HYDROXY- AND ACETOXY-MERCURATION OF D-GLUCAL TRIACETATE

K. TAKIURA AND S. HONDA

Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka-fu (Japan)

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ABSTRACT

Hydroxy- and acetoxy-mercuration of D-glucal triacetate (**1**) afforded 2-acetoxymercuri-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucose (**2**) and 2-acetoxymercuri-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (**3**), respectively. On demercuration with sodium borohydride, compound **2** gave at first the acyclic 4,6-di-*O*-acetyl-D-*erythro*-hex-2-enose (**4**), which was further reduced to the corresponding hex-2-enitol derivative (**5**). Demercuration of **3** with borohydride gave a mixture of **1** and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose (**6**). On the other hand, demercuration of **2** and **3** with thiourea yielded **4** and **1**, respectively. The reaction mechanisms of both oxymercurations are also discussed.

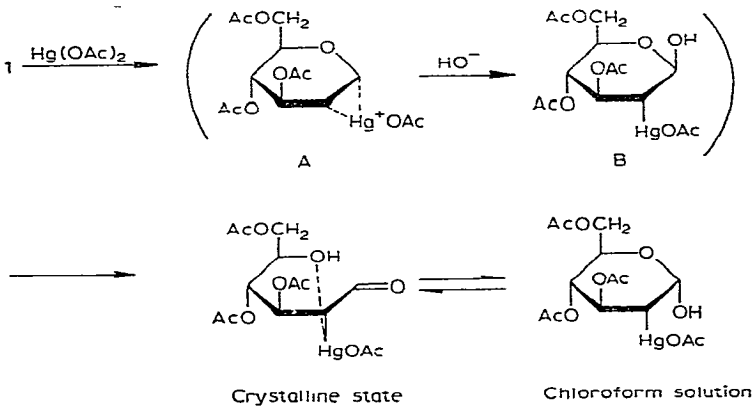
INTRODUCTION

In the previous paper[1] we described details of the methoxymercuration of glycal acetates and suggested the usefulness of this reaction for the synthesis of such important carbohydrate derivatives as 2,3-unsaturated sugars and 2-deoxy sugars. The advantages of the methoxymercuration–borohydride-reduction method over the Fischer glycal synthesis of 2-deoxy sugars were demonstrated especially by the preparation of 2-deoxy-D-*erythro*-pentose[2]. In continuation of our studies of the synthesis and reactions of mercurial sugars, we have examined two oxymercuration reactions of the title compound.

RESULTS AND DISCUSSION

Hydroxymercuration of D-glucal triacetate (**1**) was performed in aqueous acetone by using mercuric acetate, and a crystalline mercurial product (**2**) having the molecular formula $C_{14}H_{20}HgO_{10}$ was obtained in 85% yield. The i.r. spectrum of crystalline **2** showed an intense OH band at 3430 cm^{-1}. Marked mutarotation ($+66.4° \rightarrow -0.03°$) indicated that the hydroxyl group was at C-1. The n.m.r. spectrum, measured in chloroform-d_6, gave, together with the signals of twelve acetyl protons

at τ 7.9–8.0, a well-resolved quartet for H-2 at τ 7.37 that resembled the H-2 proton signals of the methoxymercuration products of glycal acetates[1]. Tentative assignments of other protons, and the observed spacings in the spectra (Table I), were consistent with the structure of 2-acetoxymercuri-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose in the *C1* conformation. The i.r. spectrum of **2**, measured in chloroform, was notably different from that measured in the crystalline state (in KCl or Nujol). The former was much simpler; the only absorption bands observed in the region of 1500–4000 cm^{-1} were two C=O bands, at 1750 (C–OAc) and at 1590 cm^{-1} (Hg–OAc). Neither the OH band nor an intense band at 1705 cm^{-1}, which was observed in the solid-state spectrum and was presumably due to a free aldehyde group, were seen in the solution spectrum. The disappearance of these two bands in solution may be attributed to the formation of an intramolecular, chelate bond between the C-1 hydroxyl group and the C-2 mercury atom, as indicated in Scheme 1. The presence of a C=O band at 1705 cm^{-1} in the crystalline compound suggests that



