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Formation of dihydrofuran derivatives by intramolecular substitution of the *manno* adducts formed by Michael reaction of a 1-*O*-acetyl-3-*C*-nitro-2-enopyranose derivative with 2,4-pentanedione and dibenzoylmethane

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ABSTRACT

Michael reaction of 1-*O*-acetyl-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-α-D-*erythro*-hex-2-enopyranose with 2,4-pentanedione afforded two cyclized products, together with adducts having the α-D-*gluco* and α-D-*manno* configurations. The dihydrofuran structures of the cyclized products were determined from spectral data, supported by semi-empirical molecular orbital (AM1) calculations. Cyclization occurred from the *manno* adduct through nucleophilic expulsion of the anomeric acetoxyl group by an enolate generated from the C-2 substituent. Such a proposed intramolecular SN2 mechanism was supported by a similar reaction with dibenzoylmethane.

INTRODUCTION

Remarkable solvent effects have been observed on the direction of approach of a nucleophile, generated from 2,4-pentanedione and sodium hydroxide, to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-β-D-*erythro*-hex-2-enopyranoside. In 1,4-dioxane the nucleophile attacks preferentially from the equatorial side of C-2 to give the α-D-*gluco* product, whereas in acetone or in a heterogeneous system (benzene–0.2M sodium hydroxide in the presence of a phase-transfer catalyst) it attacks from the axial side to give the α-D-*manno* product[1].

To study whether or not similar solvent effects occur with other Michael acceptors, 1-*O*-acetyl-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-α-D-*erythro*-hex-2-enopyranose (**1**) was treated with 2,4-pentanedione.

RESULTS AND DISCUSSION

The 3-nitro-2-enopyranose **1**, treated with 2,4-pentanedione in 1,4-dioxane in the presence of 0.2M sodium hydroxide for 2.5 h, afforded 24% of a cyclized product **6**, along with the α-D-*gluco* adduct **4** (33%) and unreacted starting material **1** (19%). Formation of the *gluco* adduct **4** in 1,4-dioxane was expected from the results observed in a similar reaction with the 1-*O*-methyl analogue of **1**. The yield of cyclized product **6**

