and 4.87 (H-3) for **15**] (Tables I and II).

TABLE I

CHEMICAL SHIFTS (δ) OF THE PRODUCTS AT 100 MHz IN CHLOROFORM-*d* (Me_4Si AS INTERNAL STANDARD)

Compound	*H-1a*	*H-1e*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6e*	*PhCH*
3	3.63	4.03	~4.26	4.63	~4.60	3.41	3.86	4.35	5.68
4[a]	3.31	4.06	~4.60	←4.75–4.85→		3 64	4.20	4.20	5.64
6	3.66	4.15	5.60	2.78	4.58	3 43	3.88	4.38	5.71
9[a]	3.76	5.19	4.29	5.25	4.33	3.68	3.85	4.39	5.72
10		6.71	4.93	5.26	4.08	4.74	3.80	4.49	5.62
13	3.59	4.40	5 45	5.28	5.03	3 79	4.22	4.22	5.72
14	4 74	4.37	~7.49		5.04	3.37	4.22	4.44	5.71
15		6.78	5.07	4.87	4.68[b]	4.03[b]	4.13	4 46	5.65

[a]Recorded in acetone-d_6. [b]The possibility of H-4 (4.03) and H-5 (4.68) is not excluded.

*As is often observed in heterogeneous reaction-media (solid–liquid), slight variations of the conditions affected the reaction rates, and therefore, the reaction was monitored by t.l.c.

TABLE II

FIRST-ORDER COUPLING-CONSTANTS (Hz) AT 100 MHz IN CHLOROFORM-*d*

Compound	$J_{1a,1e}$	$J_{1a,2}$	$J_{1e,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6e}$	$J_{6a,6e}$
3	12.9	1.1	1.8	2.1	2.1	9.1	10.6	4.5	10.6
4[a]	11.7	9.8	5.3			1.5	1.5	1.5	~0
6	13.5	1.2	1.5	3.4	10.5	8.6	10.1	4.5	10.1
9[a]	10.5	9.0	7.5	10.5	9.8	9.8	9.8	4.5	9.8
10	6.1 ($J_{1,2}$)	~0.6 ($J_{1,3}$)		6.1	5.3	10.6	10.2	5.3	10.2
13[a]	11.3	9.8	5.3	9.8	3.8	~1.0	~1.0	~1.0	~0
14[b]	19.7	3.8	2.3			1.5	2.3	1.1	13.6
15[c]	6.0 ($J_{1,2}$)	≤1.0 ($J_{1,3}$)		5.4	~1.1	~1.5	1.5	1.5	12.8

[a]Recorded in acetone-d_6. [b]$J_{1e,4}$ 1.5 Hz. [c]$J_{2,4}$ 1.8 Hz.

The nitro alkenes **7** and **14** thus prepared were treated with triethylamine in chloroform-*d* and the reactions were monitored by n.m.r. spectroscopy. Within 5 min, compound **7** was completely converted into the glucal derivative **8**, which slowly epimerized to the allal derivative **10**, giving a mixture of **8** and **10** in the ratio of 2.5:1 after 3 and 24 h. This was an equilibrated mixture, because the glucal (**8**) and allal (**10**) derivatives epimerized to yield a mixture of **8** and **10** (2.5:1) by similar treatment with triethylamine. On the other hand, compound **14** was changed into the *aci*-salt **16** within 5 min, and this was stable even after 24 h. Although the *aci*-salt corresponding to **16** was not detectable during the reaction of **7** with triethylamine, the sodium salt **17** was generated in the reaction of the glucal derivative **8** with sodium borohydride. The *aci*-salt structure for **16** and **17** was deduced by n.m.r. spectroscopy (only six protons for the sugar moiety and the signals of H-1 and H-2 appeared as a doublet) and by isolation of the glycal (**15**) and glucal (**8**) derivatives, respectively, by treatment with dilute hydrochloric acid.

