THE PRODUCTS OF THE PREVOST REACTION ON D-GLUCAL TRIACETATE

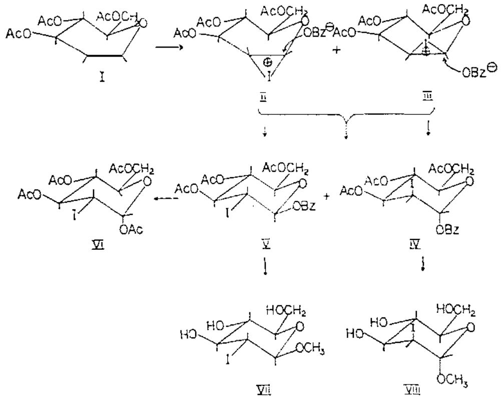
R. U. LEMIEUX[1] AND S. LEVINE[2]
Department of Chemistry, University of Ottawa, Ottawa, Ontario

Received May 7, 1962

ABSTRACT

The compound reported by Stanek and Schwarz (Collection Czechoslov. Chem. Communs. **20**, 42 (1955)) to be 1-*O*-benzoyl-2-iodo-2-deoxy-α-D-glucopyranose triacetate is actually an approximately equimolar mixture of 1-*O*-benzoyl-2-iodo-2-deoxy-β-D-glucopyranose triacetate and the stereoisomer with the α-D-manno configuration. Methanolysis of these compounds yielded methyl 2-iodo-2-deoxy-β-D-glucopyranoside and methyl 2-iodo-2-deoxy-α-D-mannopyranoside, respectively. Hydrogenolysis of the latter iodoglycosides using a palladium catalyst gave near-quantitative yields of the corresponding methyl 2-deoxy-D-glucopyranosides. Several other properties of the iodides are reported.

In 1955, Stanek and Schwarz (1) reacted D-glucal triacetate (I) with iodine and silver benzoate in dry benzene to form a substance termed 1-*O*-benzoyl-2-iodo-2-deoxy-α-D-glucopyranose triacetate, m.p. 129–130°, $[\alpha]_D^{31}$ +21.7° in chloroform. On repeating the experiment, we obtained a nicely crystalline product, $[\alpha]_D$ +25.9° in chloroform, in 96% yield. However, although the product possessed the expected iodine content, the melting point (microstage) was 123–148°.



From a mechanistic point of view, it would be anticipated that, in the first stage of the reaction, both the 1,2-iodonium ions II and III would form. These would subsequently undergo nucleophilic attack by benzoate ion to form 1,2-*trans* adducts of the D-glucal triacetate (I). The positive charge of the iodonium ions should be localized mainly at the anomeric center in view of the ability of the ring oxygen to participate in the delocalization. Certainly, for this reason, nucleophilic attack by benzoate ion should occur largely at the 1-position. It may be noted in this regard that 1,2-anhydro-α-D-glucopyranose triacetate undergoes attack exclusively at the 1-position (2). Therefore, the Prevost reaction (3) would be expected to form, from D-glucal triacetate (I), a

---

[1] *Present address: Department of Chemistry, University of Alberta, Edmonton, Alberta.*

[2] *Present address: Department of Chemistry, University of Saskatchewan, Regina Campus, Regina, Saskatchewan.*

mixture of the two 1-*O*-benzoyl-2-iodo-2-deoxyhexose triacetates IV and V. The relative amounts of these two products presumably would depend either on the relative stabilities of the transition states leading to the two iodonium ions, if these are formed essentially irreversibly in the slow stage of the reaction, or the relative stabilities of the transition states for the nucleophilic attack on the iodonium ions, if the formation of the ions is relatively rapid and reversible. There appears to be no definitive information as to which of these two stages is rate controlling.