2

Scheme 1

2 exists in the aldehyde form, a behavior reminicent of the hydroxymercuration of vinyl ethers to yield 2-mercuriacetaldehyde[3]. The formation of the aldehyde form may be rationalized by postulating chelation between the C-2 mercury atom and the C-5 hydroxyl group, somewhat as in the 2,5-anhydrohexoses, which tend to exist in the aldehyde form[4]. Accordingly, the downward mutarotation observed may be attributed to transformation from the aldehyde form to the chelated, cyclic form. It is generally accepted that most solvomercuration reactions proceed through rear-side attack of oxide nucleophiles upon intermediate mercurinium ions, giving rise to *trans*-addition products[5]. This orientation was also demonstrated in the methoxymercuration of glycal acetates[1]. Hence, hydroxymercuration of **1** may similarly be assumed to proceed by *trans*-addition to yield, via the mercurinium ion A, at first the β-anomer B, which is then converted, presumably via the crystallizable aldehyde form, into the α-anomer having intramolecular, chelate bonding. The high yield (85%) of D-*gluco*

TABLE I

N.M.R. PARAMETERS OF MERCURIAL ADDUCTS, MEASURED AT 100 MHz IN CHLOROFORM-d_6

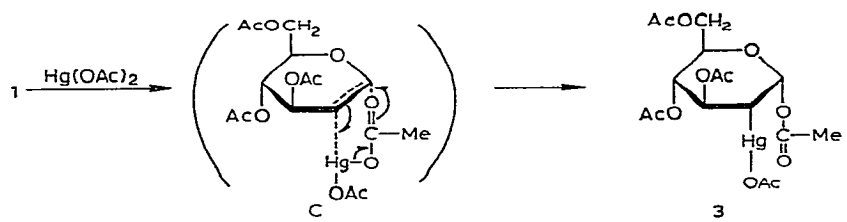
Mercurial adduct	*Chemical shifts* (τ) *and multiplicities*[a] *of signals*								
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*OH*	*OAc*[b]
2	4.45d	7.37q	4.67q	4.97t	———	5.6–6.0m	———	6.26m	7.92(1) 7.95(3)
3	3.68d	7.32q	4.59q	4.92t	———	5.6–6.1m	———		7.85(1) 7.95(1) 7.98(1) 8.02(1)

	Spin-spin coupling constants (Hz)			
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
2	3.3	11.5	9.1	9.0
3	3.3	11.5	9.0	9.0

[a]Multiplicities are designated: d, doublet; t, triplet; q, quartet; m, multiplet. [b]The number of acetyl groups is shown in parentheses.

derivative is noteworthy when compared with the D-*gluco* to D-*manno* proportion (45:55) obtained[1] in the methoxymercuration of 1. There was observed some difference in the specific rotation of **1** in 1:1 aqueous acetone (+0.7°) and in methanol (−9.9°). This difference is considered to reflect a conformational change in **1**, and it appears possible that such a change might be responsible, at least in part, for the increased yield of D-*gluco* derivative in the hydroxymercuration in aqueous acetone, favoring formation of a mercurinium ion at one side of the double bond.