As the reaction of the *threo* isomer **14** stopped at the intermediary *aci*-salt **16**, the thermodynamic stability between the nitro alkene **14** and glycal **15** could not be determined. The role of $A^{(1,2)}$ strain, therefore, in determining the stability between the nitro alkene **7** and glucal **8** also could not be clarified.

In contrast to the case with the *erythro* isomer **7**, formation of the stable *aci*-salt **16** from the *threo* isomer **14** is explicable in terms of $A^{(1,3)}$ strain[5,12]; compound **16** is free from $A^{(1,3)}$ strain, whereas the corresponding *aci*-salt derived from **7** has this strain.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 polarimeter. I.r. spectra were recorded for potassium bromide discs with a Hitachi 285 grating i.r. spectrophotometer, and n.m.r. spectra were recorded, for solutions in chloroform-*d*, with tetramethylsilane as the

internal standard with a JNM-PS-100 (JEOL) spectrometer, unless otherwise stated. Solutions were evaporated under diminished pressure. Column chromatography was conducted on silica gel (C-300, Wakogel, Japan). T.l.c. was performed with Merck (Darmstadt) silica gel GF254.

*1,5-Anhydro-4,6-O-benzylidene-3-deoxy-3-nitro-*D*-glucitol* (**2**), *-*D*-mannitol* (**3**), *and -*D*-galactitol* (**4**). — (*a*) Oxidation of 1,5-anhydro-D-mannitol[7] (**1**) (16.4 g, 0.1 mol) with sodium metaperiodate, followed by nitromethane cyclization in the presence of a catalytic amount of sodium methoxide, and subsequent benzylidenation[3] afforded the glucitol derivative **2** (6.89 g, 24.5% from **1**) after recrystallization from ethanol. The ethanolic filtrate was evaporated and the syrup chromatographed with 10:1 (v/v) benzene–ethyl acetate as eluant. The first fraction was benzaldehyde, the second (1.80 g, 6.4%) was **2** (total yield 30.9%), the third (1.77 g, 6.3%) was a mixture of **2** and **3** in the ratio of 1:1, and the fourth (2.39 g, 8.5%) was pure **4**. Compound **4** was recrystallized from chloroform–hexane; m.p. 212–214° $[\alpha]_D^{22}$ +126° (*c* 1, acetone); ν_{max} 3400 (OH) and 1555 cm^{-1} (NO_2).

Anal. Calc. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38; N, 4.98. Found: C, 55.38; H, 5.25; N, 5.00.

(*b*) Oxidation of **1** (6 g, 36.9 mmol) as in (*a*) afforded a syrup that was dissolved in methanol (36 mL)–nitromethane (2.1 mL), and then the solution was cooled with ice–water. To the solution was added, during 5 min, 0.8M sodium methoxide (36 mL) with stirring. After stirring for 30 min at 0° and for 1 h at room temperature, the mixture was deionized by Amberlite IR-120 (H^+) cation-exchange resin. After removal of the resin, the mixture was completely evaporated by azeotropic distillation with benzene. Without further purification, the syrup was benzylidenated with benzaldehyde (24 mL) in the presence of zinc chloride (12 g). The mixture was stirred for 20 h at room temperature and then hexane (500 mL) and water (300 mL) were added. After decantation, 500 mL of hexane was again added and decantated off. The products were extracted with chloroform and the extracts dried ($MgSO_4$) and evaporated. The syrup was similarly chromatographed to afford 3.93 g (38.2%) of **2**, 1.18 g (11.5%) of **3**, and 1.31 g (12.7%) of **4**. Compound **3** was recrystallized from chloroform–hexane; m.p. 126–127°, $[\alpha]_D^{22}$ −99.6° (*c* 1, acetone); ν_{max} 3300 (OH) and 1560 cm^{-1} (NO_2).

Anal. Calc. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38; N, 4.98. Found: C, 55.56; H, 5.26; N, 5.24.