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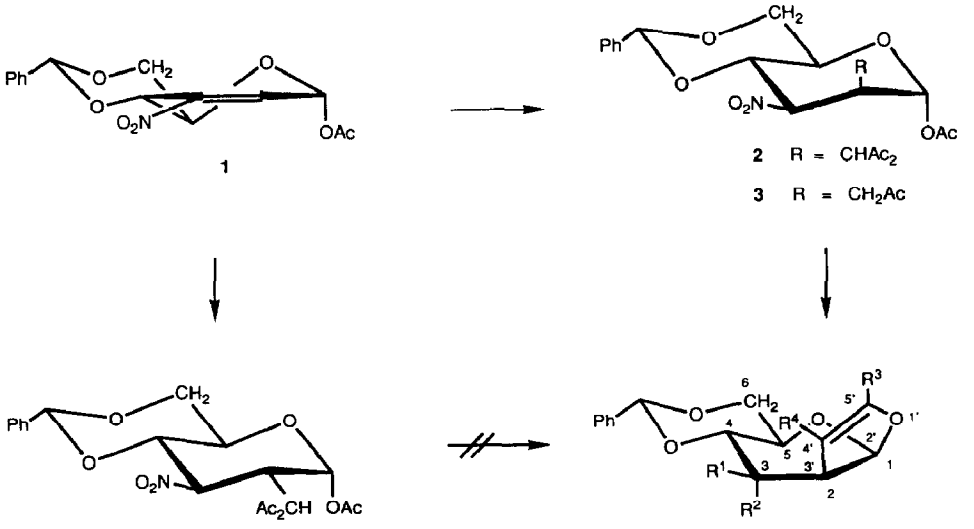
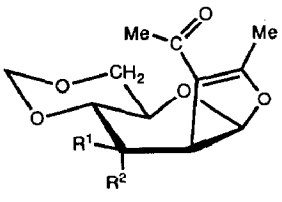
was raised to 68% by treatment of **1** in benzene–0.2M sodium hydroxide for 20 h at room temperature in the presence of tributylhexadecylphosphonium bromide as a phase-transfer catalyst. However, under milder, heterogeneous conditions (0.05M sodium hydroxide, 7.5 h for reaction time), another cyclized product (**5**, 18%) was isolated along with the α-D-*manno* adduct **2** (11%) and the starting nitro alkene **1** (37%). For **2** and **4**, respectively, the α-D-*manno* and α-D-*gluco* configurations having the $^4C_1$ conformation were assigned from the values of the coupling constants. Elemental analyses of the cyclized products **5** and **6** agreed with the formula, $C_{18}H_{19}NO_7$, which was confirmed by the molecular-ion peak at m/z 361. I.r. spectra suggested the presence of a β-alkoxy-α,β-unsaturated carbonyl group and the absence of ester and saturated carbonyl groups. In the ^{1}H-n.m.r. spectrum ($CDCl_3$), the H-1 and H-3 signals of **5** were observed respectively at δ 5.83 as a doublet having $J_{1,2}$ 6.3 Hz, and δ 5.07 as a doubled doublet having $J_{2,3}$ 8.4 and $J_{3,4}$ 10.4 Hz. The corresponding signals of **6** were observed at δ 6.11 as a doublet having $J_{1,2}$ 5.3 Hz and δ 6.19 as a double doublet having $J_{2,3}$ 1.4 and $J_{3,4}$ 5.0 Hz; the H-3 signals appeared at exceptionally low field[2]. The assignment of the H-3 signals for **6** was confirmed by comparison with the sepctrum of its C-3 deuterated derivative. Except for C-2, the pyranose ring-carbon atoms of **6** resonate at higher fields than the corresponding carbon atoms of **5**. The difference for C-5 amounts to 6.4 p.p.m., suggesting that C-5 of **6** is sterically compressed[3] compared with C-5 in **5**. These physical data indicate that **5** and **6** incorporate a dihydrofuran ring at C-1 and C-2 of the pyranose ring. The signals of H-2 and H-5 were examined in n.O.e. difference spectra with irradiation of the H-1 signal, and indicated the β-D and not the α-D-structure for **6**,