Reaction of **1** with mercuric acetate in inert solvents led to acetoxymercuration, with the introduction of an acetoxyl group at C-1. The reaction proceeded with difficulty in chloroform, but readily in acetonitrile. In both cases, a crystalline mercurial compound (**3**) having the molecular formula $C_{16}H_{22}HgO_{11}$, was obtained in good yield. The n.m.r. spectrum of **3** gave well-resolved signals for H-1, H-2, H-3, and H-4, together with signals of fifteen acetyl protons at τ 7.85–8.05 (Table I). The large $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ values indicate that **3** in chloroform-d_6 has D-*gluco* configuration in the *CI* conformation, and the small $J_{1,2}$ value suggests that the C-1 acetoxyl group is oriented axially rather than equatorially, indicating the α-anomeric configuration. Consequently, the structure of **3** is considered to be 2-acetoxymercuri-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose. *cis*-Addition in oxymercuration is an abnormal reaction. However, the reaction may be readily explained by the formation of a cyclic intermediate C (Scheme 2). As **3** is the 1-*O*-acetyl derivative of **2**, an attempt was

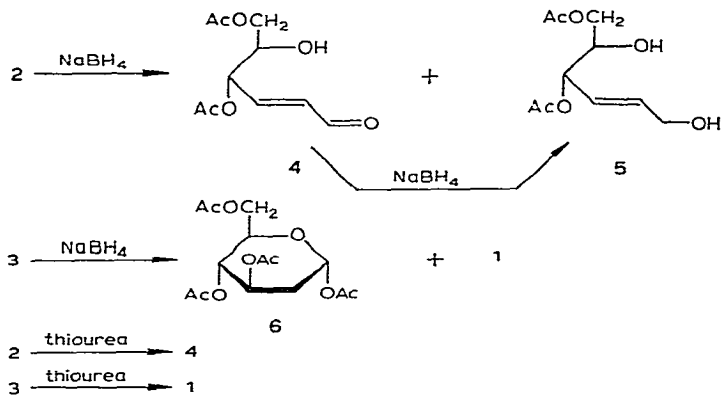


Scheme 2

made to obtain **3** by acetylation of **2** with acetic anhydride–pyridine, but the mercurial compound was so labile that the acetylation caused rapid demercuration, and gave **1** in high yield.

Addition of sodium borohydride to a methanolic solution of **2** until no further precipitation of metallic mercury occurred yielded two demercuration products, which were separated by silica-gel column chromatography. The fast-moving component (**4**) was a syrup that was very sensitive to sulfuric acid spray and consumed bromine rapidly. Its characteristic, intense absorption at 1685 cm^{-1}, and a weak absorption appearing as a shoulder at 1650 cm^{-1} indicated the presence of an α,β-unsaturated aldehyde group. The observation from the i.r. spectrum accorded with the presence of two absorption maxima in the u.v. spectrum at 218 (ε_{max}^{MeOH} 7180) and 329 nm (ε_{max}^{MeOH} 15.3). The n.m.r. spectrum of **4** showed a doublet of H-1 at τ 0.43, two well-resolved signals for olefinic protons at τ 3.77 (H-2) and 3.09 (H-3), a broadened singlet for an OH proton at τ 6.55, and the signals of six acetyl protons at τ 7.85–

7.95. On the basis of these data, the open-chain structure of 4,6-di-*O*-acetyl-D-*erythro*-hex-2-enose is proposed for **4**. The microanalytical data also supported this structure, and further proof was provided by preparation of the corresponding 2,4-dinitrophenylhydrazone.



Scheme 3

The slow-moving component (**5**) was a crystalline compound that consumed bromine but had no enol group, as evidenced by negative ferric chloride and bromine–iodide–starch tests[6]. The i.r. spectrum of **5** showed absorptions assigned to OH, C=O, and C=C vibrations at 3430, 1735, and 1650 cm^{-1}, respectively. In the n.m.r. spectrum, two signals at τ 6.53 and 6.92, which were eliminated by deuteration, indicated that two kinds of hydroxyl groups were present. On the basis of this evidence, together with the microanalytical data, compound **5** was considered to be a reduction product of **4**, namely 4,6-di-*O*-acetyl-D-*erythro*-hex-2-enitol. Compound **5** was deacetylated in methanolic sodium methoxide, and the deacetylation product gave a tetra-*p*-nitrobenzoate. With an excess of sodium borohydride, the mercurial compound **2** gave compound **5** exclusively, in nearly quantitative yield. Consequently, demercuration of **2** with sodium borohydride was initiated by elimination of mercuric acetate from the C-2 acetoxymercuri group and the *trans*-disposed C-3 acetoxyl group, yielding an α,β-unsaturated aldehyde derivative **4**. Concurrent reduction of the aldehyde group occurred rather slowly to give **5**. Demercuration of **2** with thiourea also yielded **4**, as expected from the results obtained[1] with the methoxymercuration product of **1**.