*2-O-Acetyl-1,5-anhydro-4,6-O-benzylidene-3-deoxy-3-nitro-*D*-glucitol* (**5**) *and -*D*-mannitol* (**6**). — To a solution of the glucitol derivative **2** (281 mg, 1 mmol) in dichloromethane (5 mL) and pyridine (0.6 mL) was added acetic anhydride (0.74 mL) dropwise with stirring. After 30 min at room temperature, the mixture was evaporated. A precipitate, separated by the addition of water (50 mL), was collected by filtration and washed well with water to give 304 mg (94%) of **5** (ref. 3), pure enough for further reactions.

Similar acetylation of the mannitol derivative **3** (281 mg, 1 mmol), but with a reaction time of 2 h, afforded 321 mg (99%) of **6** as a precipitate. An analytical

sample was prepared by recrystallization from ethanol; m.p. 114–115°, $[\alpha]_D^{22}$ −112° (*c* 1, acetone); ν_{max} 1740 (CO) and 1560 cm^{-1} (NO_2).

Anal. Calc. for $C_{15}H_{17}NO_7$: C, 55.72; H, 5.30; N, 4.33. Found: C, 55.82; H, 5.42; N, 4.40.

1,5-Anhydro-4,6-O-benzylidene-3-deoxy-2-O-(methylsulfonyl)-3-nitro-D-*glucitol* (**9**). — To a solution of **2** (281 mg, 1 mmol) in oxolane (6 mL) were successively added methanesulfonyl chloride (252 mg, 2.2 mmol) and triethylamine (111 mg, 1.1 mmol) with stirring at room temperature, and the mixture was stirred for 30 min. To the mixture were added additional methanesulfonyl chloride (252 mg) and triethylamine (111 mg). After stirring for 30 min, the mixture was evaporated and partitioned between chloroform and water. The organic layer was dried ($MgSO_4$) and evaporated. The syrup was chromatographed by successive elution with benzene and 10:1 (v/v) benzene–ethyl acetate to afford 118 mg (33%) of the sulfonate **9** as a fast-running fraction, and 157 mg (56%) of the alcohol as a slow-running fraction. An analytical sample of **9** was obtained by recrystallization from acetone–ethanol; m.p. 190.5–191°, $[\alpha]_D^{22}$ −14.1° (*c* 1, acetone); ν_{max} 1560 (NO_2) and 1340, 1100 cm^{-1} (SO_2).

Anal. Calc. for $C_{14}H_{17}NO_8S$: C, 46.79; H, 4.77; N, 3.90; S, 8.92. Found: C, 47.05; H, 4.72; N, 3.99; S, 8.75.

1,5-Anhydro-4,6-O-benzylidene-2,3-dideoxy-3-nitro-D-erythro-*hex-2-enitol* (**7**). — (*a*) To an ice-cooled solution of the glucitol derivative **2** (281 mg, 1 mmol) in dichloromethane (8 mL) were successively added methanesulfonyl chloride (126 mg, 1.1 mmol) and triethylamine (222 mg, 2.2 mmol). After removal of the ice–water bath, the mixture was stirred for 20 min and diluted with chloroform and water. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed successively with benzene and 10:1 (v/v) benzene–ethyl acetate as eluant to afford in turn 32 mg (12%) of the glucal derivative **8**, 116 mg (44%) of the nitro alkene **7**, and 81 mg (29%) of the alcohol **2**, which were identical with the respective authentic samples.

(*b*) The acetate **5** (323 mg, 1 mmol) and sodium carbonate (646 mg) in oxolane (20 mL) were boiled under reflux with stirring. The reaction was frequently checked by t.l.c. After 13 h, the mixture was cooled and filtered. The filtrate was evaporated to a syrup, which was chromatographed with benzene as eluant to give successively 20 mg (8%) of **8**, 197 mg (75%) of **7**, and 44 mg (14%) of the acetate **5**.