because H-1, H-2, and H-5 are sterically close. The H-4 signal was observed by irradiation of the H-3 signal, and suggested the *altro* configuration, and this is supported by the coupling constants. Two conformers are possible for the acetyl moiety, one having the carbonyl oxygen atom close to the carbon–carbon double bond and the other having the oxygen atom remote. In the latter, hydrogen bonding through a six-membered ring is possible between H-3 (acidic because of the nitro group) and the carbonyl oxygen atom. If this is the case, the appearance of H-3 at exceptionally low field is understandable. However, the former (close to the double bond) is the more likely from the n.O.e. difference spectrum. The H-2 and H-3 signals were not enhanced upon irradiation of the doublet methyl signals at δ 2.36, but were enhanced weakly upon irradiation of the singlet methyl signal at δ 2.40. These results also suggest that the doublet methyl signals may be assigned to the group attached to C-5′, which is coupled by H-2 through homoallylic coupling ($J_{2,Me}$ 2.0 Hz). The methyl signals at δ 16.1 and 30.0 in the ^{13}C-n.m.r. spectrum were correlated with the doublet and singlet methyl signals in the ^{1}H-n.m.r. spectrum (^{1}H–^{13}C-COSY). Although the two methyl signals of **5** were almost completely overlapped in cloroform-*d*, they were separated in benzene-d_6. When one of the methyl groups was irradiated, the other one was observed in the n.O.e. difference spectrum and *vice versa*, indicating that the carbonyl oxygen atom of **5** is remote from the double bond. These structural assignments are in good agreement with the results obtained by molecular-orbital calculations (AM1 method[4]) as described later. The nitro group of **6** is *exo*-disposed, whereas that of **5** is in the sterically crowded *endo* position, and therefore **6** should be thermodynamically more stable than **5**. In fact, under the basic conditions, the cyclized product **5** was readily epimerized to give the other cyclized product **6**. Conversion of **6** into **5**, however, did not occur under the same conditions. Furthermore, treatment of **5** and **6**, respectively, with 0.2M sodium hydroxide-*d* (in D_2O) in acetone-d_6 afforded exclusively the 3-deuterio derivative of **6**, revealing that the protons at C-3 of both compounds were acidic enough to be abstracted. Thus compound **5** should be formed as a preliminary product, which should then be epimerized to the thermodynamically more stable 3-epimer **6**. This hypothesis was chemically confirmed as follows. The reaction of the α-D-*manno* adduct **2** with 0.2M sodium hydroxide-*d* in acetone-d_6 was monitored by n.m.r. spectroscopy. Within 3 min, **2** had mostly disappeared and **5** was detected as the major product. The reaction was quenched with a cation-exchange resin and the ^{1}H-n.m.r. spectrum of **5**, isolated as the major product, revealed that its H-3 was not replaced by deuterium, indicating that epimerization of the nitro group did not occur during the formation of **5**, compound **5** should therefore have the *manno* configuration. When the reaction time was extended to 26 min, the other cyclized product (**6**) preponderated. The ^{1}H-n.m.r. spectrum of **6** as isolated showed that the H-3 signal was completely absent. In contrast, similar treatment of the α-D-*gluco* adduct **4** gave no evidence for formation of the cyclized products **5** and **6** even after 40 min, revealing that **4** was not a precursor to the cyclized products. Although the 3 position of the recovered **4** was completely deuterated, its H-2′ (diacetylmethine) proton was not replaced by deuterium.

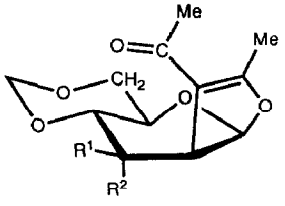
In order to obtain further structural information semi-empirical molecular orbi-

tal (AM1) calculations were performed on 4,6-*O*-methylene derivatives used as model compounds for **5** and **6**. Two conformers of the acetyl moiety, in which the carbonyl group is close to the double bond in one conformer (**5c** and **6c**) and remote in the other (**5r** and **6r**), were calculated for the β-D-*manno* and β-D-*altro* isomers with full optimization (bond length, bond angle, and dihedral angle). The optimized structure adopted the half-chair conformation and the stabilities decreased through to the sequence: **6c** > **6r** > **5r** > **5c**. The heats of formation thus calculated were in good agreement with the experimental results. In these conformers, the *altro* isomers (**6c** and **6r**) are always more stable than the *manno* isomers (**5r** and **5c**). As suggested by the n.O.e. difference spectrum, the present calculation shows that **6c** is more stable than **6r** by 0.8 kcal/mol. Furthermore, calculation reveals that the methyl group of the acetyl moiety, which deviates by 24° from the plane of the double bond, is close to H-2. Also as indicated by the n.O.e. difference spectrum, the calculation reveals that **5r** is more stable than **5c** by 1.5 kcal/mol.



