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PREPARATION OF METHYL 4,6-*O*-BENZYLIDENE-2,3-DIDEOXY-2,3-DINITRO-α-D-GLUCOPYRANOSIDE AND ITS SELECTIVE CONVERSION INTO THE CORRESPONDING 2-NITRO-2-ENOPYRANOSIDE*

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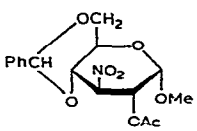
ABSTRACT

Treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside (**3**) with sodium nitrite in benzene–water in the presence of small amounts of tributylhexadecylphosphonium bromide as a phase-transfer catalyst afforded the 2-nitro alkene **4** in 47% yield. A similar reaction in the presence of 1.3 equiv. of acetic acid gave the 2,3-dinitro derivative **5** in 58% yield; it was selectively converted into the 2-nitro alkene **4**. In these reactions, nitrite ion undergoes addition from the axial and equatorial sides of **3** and **4**, respectively.

INTRODUCTION

We have shown[2] that the phase-transfer-catalyzed reaction of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (**1**) with sodium nitrite, or the reaction of the 3-nitro alkene derived from **1** by elimination of acetic acid, with sodium nitrite in the presence of tributylhexadecylphosphonium bromide, affords methyl 4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside as a major product and the isomeric 2-nitro alcohol as a minor product. The latter was assumed to arise *via* the 2,3-dinitro intermediate and the 2-nitro alkene. In this paper, we report the preparation of the α anomers of these presumed intermediates, namely, the 2-nitro alkene **4** and the 2,3-dinitro compound **5**, and the selective conversion of **5** into **4**.



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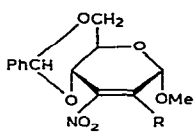

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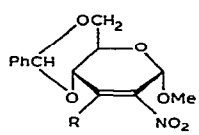
3a R = D



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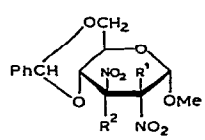
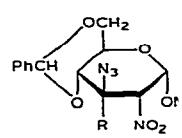
4a R = D



5 $R^1 = R^2 = H$
5a $R^1 = R^2 = D$
5b $R = D, R^2 = H$
5c $R^1 = H, R^2 = D$



6 R = H
6a R = D

*Stereochemistry of Nucleophilic Addition Reactions, Part VII. For part VI, see ref. 1.

RESULTS AND DISCUSSION

In contrast to the situation with **1**, treatment of the α-anomeric nitro acetate **2** with sodium nitrite in benzene–water in the presence of tributylhexadecylphosphonium bromide for 4 days at room temperature resulted only in the recovery of **2**. However, a similar, heterogeneous reaction of the nitro alkene **3** for 2 h gave a mixture that consisted mainly of **3** and **4**, and from which **4** was isolated in 47% yield.

The nitro-alkene structure was deduced from the results of elemental analysis, i.r. (1527 cm^{-1}, conjugated nitro-alkene), and n.m.r. spectroscopy (alkenic proton at δ 7.52 in Me_2SO-d_6).

Similar treatment of **3** with sodium nitrite in the presence of 1.3 equiv. of acetic acid immediately afforded a precipitate. After 15 min, the precipitate (which gradually disappeared at longer reaction-times) was collected by filtration and washed with benzene to give the dinitro derivative **5** in 72% yield (58% after recrystallization). Elemental analysis and i.r. bands at 1567 and 1552 cm^{-1} (saturated nitro groups) supported the assigned structure. Attempts to record the n.m.r. spectrum of pure **5** failed because the compound was insufficiently soluble in such relatively nonpolar solvents as chloroform-*d*, and partial conversion of **5** into **4** occurred in such a polar solvent as dimethyl sulfoxide-d_6. Nevertheless, by means of spin decoupling as well as by comparison with 2-deuterated (**5b**) and 3-deuterated (**5c**) derivatives of **5**, the ring-proton signals could be assigned, and the *gluco* configuration ($^4C_1$ conformation) was deduced from the coupling constants, $J_{1,2}$ 4.0, $J_{2,3}$ 10, and $J_{3,4}$ 11.5 Hz.