The demercuration of compound **3** was interesting from a stereochemical viewpoint, since this compound possesses two acetoxyl groups at C-1 and C-3 adjacent to the C-2 acetoxymercuri group. Elimination of mercuric acetate by thiourea was favored between positions **1** and **2**, yielding **1** as a predominant product. A contaminant, minor product was assumed on the basis of microanalysis to be the 2,3-unsaturated hexose derivative, but it amounted only to an estimated 15% of **1**. Thus, the axial C-1 acetoxyl group was more susceptible to elimination than the equatorial C-3

acetoxyl group. The susceptibility of the C-1 acetoxyl group to demercuration was encountered also in the reaction with sodium borohydride in methanol, in which reaction **1** was obtained in considerable yield together with the 2-deoxy sugar deriative (**6**).

EXPERIMENTAL

General. — Melting points were determined on a hot stage by using a Yanagimoto micro melting-point apparatus, and are uncorrected. Specific rotations were measured in a 1-dm tube. I.r. spectra were obtained with a Hitachi–Perkin–Elmer EPI G-2 i.r. spectrophotometer. N.m.r. spectra were recorded at 100 MHz with a JEOL JNM-4H spectrometer. Chemical shifts are expressed on the τ-scale for 10% solutions in chloroform-d_6 at 35°, with tetramethylsilane as the internal standard. T.l.c. was performed on glass plates coated with Wakogel B-5. Descending paper chromatography was conducted on Whatman No. 1 filter paper by using 4:1:5 butyl alcohol–acetic acid–water (upper phase, solvent *A*) and 6:4:3 butyl alcohol–pyridine–water (solvent *B*) at 25°, and the spots were detected with alkaline silver nitrate[7]. R_G denotes the mobility relative to D-glucose. G.l.c. was carried out with a Hitachi K-23 instrument equipped with a hydrogen-flame ionization detector. A stainless-steel column (2 m) containing 3% SE-30 was used at 120°, and the carrier gas (nitrogen) was regulated at a flow rate of 60 ml/min. Microanalysis for C, H, and Hg was performed as described in the previous paper[1]. All evaporations were performed below 40° under diminished pressure.

Hydroxymercuration of D-*glucal triacetate* (**1**). — Mercuric acetate (3.19 g, 10.0 mmoles) and **1** (2.72 g, 10.0 mmoles) were dissolved in 1:1 aqueous acetone (40 ml), and the solution was kept overnight. The solution was then evaporated and the residue was dried over sodium hydroxide *in vacuo*. The thick syrup resulting was crystallized from acetone–isopropyl ether to give compound **2** (4.68 g, 85%). Recrystallization from the same solvents afforded needles, m.p. 128–128.5°, $[\alpha]_D^{29}$ (*c* 1.25, 1:1 aqueous acetone) +66.4° (10 min)→−0.03° (equil.) $\nu_{max}^{KCl\ (Nujol)}$ 3430 (OH), 1735 (C=O of C–OAc), 1705 (C=O of –CHO), 1625, 1600 (C=O of Hg–OAc), 1240–1260 cm^{-1} (C=O of OAc); $\nu_{max}^{chloroform}$ 1750 (C=O of C–OAc), 1590 (C=O of Hg–OAc), 1240 cm^{-1} (C=O of OAc).

Anal. Calc. for $C_{14}H_{20}HgO_{10}$: C, 30.63; H, 3.67; Hg, 36.55. Found: C, 30.49; H, 3.58; Hg, 36.92.