5c $R^1 = NO_2$, $R^2 = H$

6c $R^1 = H$, $R^2 = NO_2$



5r $R^1 = NO_2$, $R^2 = H$

6r $R^1 = H$, $R^2 = NO_2$

The following two mechanisms for formation of **5** were taken into the consideration: (*a*) an enolate ion directly attacks the anomeric carbon atom from the rear side of the acetoxyl group (SN2 mechanism) or (*b*) after anomerization, a carbanion attacks the carbonyl carbon atom of the acetoxyl moiety, with subsequent deacetylation and dehydroxylation to give **5**. Although an anomeric acetoxyl group is employed as a leaving group under acidic conditions, it is seldom used under neutral or basic conditions because of its poor leaving-group ability. Despite these facts, cyclization of **2** occurred to some extent even during isolation of **2** by fractional crystallization from 2-propanol. We therefore, first excluded the possibility of route (*a*) and anomerization in route (*b*); and thus **5** and **6** were initially assigned incorrectly to the α-D-*manno* and α-D-*altro* configurations having the $^{1,4}B$ conformations, respectively, without the n.O.e. difference spectra data*. If the former mechanism operates, the methyl group at C-5′ arises from the diacetylmethyl moiety, whereas if the latter one operates it does so from the anomeric acetoxyl group. In order to clarify the mechanism, therefore, a reaction of **1** with dibenzoylmethane was performed under conditions similar to those employed for

* We thank one of referees who pointed out the possibility of the β-D-*manno* and β-D-*altro* structure for **5** and **6**, respectively. According to this suggestion we reinvestigated and revised our structural assignments.

the preparation of **6**. Compound **7**, isolated as the major product, has the *β*-D-*altro* configuration and has phenyl and benzoyl groups at C-5′ and C-4′, respectively. Thus it is concluded that the cyclization occurred through the SN2 mechanism [route (*a*)]. It is noteworthy that, even under such mild conditions, the anomeric acetoxyl group acts as an excellent leaving group.

If the enolate is formed from the 2-*C*-acetonyl moiety of 2-*C*-acetonyl-1-*O*-acetyl-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-α-D-mannopyranose (**3**), a similar SN2 reaction should occur to give the corresponding cyclized product. However, similar treatment of **3**, prepared from **1** and acetone in the presence of NaOH, under the same conditions employed for conversion of **2** into **6** resulted in the recovery of the 3-deuterio derivative of **3**.