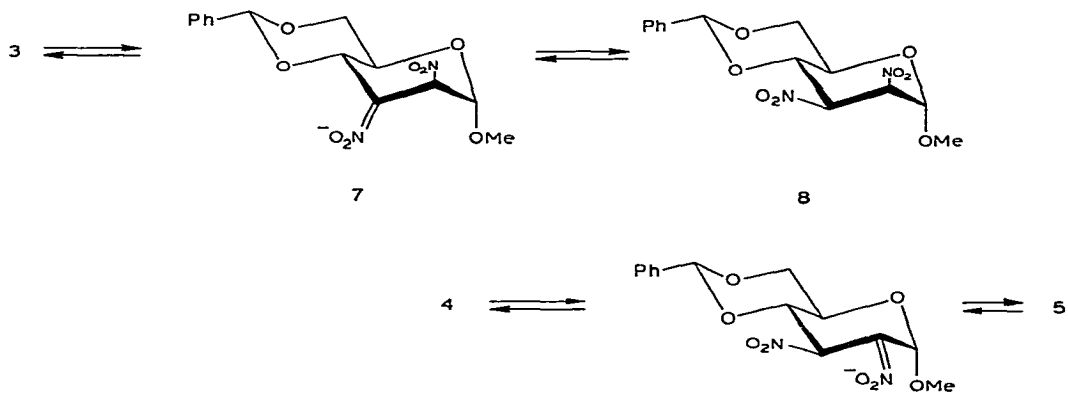
When the dinitro derivative **5** was heated in refluxing benzene in the presence of sodium hydrogencarbonate, the 2-nitro alkene **4** was selectively formed within 6 h. Treatment of **5** with triethylamine for 15 min at 0° also afforded **4** in 87% yield, together with traces of the 3-nitro alkene **3**. Such a highly regioselective elimination of nitrous acid may be explained as follows: (*i*) H-2 is more acidic than H-3 because of the electron-withdrawing character of the anomeric carbon atom[3], and (*ii*) abstraction of H-3 is disfavored by steric hindrance from the anomeric methoxyl group.

In order to confirm the aforementioned assignment of the n.m.r. spectrum of **5**, we attempted the preparation, from **3**, of the C-3 deuterated derivative (**5c**) of **5** by use of deuterium oxide and acetic acid-*O*-*d*. The product (**5a**) was, however, deuterated at both C-2 and C-3. Therefore, in order to obtain information on the reaction mechanism, we prepared the 2-deuterated derivative (**3a**) of **3** from methyl 2-*C*-deuterio-α-D-glucopyranoside[4] (**10**) and the 3-deuterated derivative (**4a**) of **4** by treating **3** with sodium nitrite in benzene–deuterium oxide, and performing the following experiments.

When the 2-nitro alkene **4** was treated with sodium nitrite in benzene–water with the phase-transfer catalyst in the absence of acetic acid for 25 min at room temperature, almost all of the starting material **4** was recovered. On the other hand, the same reaction of the 3-nitro alkene **3** afforded a mixture of **4** and **3** in the ratio of 1:0.6. When deuterium oxide was used instead of water, the reaction was slightly retarded and gave **4a** and **3** in the ratio of 1:1.6. A similar reaction of **3a** in benzene–

water was much slower, yielding **4** and **3a** in a ratio of 1 : 10, whereas it was somewhat accelerated in benzene–deuterium oxide, affording **4a** and **3a** in 1:6 ratio. Such remarkable isotope-effects suggest that proton abstraction from C-2 plays an important role in determining the reaction rate.

Similar reaction of **3** or **3a** in the presence of acetic acid afforded the dinitro compound **5**, but, in benzene–deuterium oxide containing acetic acid-*O-d*, the 2,3-dideuterated derivative **5a** was produced. Therefore, the hydrogen or deuterium atoms that were introduced at C-2 and C-3 of the product came from the solvent or acid. These facts are best explained in terms of epimerization; nitrite ion initially approaches from the axial side of **3**, to give an adduct having an axial nitro group at C-2, and this intermediary adduct then epimerizes to the more stable *gluco* isomer **5** (Scheme I). The predominance of axial over equatorial approach to **3** is in accord with previous examples[1]. It is likely that protonation of the intermediary nitronate **7** occurs predominantly from the axial side, yielding the 2,3-dinitromannopyranoside **8**; this approach is sterically hindered by the methoxyl group, but the alternative approach would cause a more serious 1,3-diaxial interaction between the methoxyl and nitro groups.