Acetoxymercuration of **1**. — Mercuric acetate (3.19 g, 10.0 mmoles) was heated under reflux in a chloroform solution (100 ml) of **1** (2.72 g, 10.0 mmoles) whereby the former dissolved gradually within 2 h. After 5 h at reflux, the solution was evaporated, and the residue was dried over sodium hydroxide *in vacuo*. The thick syrup resulting was crystallized from acetone–isopropyl ether to give compound **3** (1.72 g, 29%). Recrystallization from methanol afforded needles, m.p. 131–132°, $[\alpha]_D^{27}$ +70.9° (*c* 1.0, chloroform); ν_{max}^{KCl} 1740 (C=O of C–OAc), 1600 (C=O of Hg–OAc), 1220–1260 cm^{-1} (C=O of OAc).

Anal. Calc. for $C_{16}H_{22}HgO_{11}$: C, 32.52; H, 3.75; Hg, 33.94. Found: C, 32.39; H, 3.62; Hg, 33.92.

The mercurial compound **3** was also obtained, in a yield of 23%, when an acetonitrile solution (20 ml) containing the same amounts of **1** and mercuric acetate was kept for 2 h at room temperature and processed in similar fashion.

Reaction of **2** *with a minimum amount of sodium borohydride.* — The mercurial compound **2** (1.10 g, 2.00 mmoles) was dissolved in methanol (10 ml), and sodium borohydride was added in small portions. The reaction temperature was kept below 0°. The amount of sodium borohydride that was required, until further addition of the reagent ceased to precipitate metallic mercury, was 60 mg (1.6 mmoles). The reaction mixture was filtered, and the filtrate decationized by stirring with Amberlite IR-120 (H^+, 1 g). The decationized solution was evaporated to dryness, the residual syrup redissolved in methanol, and this solution was evaporated. This procedure was repeated three times, and finally there was obtained a thick syrup (450 mg) that was fractionated on a silica gel column (Wakogel C-200, 2.0 × 35 cm) by using 9:1 ethyl acetate–benzene as an eluant. From the 90–160 and 170–250 ml fractions, compound **4** (283 mg, 61%) and compound **5** (99 mg, 22%) were obtained after evaporation of the solvent.

Compound **4** was a syrup having $[\alpha]_D^{18}$ +4.2° (*c* 1.8, chloroform); R_F 0.63 (9:1 ethyl acetate–benzene); λ_{max}^{MeOH} 218 (ε_{max} 7180), 329 nm (ε_{max} 15.3); ν_{max}^{film} 3460 (OH), 1740 (C=O of OAc), 1685 (C=O of C=C–CHO), 1650 (C=C), 1240 cm^{-1} (C=O of OAc); n.m.r.: τ 0.42 (1-proton doublet, $J_{1,2}$ 8.3 Hz, H-1 of C=C–CHO), 3.09 (1-proton quartet, $J_{3,4}$ 4.5 Hz, H-3), 3.77 (1-proton octet, $J_{2,3}$ 15.5 Hz, $J_{2,4}$ 0.1 Hz, H-2), 4.42 (1-proton sextet, $J_{4,5}$ 4.5 Hz, H-4), 5.65–5.98 (3-proton multiplet, H-5, H-6 and H-6′), 6.55 (1-proton broadened singlet, OH), 7.86 (3-proton singlet, OAc), 7.92 (3-proton singlet, OAc). Compound **4** consumed bromine rapidly.

Anal. Calc. for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.06; H, 6.32.

The 2,4-dinitrophenylhydrazone of **4** gave orange leaflets from aqueous ethanol, m.p. 138–139°.

Anal. Calc. for $C_{16}H_{18}N_4O_9$: C, 46.83; H, 4.42; N, 13.66. Found: C, 46.74; H, 4.37; N, 13.77.