The large melting point range that we observed for the product suggested that the substance was a mixture of the isomers IV and V. This condition was clearly substantiated by the nuclear magnetic resonance spectrum of the product, which is reported in Fig. 1. The spectra of the pure compounds are also reproduced in Fig. 1 since this application clearly illustrates the power of this relatively new physical tool in the solution of problems related to purity in the field of carbohydrate chemistry. It was at once evident from the appearance of two doublets, at 7.16 and 6.58 p.p.m., in the general region characteristic of anomeric hydrogens for 1-*O*-acyl aldoses (4) that the substance was an approximately 1:1 mixture of two isomeric compounds. The doublet at 6.58 p.p.m. has a spacing of 9.6 c.p.s. and must therefore arise from the isomer (V) with the β-gluco configuration,

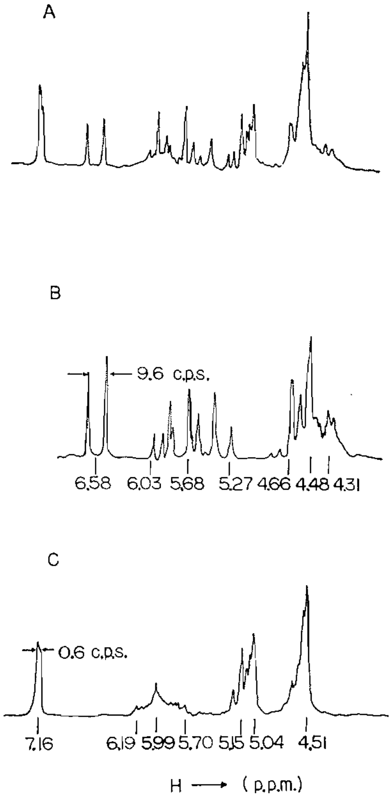


FIG. 1. The proton magnetic resonance spectra measured at 60 Mc/s in chloroform, with tetramethylsilane as an internal standard, of the products which are formed on reacting D-glucal triacetate with iodine and silver benzoate in benzene. Spectrum A is of the crude reaction product and shows that the material is an approximately equimolar mixture of the compounds whose spectra are reproduced in B and C. Spectrum B is of 1-*O*-benzoyl-2-iodo-2-deoxy-β-D-glucopyranose triacetate (V) and spectrum C is of the α-D-manno stereoisomer (IV).

wherein the 1-hydrogen is in axial orientation and 1- and 2-hydrogens define a dihedral angle of about 180°. The doublet at lower field has a spacing of only about 0.6 c.p.s. and must arise from a compound with 1- and 2-hydrogens in gauche orientation. From the above-mentioned mechanistic considerations, the signal would be expected to arise from the compound (IV) which has the α-manno configuration. Definitive evidence for this assignment of structure is given below.

A scheme for the separation of IV and V by fractional crystallization was evolved. Compound IV melted at 159.5–160° with $[\alpha]_D$ +45.3° in chloroform whereas compound V melted at 150–151.5° with $[\alpha]_D$ +2.2° in chloroform.

Evidence that compounds IV and V were not anomeric was provided by the following acetolysis and methanolysis experiments. Treatment of V with 1:1 acetic acid – acetic anhydride containing sulphuric acid to constant rotation led to the formation of a substance, m.p. 109.5–111.5°, $[\alpha]_D$ +125° in chloroform, which, in view of its rotation and the fact that the signal for the anomeric hydrogen has a half-band width of only 3 c.p.s., must be 2-iodo-2-deoxy-α-D-glucopyranose tetraacetate (VI). On the other hand, a similar acetolysis of compound IV gave a viscous oil in 91% yield with $[\alpha]_D$ +41.5°. The nuclear magnetic resonance spectrum of this oily substance showed it to be a mixture of presumably anomeric compounds devoid of the benzoate group. The signals for the anomeric hydrogens were at 6.74 and 6.30 p.p.m., whereas the position of the signal for the anomeric hydrogen in compound VI was at 6.85 p.p.m. Therefore, it is highly improbable that compounds IV and V are anomeric since, if they were, they would be expected to yield common products on acetolysis. Treatment of compound V with methanolic hydrogen chloride produced methyl 2-iodo-2-deoxy-β-D-glucopyranoside (VII), m.p. 189–189.5° and $[\alpha]_D$ +6.9° in methanol. The identity of this substance was firmly established by ammonolysis followed by acetylation to methyl 3-amino-3-deoxy-β-D-altropyranoside tetraacetate (5–7). On the other hand, methanolic hydrogen chloride converted compound IV to a methyl 2-iodo-2-deoxyglycoside, VIII, m.p. 146–147° and $[\alpha]_D$ +49.2° in methanol, in 72% yield. Ammonolysis of this compound led to deep-seated degradation without the formation of an aminoglycoside. Further evidence for the configurations of compounds IV and VIII is available from a consideration of the optical rotations shown in Table I. It is seen that there is very good agreement between the molar rotations of compounds IV and VIII and those observed for the corresponding derivatives of α-D-mannose. Although the molar rotations for the configurationally related derivatives of D-glucose do not agree nearly as well, the general agreement is sufficiently good for the present purpose of assigning configurations to the various 2-iodo-2-deoxysugar derivatives. That compounds VII and VIII are in fact 2-iodo-2-deoxyglycosides was firmly established by their hydrogenolysis in near-quantitative yield to the methyl 2-deoxy-β- and -α-D-glucopyranosides, respectively.