Although **4** and **4a** did not react with sodium nitrite in benzene–water or benzene–deuterium oxide in the absence of acetic acid, they gave dinitro derivatives (**5**, **5a**, **5b**, or **5c**) when the reactions were performed in the presence of acetic acid. In these products, the hydrogen or deuterium atom at C-2 was introduced from the medium, and that at C-3 originated from the starting alkene. The latter facts strongly suggest that nitrite ion approaches from the equatorial side of the 2-nitro alkene and the nitro group thus introduced at C-3 did not epimerize.

In these reactions, it was not easy to determine the ratios of deuteration of **4** at C-3, because the H-3 signal appears near those of phenyl protons, and its coupling constants are small ($J_{1,3}$ and $J_{1,4}$ 0, $J_{3,4}$ 2.0 Hz). The ratios of deuteration at C-3 were, therefore, determined after conversion of the compound into the azide **6** or **6a**, by treatment with sodium azide in the presence of acetic acid.

EXPERIMENTAL

General methods. — Melting points were determined in capillaries and are uncorrected. I.r. spectra were recorded for potassium bromide discs, and n.m.r. spectra were determined in chloroform-*d* and/or dimethyl sulfoxide-d_6 with tetramethylsilane as internal standard on either a Varian EM-360A or JNM-PS-100 (JEOL) spectrometer. 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 GF 254. The catalyst used refers to tributylhexadecylphosphonium bromide.

Methyl 3-O-benzoyl-4,6-O-benzylidene-2-deuterio-α-D-glucopyranoside (**9**). — To a suspension of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-2-ulose[5] (2.30 g, 6.0 mmol) in methanol (40 mL)–water (4 mL) was added sodium borodeuteride (250 mg, 6.0 mmol) and the resulting solution was stirred for 1 h at room temperature. After the addition of water (150 mL), a precipitate was collected by filtration and washed with water. Recrystallization from acetone afforded 1.92 g of **11** (83%), m.p. 221.5–223.5° (lit.[6] undeuterated compound, m.p. 219–220°); n.m.r. (Me_2SO-d_6): δ 8.3–7.2 (10 H, m, Ph), 5.70 (1 H, s, PhC*H*), 5.47 (1 H, m, H-3), 5.40 (1 H, s, OH), 4.83 (1 H, s, H-1), 4.5–3.6 (4 H, m, H-4, 5, 6a, 6e), and 3.40 (3 H, s, OMe).

Methyl 2-C-deuterio-α-D-glucopyranoside (**10**). — To a suspension of **9** (1.9 g, 4.9 mmol) in methanol (20 mL) was added M sodium methoxide (2 mL). The solution was warmed briefly until the crystals dissolved and then kept for 15 h at room temperature. After deionization with Amberlite IR-120 (H^+) cation-exchange resin, the mixture was evaporated, and 80% aqueous acetic acid (20 mL) added to the residue. The solution was warmed for 1 h in a water bath (~90°) and then evaporated. The residue was dissolved in 40 mL of water and washed with chloroform (3 × 20 mL). The aqueous layer was evaporated, and recrystallization of the residue from methanol afforded 730 mg of **10** (87%), m.p. 167.5–169.5° (lit.[4] m.p. 169–171°).

Methyl 4,6-O-benzylidene-3-deoxy-2-deuterio-3-nitro-α-D-glucopyranoside (**11**). — A mixture of sodium metaperiodate (2.24 g, 10.5 mmol) and sodium hydrogencarbonate (0.44 g, 5.23 mmol) was added to an ice–water-cooled aqueous solution (8 mL) of **10** (1.02 g, 5.23 mmol) in portions during 15 min with stirring. The resulting solution was allowed to warm to room temperature and kept for 1 h. Ethanol was added and the precipitate that separated was filtered off and washed with small amounts of ethanol. The filtrate was evaporated and ethanol added to the residue. The salt was filtered off and the filtrate evaporated. This procedure was repeated twice more. To an ice–water-cooled solution of the dialdehyde in 10 mL of methanol were successively added nitromethane (0.37 mL, 6.80 mmol) and M sodium methoxide (5.3 mL). After 1 h at room temperature, the solution was deionized by addition of Amberlite IR-120 (H^+) cation-exchange resin. The resin was removed and the solution evaporated. Anhydrous zinc chloride (1 g) and benzaldehyde (4 mL) were added to the residue and the resulting solution stirred for 28 h at room temperature. Water