(*c*) To a solution of the sulfonate **9** (35.9 mg, 0.1 mmol) in oxolane (2 mL) was added sodium carbonate (100 mg). The mixture was stirred for 66 h at room temperature and filtered, and the filtrate was evaporated. The syrup was chromatographed with benzene as eluant to give 23 mg (87%) of **7**.

(*d*) To a solution of the 2-*O*-acetylmannitol derivative **6** (32.3 mg, 0.1 mmol) in oxolane (2 mL) was added sodium carbonate (100 mg). The mixture was stirred for 48 h at room temperature and filtered, and the filtrate was evaporated. The syrup was chromatographed with benzene as eluant to yield, 20 mg (76%) of **7**.

(*e*) To an ice-cooled solution of **11** (87 mg, 0.33 mmol) in oxolane (2 mL) was added butyllithium (0.2 mL of hexane solution, ~0.66 mmol) under nitrogen, and the mixture was stirred for 20 min at 0°. To the mixture was added a solution of phenylselenenyl bromide (170 mg, 0.72 mmol) in 2 mL of oxolane and the mixture was stirred for 1 h at 0°, and then 35% aqueous hydrogen peroxide (1.0 mL) was added dropwise at that temperature. The mixture was stirred overnight and then diluted with water (5 mL), and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated. The syrup was chromatographed with 50:1 (v/v) benzene–ethyl acetate as eluant to provide 62 mg (72%) of **7**. Compound **11** was prepared as follows. To a suspension of sodium borohydride (185 mg) in 5 mL of dimethyl sulfoxide was added a solution of the acetate **5** (790 mg, 2.45 mmol) in 7.5 mL of dimethyl sulfoxide. After stirring for 1 h at room temperature, the mixture was poured into water (400 mL) and the precipitate formed was filtered off and washed with water to give 636 mg (98%) of **11** (ref. 3), pure enough for the next reaction.

4,6-O-Benzylidene-3-deoxy-3-nitro-D-*glucal* (**8**) *and* -D-*allal* (**10**). — (*a*) To a solution of the nitro alkene **7** (369 mg, 1.4 mmol) in dichloromethane (10 mL) was added triethylamine (0.1 mL). After stirring for 3 h at room temperature, the mixture was diluted with chloroform and water. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The syrup was chromatographed with 1:1 (v/v) benzene–carbon tetrachloride as eluant to give successively 240 mg (65%) of **8** and 88 mg (24%) of **10**. An analytical sample of **10** was recrystallized from ethanol; m.p. 98–99°, $[\alpha]_D^{22}$ +314° (*c* 1, acetone); ν_{max} 1635 (C=C) and 1550 cm^{-1} (NO_2).

Anal. Calc. for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.46; H, 4.89; N, 5.43.

(*b*) To a solution of the acetate **5** (323 mg, 1 mmol) in dichloromethane (10 mL) was added triethylamine (555 mg, 5 mmol). The mixture was stirred for 70 min at room temperature and diluted with chloroform and water. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The syrup was chromatographed as already described to give 199 mg (76%) of **8** and 59 mg (22%) of **10**.

Methanesulfonylation of the galactitol derivative **4**. — To an ice-cooled solution of **4** (281 mg, 1 mmol) and triethylamine (204 mg, 2.02 mmol) in oxolane (10 mL) was added methanesulfonyl chloride (126 mg, 1.1 mmol) dropwise with stirring. The mixture was stirred for 30 min at 0° and for 30 min at room temperature, evaporated, and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated. The syrup was chromatographed with 10:1 (v/v) benzene–ethyl acetate to afford successively 15 mg of the glycal **15**, 81 mg of the nitro alkene **14**, 97 mg of the sulfonate **13**, and 87 mg (31%) of the alcohol **4**. The glycal **15** was recrystallized from 2-propanol to afford 8 mg (3%) of **15**; m.p. 140–141.5°, $[\alpha]_D^{22}$ +376° (*c* 1, chloroform); ν_{max} 1650 (C=C) and 1545 cm^{-1} (NO_2).