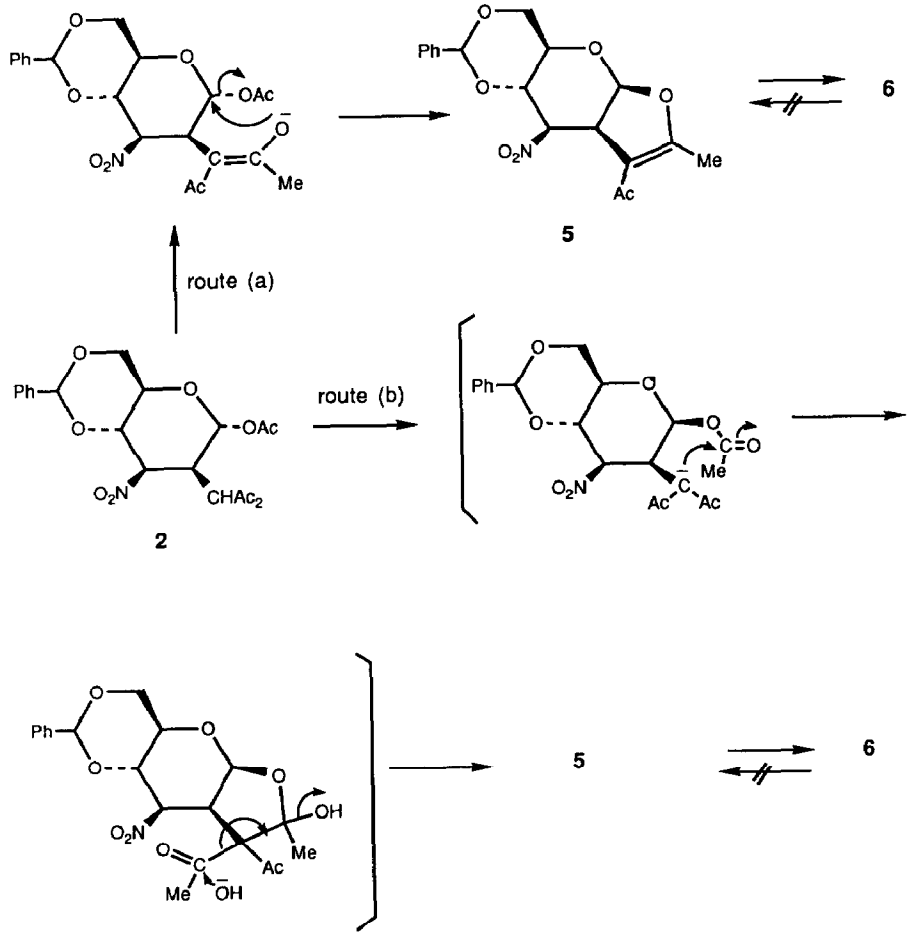


TABLE I

Chemical shifts from ^{1}H n.m.r. spectra[a]

Compd.	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*a	*H-6*e	*PhCH*	*OAc*	*CAc*		*Other(s)*
2[b]	5.96	3.76	5.18	4.40	4.02	3.88	4.33	5.67	2.35	2.22	2.19	4.44 (H-2′
	(s)	(oct)	(dd)	(t)	(dt)	(t)	(dd)	(s)	(s)	(s)	(s)	(d)
3[c]	5.97	3.33	5.16	4.31	3.96	3.83	4.32	5.67	2.19	2.19		ca. 2.74 (CH_2)
	(s)	(br.s)	(dd)	(t)	(dt)	(t)	(dd)	(s)	(s)	(s)		(2 H)
4[c]	6.18	3.53	4.96	4.29	3.94	3.82	4.33	5.61	2.26	2.18	2.14	3.94 (H-2′)
	(s)	(oct)	(dd)	(t)	(dt)	(t)	(dd)	(s)	(s)	(s)	(s)	(s)
5[b]	5.83	4.23	5.07	4.49	3.74	3.84	4.39	5.60		2.29		2.29 (Me)
	(d)	(m)	(dd)	(dd)	(dt)	(t)	(dd)	(s)		(s)		(d)
6[d]	6.11	3.85	6.19	3.84	4.09	3.67	4.33	5.56		2.40		2.36 (Me)
	(d)	(m)	(dd)	(dd)	(dt)	(t)	(dd)	(s)		(s)		(d)
7[d]	6.34	4.33	5.82	3.92	4.25	3.78	4.44	5.54				7.7-7.1(Ph × 3)
	(d)	(dd)	(dd)	(dd)	(dt)	(t)	(dd)	(s)				

[a] All spectra run in $CDCl_3$; chemical shifts are in δ values relative to internal $MeSi_4$. [b] Measured at 270 MHz. [c] measured at 200 MHz. [d] Measured at 500 MHz.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were determined with a Horiba High Sensitivity Polarimeter (SEPA-200). ^{1}H-N.m.r. spectra were recorded at 200 MHz with a Jeol spectrometer (JNM-FX200), 270 MHz (JNM-EX270), or 500 MHz (JNM-GSX500) in $CDCl_3$ with Me_4Si as the internal standard. N.O.e. Difference spectra of **5** ($CDCl_3$) and **6** (C_6D_6) were recorded at 500 MHz. The ^{1}H–^{13}C-COSY experiments were performed with the 270-MHz spectromter. I.r. spectra were recorded for KBr pellets. Mass spectra (e.i.) were obtained with a Hitachi M-70 mass spectrometer. Calculations were performed by the AM1 method included in the MOPAC program[4] with full optimization by the FACOM M-360 AP computer at the Education Center for Information Processing of Yokohama City University. Solutions were dried over $MgSO_4$ and evaporated under diminished pressure. Column chromatography was conducted on silica gel (Wakogel C-300). The catalyst refers to tributylhexadecylphosphonium bromide.