Compound **5** gave needles from ether–petroleum ether, m.p. 61–63°, $[\alpha]_D^{26}$ +18.7° (*c* 3.9, chloroform); R_F 0.53 (9:1 ethyl acetate–benzene); ν_{max}^{film} 3430 (OH), 1735 (C=O of OAc), 1650 (C=C), 1240 cm^{-1} (C=O of OAc); n.m.r.: τ 3.96–4.38 (2-proton multiplet, H-2 and H-3), 4.71 (1-proton triplet, $J_{3,4}$ 4.7 Hz, $J_{4,5}$ 4.7 Hz, H-4), 5.6–6.1 (5-proton multiplet, H-1, H-1′, H-5, H-6 and H-6′), 6.53 (1-proton broadened singlet, OH), 6.92 (1-proton broadened singlet, OH), 7.97 (6-proton singlet, 2 OAc). Compound **5** consumed bromine but gave a negative bromine–iodide–starch test[6], as well as a negative ferric chloride test, indicating the absence of an enol group.

Compound **5** (58 mg, 0.25 mmoles) was dissolved in 0.1M methanolic sodium methoxide (2.5 ml), and the solution was kept for 2 h. Decationization by stirring with Amberlite IR-120 (H^+, 0.5 g), followed by evaporation of the decationized solution, afforded the deacetylated product as a syrup (35 mg, 95%), $[\alpha]_D^{22}$ −2.1°

(*c* 1.4, water); R_G 2.00 (solvent *A*). The syrup (35 mg) was treated with *p*-nitrobenzoyl chloride (186 mg. 1.00 mmole) in pyridine to give the *p*-nitrobenzoate (180 mg, 97%). Recrystallization from ethanol afforded minute needles, m.p. 177–178°, $[\alpha]_D^{20}$ +9.6 (*c* 1.1, chloroform).

Anal. Calc. for $C_{34}H_{24}N_4O_{16}$: C, 54.84; H, 3.24; N, 7.53. Found: C, 54.75; H, 3.07; N, 7.44.

Reaction of **2** *with an excess amount of sodium borohydride.* — The mercurial compound **2** (1.10 g, 2.00 mmoles) was dissolved in methanol (10 ml) and sodium borohydride (379 mg, 10.0 mmoles) was added in small portions. The reaction mixture was processed as described previously to give compound **5** (455 mg, 99%) in almost homogeneous form. Purification on a column of silica gel by using 9:1 ethyl acetate–benzene as an eluant afforded an analytically pure sample. Identity with the slow-moving component in the preceding experiment was confirmed by m.p., $[\alpha]_D$, chromatographic behavior, and microanalysis, as well as by spectrometric data.

Reaction of **2** *with thiourea.* — The mercurial compound **2** (1.10 g, 2.00 mmoles) was dissolved in methanol (10 ml) and thiourea (761 mg, 10.0 mmoles) was added. After 2 h, the reaction mixture was evaporated to dryness to give a syrup, which was fractionated on a silica gel column (Wakogel C-200, 2.0 × 40 cm) by using 7:1 chloroform–methanol as eluant. From the 60–110-ml fraction a syrupy product (333 mg, 72%) was obtained after evaporation of the solvent. The crude product was purified on a silica-gel column by using 9:1 ethyl acetate–benzene as eluant. The $[\alpha]_D$, chromatographic behavior, microanalysis, and spectrometric data of the purified product were identical with those of **4**.

Attempted acetylation of **2**. — The mercurial compound **2** (549 mg, 1.00 mmole) was dissolved in pyridine (2 ml) and acetic anhydride (1 ml) was added. After 2 h, the solution was poured into ice–water (50 ml), and the resulting solution was extracted with chloroform (20 ml). The extract was washed three times with 20-ml portions of a saturated aqueous solution of sodium hydrogen carbonate, and then with water. Drying and evaporation of the solution gave a syrup that did not contain mercury (109 mg, 80%). T.l.c. with 7:3 benzene–ethyl acetate gave chiefly a dense spot having R_F 0.61, together with more slow moving faint spots (R_F of **1**, 0.61). The n.m.r. spectrum of the syrup was almost identical with that of **1**.