TABLE I

CHEMICAL SHIFTS (δ)[a] AND FIRST-ORDER COUPLING CONSTANTS (Hz) AT 100 MHz

Compound	*Solvent*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6e*	*PhCH*	*Ph*	*OMe*
4	$CDCl_3$	5.42(s)		[b]	~4.38(m)	~4.04(m)	3.84(q)	~4.38	5.58(s)	7.28–7.56	3.56(s)
		$J_{1,3} = J_{1,4} \sim 0$, $J_{3,4}$?, $J_{4,5}$ 9.0, $J_{5,6a}$ 9.5, $J_{5,6e}$ 4.5, $J_{6a,6e}$ 8.5									
4	Me_2SO-d_6	5.5(s)		7.52(d)	4.64(d)[c]	← 3.6–4.2(m) →		4.32(q)	5.80(s)	~7.40	3.48(s)
		$J_{1,3} = J_{1,4} \sim 0$, $J_{3,4}$ 2.0, $J_{4,5}$ 9.0, $J_{5,6a}$?, $J_{5,6e}$ 5.0, $J_{6a,6e}$ 9.0									
5	Me_2SO-d_6	5.55(d)	6.16(q)	5.53(q)	4.27(q)	← 3.6–4.5(m) →			5.77(s)	~7.40	3.40(s)
		$J_{1,2}$ 4.0, $J_{2,3}$ 10, $J_{3,4}$ 11.5, $J_{4,5}$ 10									
6	$CDCl_3$	5.20(d)	4.38(q)	4.59(q)	3.53(t)	~3.92(m)	3.73(t)	4.33(q)	5.58(s)	7.28–7.60	3.39(s)
		$J_{1,2}$ 4.5, $J_{2,3}$ 10.5, $J_{3,4}$ 9.5, $J_{4,5}$ 10, $J_{5,6a}$ 10, $J_{5,6e}$ 3.5, $J_{6a,6e}$ 9.5									

[a] Me_4Si as internal standard. [b] The signal was overlapped with the phenyl signals. [c] The doublet was broad.

and hexane were added to the solution and most of the organic layer was decanted. After repetition of the decantation twice more, the product was extracted with chloroform. The extract was dried (magnesium sulfate) and evaporated. The syrup was chromatographed on silica gel and the products were successively eluted with benzene and benzene–ethyl acetate (50:1, 20:1, and 10:1, v/v). The fractions containing the products were combined and evaporated to give crystalline material. Recrystallization from ethanol afforded 270 mg of the *gluco* isomer **11** (19% from **10**). The mother liquor consisted mainly of the *manno* **12** and *gluco* **11** isomers in the ratio 3:1, as judged from n.m.r. spectroscopy conducted directly after evaporation (566 mg, 40%). The *gluco* isomer **11** had the following physical data: m.p. 167–168° (lit.[7] undeuterated compound, m.p. 167°); n.m.r. ($CDCl_3$): δ 7.17 (5 H, s, Ph), 5.50 (1 H, s, PhC*H*), 4.80 (1 H, s, H-1), 4.77 (1 H, m, H-3), 4.47–3.60 (4 H, m, H-4,5,6a,6e), 3.42 (3 H, s, OMe), and 2.48 (1 H, m, OH).

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-deuterio-3-nitro-*α*-*D*-*erythro*-hex-2-enopyranoside* (**3a**). — (*a*) To a solution of the syrupy mixture of **11** and **12** (536 mg, 1.72 mmol) and methanesulfonyl chloride (220 mg, 1.91 mmol) in dichloromethane (6 mL) was added triethylamine (382 mg, 3.78 mmol)[8] dropwise with stirring at 0°. After stirring for 15 min, the solution was chromatographed directly on silica gel, with benzene as eluant. The eluate was evaporated to a solid that was recrystallized from isopropyl alcohol to give 368 mg of **3a** (72%), m.p. 183–184.5° (lit.[9] undeuterated compound, m.p. 183°); n.m.r. ($CDCl_3$): δ 5.17 (1 H, d, H-1) and 4.70 (1 H, m, H-4).