Anal. Calc. for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.26; H, 4.97; N, 5.27.

Recrystallization from chloroform–hexane provided 40 mg (15%) of **14**; m.p. 163° (dec.), $[\alpha]_D^{22}$ −61.6° (*c* 0.5, dichloromethane); ν_{max} 1520 (C=C-NO_2).

Anal. Calc. for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.48; H, 4.92; N, 5.59.

Recrystallization from 2-propanol gave 54 mg (15%) of the sulfonate **13**; m.p. 181.5–182.5°, $[\alpha]_D^{22}$ +3° (*c* 0.8, dichloromethane); ν_{max} 1560, 1365 (NO_2), and 1345, 1105 cm^{-1} (SO_2).

Anal. Calc. for $C_{14}H_{17}NO_8S$: C, 46.80; H, 4.77; N, 3.90; S, 8.92. Found: C, 46.81; H, 4.75; N, 3.91; S, 8.66.

Epimerization of the glucal (**8**) *and allal derivatives* (**10**). — To a solution of **8** (20 mg) in chloroform-*d* (0.2 mL) in a n.m.r. sample-tube was added triethylamine (0.01 mL) and the reaction was monitored by n.m.r. spectroscopy. Epimerization of **8** to **10** was observed, giving a mixture of **8** and **10** in the ratio of 2.5:1 on the basis of the area-ratio for anomeric protons at δ 6.48 for **8** and δ 6.71 for **10** after 3 h. After 24 h, the ratio was not changed.

Similar treatment of the allal derivative **10** (20 mg) with triethylamine (0.01 mL) also afforded a mixture of **8** and **10** (ratio, 2.5:1).

Treatment of the nitro alkenes **7** *and* **14** *with triethylamine.* — To a solution of the nitro alkene **7** (20 mg) in chloroform-*d* (0.2 mL) in a n.m.r. sample-tube was added triethylamine (0.01 mL) and the reaction was monitored by n.m.r. spectroscopy. Within 5 min, compound **7** was completely converted into the glucal derivative **8**, which gradually epimerized to **10**, giving the equilibrium mixture of **8** and **10** (2.5:1) after 3 h.

Similar treatment of the nitro alkene **14** (20 mg) with triethylamine (0.01 mL) yielded the *aci*-salt **16** within 5 min. After 24 h, no change was observed by n.m.r. spectroscopy; n.m.r. (chloroform-*d* + triethylamine, 60 MHz): δ 6.47 (d, 1 H, $J_{1,2}$ 6.0 Hz, H-1), 6.04 (d, 1 H, H-2), 5.78 (s, 1 H, PhCH), and 5.42 (broad s, 1 H, H-4). To the mixture was added dilute aqueous hydrochloric acid, and the mixture was extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated to give 4 mg of a syrup. The syrup (4 mg × 4) was chromatographed with benzene as eluant to give 7 mg of the glycal **15**, identical (n.m.r. and i.r.) with an authentic sample.

Treatment of the glucal derivative **8** *with sodium borohydride.* — To a solution of **8** (52.6 mg, 0.2 mmol) in methanol (2 mL) was added sodium borohydride (10 mg) with stirring, and the mixture was stirred for 20 min and then evaporated. The n.m.r. spectrum of the crude product showed that it was the *aci*-salt **17**; n.m.r. (methanol-d_4, 60 MHz): δ 6.53 (d, 1 H, $J_{1,2}$ 6.0 Hz, H-1), 6.13 (d, 1 H, H-2), and 5.79 (s, 1 H, PhCH). To the crude product in chloroform was added dilute aqueous hydrochloric acid and the mixture was extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated to give 52 mg (95%) of **8**.

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