1-O-2-C-(1-acetyl-2-oxopropyl)-4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-α-D-mannopyranose (**2**) *and 4-acetyl-2,3-dihydro-5-methyl-(4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-β-D-mannopyranosido)[1,2-b]furan* (**5**) — A mixture of **1** (ref. 5, 145 mg, 0.45 mmol), 2,4-pentanedione (61 mg, 0.61 mmol), the catalyst (9 mg) 0.05M NaOH (0.45 mL), and benzene (13.5 mL) was stirred for 7.5 h at room temperature. After dilution with benzene, the organic layer was washed with dilute HCl and water, dried, and evaporated. The residue was chromatographed with 15:1 (v/v) benzene–EtOAc, to give successively 53 mg (37%) of starting material **1**, 19 mg (10%) of **5**, and 89 mg of **2**, which was contaminated with **5**. The last fraction was recrystallized from EtOH to give 21 mg (11%) of **2** and the filtrate from this was evaporated. The ^{1}H-n.m.r. spectrum of the residue suggested partial conversion of **2** into **5** during recrystallization. Thus additional amounts of **5** (total 30 mg, 18%) were isolated from the residue by recrystallization from EtOH. Physical data for **2**: m.p. 177.5–178.5°, $[\alpha]_D^{22}$ −182° (*c* 1, $CHCl_3$); ν_{max} 1765, 1738, 1700 (C=O), and 1560 cm^{-1} (NO_2).

Anal. Calc. for $C_{20}H_{23}NO_9$: C, 57.00; H, 5.50; N, 3.32. Found: C, 56.87; H, 5.32; N, 3.49.

Physical data for **5**: m.p. 179.5–180.5°, $[\alpha]_D^{22}$ +62° (*c* 1, acetone); ν_{max} 1645, 1615 (C=C–CO), and 1560 cm^{-1} (NO_2); *m/z* 361 (M^+); ^{1}H-n.m.r. (500 MHz, C_6D_6) δ 5.02 (d, 1 H, $J_{1,2}$ 6.1 Hz, H-1), 3.53 (m, 1 H, H-2), 4.67 (dd, 1 H, $J_{2,3}$ 8.3, $J_{3,4}$ 10.5 Hz, H-3), 4.39 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.11 (dt, 1 H, $J_{5,6a}$ 10.0, $J_{5,6e}$ 5.0 Hz, H-5), 3.40 (t, 1 H, $J_{6a,6e}$ 10.5 Hz, H-6*a*), 4.44 (dd, 1 H, H-6*e*), 5.13 (s, 1 H, PhCH), 1.95 (s, 3 H, Ac), and 1.72 (d, 3 H, $J_{2,Me}$ 1.3 Hz, Me); ^{13}C-n.m.r. (67.8 MHz, $CDCl_3$, $CDCl_3$ as internal standard) δ 102.3 (C-1, sugar numbering, see formula **5**), 43.9 (C-2), 84.1 (C-3), 74.7 (C-4), 66.5 (C-5), 68.9 (C-6), 101.7 (Ph*C*H), 114.3 (C-5′ or C-4′), 165.5 (C-4′ or C-5′), 193.2 (C=O), 15.3 (Me), 29.1 (Ac), 136.1 (*ipso*), 128.3 (*ortho* or *meta*), 126.0 (*meta* or *ortho*), and 129.3 (*para*).

Anal. Calc. for $C_{18}H_{19}NO_7$: C, 59.83; H, 5.30; N, 3.88. Found: C, 59.89; H, 5.30; N, 3.72.

TABLE II

First-order coupling-constants (Hz)[a]

Compd.[a]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6e}$	$J_{6a,6e}$	Other(s)
2	1.3	5.3	10.9	10.0	10.2	4.3	10.2	10.0 ($J_{2,2'}$)
3	ca.0	5.3	10.7	10.0	10.0	4.3	10.0	
4	3.4	11.4	10.0	9.5	9.5	3.8	9.5	7.1 ($J_{2,2'}$)
5	6.3	8.4	10.4	9.4	9.9	4.6	9.9	~1.3 ($J_{2,Me}$)
6	5.3	1.4	5.0	10.3	10.3	5.0	10.3	2.0 ($J_{2,Me}$)
7	4.8	1.5	4.8	9.5	10.3	5.1	10.3	

[a] Footnotes as in Table I.