(*b*). Similar treatment of **11** (266 mg, 0.853 mmol) afforded **3a** in 74% yield.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-nitro-*α*-*D*-erythro-hex-2-enopyranoside* (**4**). — (*a*) *From the 3-nitro alkene*[9] **3**. A mixture of **3** (147 mg, 0.5 mmol), sodium nitrite (70 mg, 1 mmol), the catalyst (10 mg), benzene (10 mL), and water (5 mL) was stirred for 2 h at room temperature. Benzene (30 mL) was added and the organic layer was separated, washed with water, and dried (magnesium sulfate) for 5 min*. After removal of inorganic material, the filtrate was evaporated. Recrystallization from isopropyl alcohol afforded 69 mg of **4** (47%), m.p. 199–199.5°, $[\alpha]_D^{22}$ +220° (*c* 1.2, dichloromethane); ν_{max} 1527 cm^{-1} (C=C–NO_2).

Anal. Calc. for $C_{14}H_{15}NO_6$: C, 57.33; H, 5.16; N, 4.78. Found: C, 57.11; H, 5.11; N, 4.58.

Similar treatment of **3** (147 mg) with sodium nitrite (70 mg) in the presence of deuterium oxide instead of water afforded 85 mg of **4a** (58%); n.m.r. ($CDCl_3$): δ 5.42 (1 H, s, H-1), ~4.38 (1 H, d, $J_{4,5}$ 9.0 Hz, H-4), and 7.28–7.56 (5 H, Ph); (Me_2SO-d_6): δ 5.55 (1 H, s, H-1) and 4.64 (1 H, d, H-4).

In order to clarify the deuterium effects, a mixture of the 3-nitro alkene **3** or **3a** (30 mg), sodium nitrite (30 mg), the catalyst (2 mg), benzene (0.8 mL), and water or deuterium oxide (0.2 mL) was stirred for 25 min at room temperature. A similar isolation as before afforded crude product. The composition of the product

*When the solution was kept overnight, the yield of **4** dramatically decreased and many spots appeared in t.l.c.

was determined by n.m.r. spectroscopy as described in the Results and Discussion section.

(*b*) *From the dinitro compound* **5**. To a stirred solution of **5** (170 mg, 0.5 mmol) and urea (12 mg, 0.2 mmol) in dichloromethane (12 mL) was added triethylamine (51 mg, 0.5 mmol) at 0°. After 15 min at 0°, the solution was washed with water, dried (magnesium sulfate), and evaporated. Recrystallization from isopropyl alcohol afforded 127 mg of **4** (87%).

Similar treatment of **5a** (171 mg, 0.5 mmol) with triethylamine afforded 128 mg (87%) of **4a**.

Compound **5** (340 mg, 1 mmol) and dry sodium hydrogencarbonate (3.4 g) in distilled benzene (40 mL) were boiled for 6 h under reflux, with stirring. The mixture was cooled and filtered, and the filtrate evaporated to give a crystalline residue. Recrystallization from isopropyl alcohol gave 197 mg of **4** (67%).

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-dinitro-α-*D*-glucopyranoside* (**5**). — To a stirred solution of **3** (750 mg, 2.56 mmol), the catalyst (50 mg), and acetic acid (200 mg, 3.33 mmol) in benzene (20 mL)–water (5 mL) was added sodium nitrite (750 mg, 10.9 mmol) at room temperature. After 15 min, a precipitate that separated immediately was collected by filtration and washed successively with water (2 × 10 mL) and benzene (10 mL). The precipitate (626 mg, 72%) was recrystallized from benzene to afford 504 mg of **5** (58%), m.p. 187–192° (dec.), $[\alpha]_D^{22}$ +92° (*c* 0.94, dichloromethane); ν_{max} 1552 and 1567 cm^{-1} (NO_2).

Anal. Calc. for $C_{14}H_{16}N_2O_8$: C, 49.41; H, 4.74; N, 8.23. Found: C, 49.40; H, 4.65; N, 8.13.

T.l.c. of the mother liquor showed strong spots of **4** and **5**, together with weak spots corresponding to the 2- and 3-nitro alcohols.

TABLE II

REACTION OF **3**, **3a**, **4**, AND **4a** WITH SODIUM NITRITE IN THE PRESENCE OF ACETIC ACID[a]

Starting material	*Solvent*	*Product*	*Yield*[b], %
3	H_2O[c]	**5**	51 (75)
3	D_2O[d]	**5a**	51 (78)
3a	H_2O	**5**	38 (60)
3a	D_2O[d]	**5a**	32 (68)
4	H_2O	**5**	32 (56)
4	D_2O[d]	**5b**	49 (77)
4a	H_2O	**5c**	46 (63)
4a	D_2O[d]	**5a**	34 (55)

[a]A mixture of the nitro alkene (75 mg), sodium nitrite (75 mg), acetic acid (20 mg), tributylhexadecylphosphonium bromide (5 mg), benzene (2 mL for **3** and **3a**, 4 mL for **4** and **4a**), and water or deuterium oxide (0.5 mL) was stirred for 25 min at room temperature. [b]Isolated yield; the figures in parentheses show the crude yield. [c]Scale was doubled. [d]Acetic acid-*O*-*d* was used instead of acetic acid.