Reaction of **3** *with sodium borohydride.* — The mercurial compound **3** (591 mg, 1.00 mmole) was dissolved in methanol, and sodium borohydride (57 mg, 1.50 mmoles) was added in small portions, with the reaction temperature being kept below 0°. The reaction mixture was evaporated to dryness and the residual syrup was fractionated on a silica-gel column (Wakogel C-200, 2.0 × 40 cm) with 7:3 benzene–ethyl acetate as an eluant. From the 100–140 ml fraction a syrup (112 mg, 41%) was obtained that was crystallized from ether–petroleum ether to give needles, m.p. and mixed m.p. 54–55° (m.p. of **1**, 54–55°), $[\alpha]_D$ +0.01° (*c* 1.0, chloroform) {$[\alpha]_D^{16}$ of **1**, +0.7° (*c* 1.0 chloroform)}. The i.r. and n.m.r. spectra of this compound were identical with those of **1**.

Anal. Calc. for $C_{12}H_{16}O_7$: C, 52.94; H, 5.92. Found: C, 52.59; H, 5.91.

From the 150–200-ml fraction, a crystalline product **6** (122 mg, 45%) was obtained. Recrystallization from ethanol afforded prisms, m.p. 110–112° (lit.[8] m.p. of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose, 111–112°), $[\alpha]_D^{22}$ +103° (*c* 1.6, chloroform) {lit.[8] $[\alpha]_D^{22}$ of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose, +104° (*c* 1.6, chloroform)}. The n.m.r. data were identical with those of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranose[9].

Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.77; H, 6.19.

Deacetylation of **6** in 0.1 M methanolic sodium methoxide yielded a syrup, R_G 1.70 (solvent *A*); 1.38 (solvent *B*). {R_G values of authentic 2-deoxy-D-*arabino*-hexose, 1.70 (solvent A); 1.38 (solvent B)}.

Reaction of **3** *with thiourea.* — The mercurial compound **3** (591 mg, 1.00 mmole) was dissolved in methanol (10 ml) and thiourea (381 mg, 5.00 mmoles) was added. After 2 h, the reaction mixture was evaporated to dryness and the residual syrup was fractionated on a silica-gel column (Wakogel C-200, 2.0 × 30 cm) by using 7:3 benzene–ethyl acetate as an eluant. From the 60–100-ml fraction a syrup (234 mg, 82%) was obtained, $[\alpha]_D^{35}$ +14.4° (*c* 1.0, chloroform). Although its i.r. and n.m.r. spectra appeared identical with those of **1**, g.l.c. showed the presence of a minor component having a retention time of 0.59 and an intensity of 0.13 relative to **1**. Attempted purification by silica-gel column chromatography with various solvent systems was unsuccessful.

Anal. Calc. for $C_{12}H_{16}O_7$: C, 52.94; H, 5.92. Found: C, 53.03; H, 6.04.

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REFERENCES

1 K. Takiura and S. Honda, *Carbohyd. Res.*, 21 (1972) 379.
2 S. Honda, K. Izumi, and K. Takiura, *Carbohyd. Res.*, 23 (1972) 155.
3 A. N. Nesmeyanov, I. F. Lutsenko, and N. I. Vereschagima, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1947) 63.
4 S. Akiya and T. Osawa, *Yakugaku Zasshi*, 74 (1954) 1259.
5 H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, 61 (1939) 3102.
6 K. Meyer and F. G. Willson, *Ber.*, 47 (1914) 832.
7 N. E. Trevelyan, D. P. Procter, and J. S. Harrison, *Nature*, 166 (1950) 444.
8 J. Janson and B. Lindberg, *Acta Chem. Scand.*, 14 (1960) 877.
9 L. D. Hall and J. F. Manville, *Can. J. Chem.*, 45 (1967) 1299.