1-O-Acetyl-2-C-(1-acetyl-2-oxopropyl)-4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-α-D-glucopyranose (**4**). — To a solution of the nitro alkene **1** (176 mg, 0.55 mmol) and 2,4-pentanedione (77 mg, 0.77 mmol) in 1,4-dioxane (96 mL) (distilled over $LiAlH_4$) was added 0.2M NaOH (0.8 mL), and the mixture was stirred for 1.5 h at room temperature and deionized with cation-exchange resin (Amberlite IR-120, H^+). After removal of the resin, the filtrate was concentrated to yield a solid residue, which was chromatographed with benzene as the eluant. The first fraction (34 mg, 19% yield) was the starting material **1** and the second consisted mainly of **4** and **6** in the ratio of 1:1. Recrystallization from EtOH afforded 77 mg (33%) of **4** as the first crop and 47 mg (24%) of **6** as the second. The ^{1}H-n.m.r. spectrum of the residue (38 mg), obtained from the mother liquor, showed that it was mainly **5** and **6** in the ratio of 1:1.3.

Physical data for **4**: 225° (dec.), $[\alpha]_D^{22}$ +176° (*c* 1, CH_2Cl_2); ν_{max} 1758, 1735, 1700 (C=O), and 1558 cm^{-1} (NO_2).

Anal. Calc. for $C_{20}H_{23}NO_9$: C, 57.00; H, 5.50; N, 3.32. Found: C, 57.01; H, 5.55; N, 3.39.

4-Acetyl-2,3-dihydro-5-methyl-(4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-β-D-altropyranosido)[1,2-b]furan (**6**). — Treatment of **1** (85 mg, 0.26 mmol) as in the preceding experiment with 2,4-pentanedione (45 mg, 0.45 mmol) in benzene (19 mL) and 0.2M NaOH (6 mL) in the presence of the catalyst (9 mg) for 20 h at room temperature and similar work-up afforded a residue, which was chromatographed with benzene as the eluant, to give successively the starting material **1** (12 mg, 14%) and **6** (65 mg, 68%). Compound **6** was recrystallized from EtOH; m.p. 160.5–161°, $[\alpha]_D^{22}$ +201°(*c* 1, $CHCl_3$); ν_{max} 1638, 1618 (C=C–CO), and 1545 cm^{-1} (NO_2); *m/z* 361 (M^+); ^{13}C-n.m.r. (67.8 MHz), $CDCl_3$, $CDCl_3$ internal standard) δ 99.3 (C-1, sugar numbering, see formula **6**), 47.0 (C-2), 80.7 (C-3), 72.9 (C-4), 60.1 (C-5), 68.8 (C-6), 112.0 (C-5′ or C-4′), 168.5 (C-4′ or C-5′), 102.3 (PhCH), 16.1 (Me), 30.0 (Ac), 193.1 (C=O), 136.3 (*ipso*), 128.3 (*ortho* or *meta*), 126.1 (*meta* or *ortho*), and 129.3 (*para*).

Anal. Calc. for $C_{18}H_{19}NO_7$: C, 59.83; H, 5.30; N, 3.88. Found: C, 59.65; H, 5.26; N, 3.84.

4-Benzoyl-2,3-dihydro-5-phenyl-(4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-β-D-altropyranosido)[1,2-b]furan (**7**). — A mixture of **1** (450 mg, 1.40 mmol), diben-

TABLE III

Heat of formation of model compounds[a] for the cyclized products

Compounds	*Heat of formation (kcal/mol)*
β-D-*altro* isomer **6c**	−185.2
β-D-*altro* isomer **6r**	−184.4
β-D-*manno* isomer **5r**	−179.6
β-D-*altro* isomer **5c**	−178.1

[a] Calculated by the AM1 method with full optimization.

zoylmethane (1010 mg, 4.51 mmol), the catalyst (90 mg), 0.2M NaOH (35 mL), and benzene (60 mL) was stirred for 26 h at room temperature. After dilution with benzene, the organic layer was washed with aq. NaCl (twice), dried, and evaporated. The resulting residue was chromatographed with PhMe and then 20:1 (v/v) PhMe–EtOAc, to give 560 mg (82%) of **7**. An analytical sample was prepared by recrystallization from ether–petroleum ether; m.p. 86–88°, $[\alpha]_D^{22}$ 170.5° (*c* 0.6, $CHCl_3$); ν_{max} 1680, 1615 (C=O), and 1555 cm^{-1} (NO_2).