Similar treatment of **3** (750 mg) in the presence of acetic acid-*O*-*d* and deuterium oxide afforded the 2,3-dideuterated derivative **5a** in 64% yield; n.m.r. (Me_2SO-d_6): δ 5.55 (1 H, s, H-1) and 4.27 (1 H, d, $J_{4,5}$ 10 Hz, H-4).

Compounds **5b** and **5c** were prepared from **4** and **4a**, respectively, as described in Table II; n.m.r. (Me_2SO-d_6) for **5b**: δ 5.55 (1 H, s, H-1), 5.53 (1 H, d, $J_{3,4}$ 11.5 Hz, H-3), and 4.27 (1 H, q, $J_{4,5}$ 10 Hz, H-4); for **5c**: δ 5.55 (1 H, d, $J_{1,2}$ 4.0 Hz, H-1), 6.16 (1 H, d, H-2), and 4.27 (1 H, d, $J_{4,5}$ 10 Hz, H-4).

Methyl 3-azido-4,6-O-benzylidene-2,3-dideoxy-2-nitro-α-D-glucopyranoside (**6**). — A mixture of **4** (88 mg, 0.3 mmol), sodium azide (29 mg, 0.45 mmol), acetic acid (50 mg, 0.83 mmol), acetonitrile (4.8 mL), and water (0.6 mL) was stirred overnight. The mixture was made neutral with sodium hydrogencarbonate and then extracted with chloroform. The extract was washed with water, dried (magnesium sulfate), and evaporated to give a solid residue in nearly quantitative yield. Recrystallization from cyclohexane afforded 62 mg of **6** (61%), m.p. 122–123.5°, $[\alpha]_D^{30}$ +180° (*c* 1.1, dichloromethane); ν_{max} 2130 (N_3) and 1570 cm^{-1} (NO_2).

Anal. Calc. for $C_{14}H_{16}N_4O_6$: C, 50.00; H, 4.80; N, 16.66. Found: C, 50.11; H, 4.75; N, 16.60.

The n.m.r. spectrum of the mother liquor revealed that it was almost pure **6**.

Similar treatment of **4a** (36 mg) or **5c** (30 mg) afforded the 3-deuterated derivative **6a** in 63 and 60% yield, respectively; n.m.r. ($CDCl_3$): δ 5.20 (1 H, d, $J_{1,2}$ 4.5 Hz, H-1), 4.38 (1 H, d, H-2), and 3.53 (1 H, d, $J_{4,5}$ 10 Hz, H-4).

REFERENCES

1 T. SAKAKIBARA AND R. SUDOH, *Bull. Chem. Soc. Jpn.*, 51 (1978) 1193–1196, and references cited therein.
2 T. SAKAKIBARA AND R. SUDOH, *Carbohydr. Res.*, 50 (1976) 197–202.
3 For example, H. H. BAER AND C.-W. CHIU, *Can. J. Chem.*, 52 (1974) 111–121.
4 A. H. HAINES, *Carbohydr. Res.*, 58 (1977) 212–216.
5 P. M. COLLINS, D. GARDINER, S. KUMAR, AND W. G. OVEREND, *J. Chem. Soc., Perkin Trans. 1*, (1972) 2596–2610.
6 R. W. JEANLOZ AND D. A. JEANLOZ, *J. Am. Chem. Soc.*, 79 (1957) 2579–2583.
7 H. H. BAER AND T. NEILSON, *Can. J. Chem.*, 43 (1965) 1829–1834.
8 Y. TACHIMORI, T. TAKAMOTO, AND R. SUDOH, *Chem. Lett.*, (1976) 483–484; H. H. BAER AND F. F. Z. GEORGES, *J. Org. Chem.*, 41 (1976) 3474–3476.
9 H. H. BAER AND F. KIENZLE, *Can. J. Chem.*, 45 (1967) 983–990.