Anal. Calc. for $C_{28}H_{23}NO_7$: C, 69.27; H, 4.78; N, 2.89. Found: C, 69.28; H, 4.86; N, 2.90.

2-C-Acetonyl-1-O-acetyl-4,6-O-benzylidene-2,3-dideoxy-3-C-nitro-α-D-manno-pyranose (**3**). — To a solution of **1** (160 mg, 0.5 mmol) in acetone (6 mL) was added 0.25 mL of M NaOH. The mixture was stirred for 6.5 h at room temperature and deionized with cation-exchange resin. After removal of the resin, the filtrate was evaporated and the residue was chromatographed with 15:1 (v/v) benzene–EtOAc, to give 47 mg (25%) of **3**. An analytical sample was recrystallized from EtOH; m.p. 173.5–174.5°, $[\alpha]_D^{22}$ +38° (*c* 0.8, acetone); ν_{max} 1750, 1710, (C=O), and 1555 cm^{-1} (NO_2).

Anal. Calc. for $C_{18}H_{21}NO_8$: C, 56.99; H, 5.58; N, 3.69. Found: C, 56.79; H, 5.55; N, 3.59.

Conversion of **2** into **5** and/or **6**. — To a solution of **2** (13 mg) in acetone-d_6 (0.3 mL) in an n.m.r. sample-tube was added 0.15 mL of 0.2M NaOD (in D_2O). After 3 min, the mixture was poured into acetone containing the cation-exchange resin. After removal of the resin, the filtrate was evaporated to give a solid residue whose ^{1}H-n.m.r. spectrum showed it to be a 1:3.6:1 mixture of **2**, **5** and **6**. Crystallization from EtOH afforded 4 mg of **5**, whose ^{1}H-n.m.r. spectrum indicated that deuteration at C-3 had not occurred.

Similar treatment of **2** for 26 min gave the C-3 deuterated derivative of **6**, together with a trace of **5**.

Similar treatment of the *gluco* isomer **4** (12.6 mg) resulted in the recovery of **4**, even after 40 min. The C-3 position of recovered **4** was completely deuterated, whereas the C-2′ position was not, as judged from the ^{1}H-n.m.r. spectrum.

Conversion of **5** *into* **6**. — To a solution of **5** (11 mg) in acetone-d_6 (0.4 mL) in an n.m.r. sample-tube was added 0.1 mL of 0.2M NaOD and the reaction was monitored by

n.m.r. spectroscopy. After 140 min, the mixture was poured into acetone containing cation-exchange resin. After removal of the resin, the filtrate was evaporated to a residue whose ^{1}H-n.m.r. spectrum showed that **5** was almost completely converted into **6** and that both methyl groups of 1-acetyl-2-oxopropyl moiety and C-3 position were deuterated.

The ^{1}H-n.m.r. spectrum of the residue, obtained by the same treatment of **6** as already described, was almost the same as that obtained from **5**, indicating that H-3 of **6** was acidic enough for abstraction.

Attempted conversion of **3** *into* **5** *and/or* **6**. — To a solution of **3** (10 mg) in acetone-d_6 (0.3 mL) in an n.m.r. sample-tube was added 0.2M NaOD (0.15 mL). After 45 min, the mixture was processed similarly. The ^{1}H-n.m.r. spectrum of the residue revealed the recovery of **3** (H-3, but not the acetonyl group, was almost completely deuterated).

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