Stanek and Schwarz (1) prepared 2-deoxy-D-glucose in low yield by reduction of the substance now known to be a mixture of IV and V using a zinc–copper couple in methanol. We observed this reaction to lead to the formation of water-soluble substances, starting either from IV or V and using the zinc–copper couple described by Shank and Schechter (8). These contained zinc and liberated D-glucal when hydrolyzed with base. Attempts to hydrogenolyze V using a palladium-on-charcoal catalyst in the presence of diethylamine in methanol led to the consumption of 2 moles of hydrogen per mole of V. The product of the reaction was not characterized.

Both the 2-iodo-2-deoxyglycosides VII and VIII rapidly consumed sodium hydroxide. The gluco compound (VII) consumed the base about three times more rapidly than the

TABLE I

Optical rotations of derivatives of D-glucose and D-mannose

Derivative	$[\alpha]_D$	Solvent	$[M]_D$
D-Glucose			
β-D-Glucopyranose pentaacetate	+ 3.8°	$CHCl_3$	+ 1,500°
1-*O*-Benzoyl-2-iodo-2-deoxy-β-D-glucopyranose triacetate (V)	+ 2.2	"	+ 1,100
Methyl β-D-glucopyranoside	− 34.2	H_2O	− 6,600
Methyl 2-iodo-2-deoxy-β-D-glucopyranoside (VII)	+ 6.9	CH_3OH	+ 2,100
Methyl β-D-glucopyranoside tetraacetate	− 18.2	$CHCl_3$	− 6,600
Methyl 2-iodo-2-deoxy-β-D-glucopyranoside triacetate (IX)	+ 6.2	"	+ 2,700
α-D-Glucopyranose pentaacetate	+101.6	"	+39,700
2-Iodo-2-deoxy-α-D-glucopyranose tetraacetate (VI)	+125	"	+57,200
D-Mannose			
α-D-Mannopyranose pentaacetate	+ 55	"	+21,500
1-*O*-Benzoyl-2-iodo-2-deoxy-α-D-mannopyranose triacetate (IV)	+ 45.3	"	+23,600
Methyl α-D-mannopyranoside	+ 79.2	H_2O	+15,400
Methyl 2-iodo-2-deoxy-α-D-mannopyranoside (VIII)	+ 49.2	CH_3OH	+15,000
Methyl α-D-mannopyranoside tetraacetate	+ 49.1	$CHCl_3$	+17,800
Methyl 2-iodo-2-deoxy-α-D-mannopyranoside triacetate (X)	+ 44.9	"	+19,300

manno epimer (VIII), presumably because of the trans configuration of the 2,3-iodohydrin group in VII. However, 1.9 equiv of base were consumed per mole of VII and 2.9 equiv per mole of VIII. These results undoubtedly are related to elimination of the iodine to form initially 2-deoxy-3-ketoglycosides, which under the influence of the base are degraded to acidic products. These reactions are under investigation.

Small amounts of methyl 2-iodo-2-deoxy-β-D-glucopyranoside (VII) were isolated from the methanolysis of pure 1-*O*-benzoyl-2-iodo-2-deoxy-α-D-mannopyranose triacetate (IV). The formation of this compound requires dissociation of the benzoyloxy group, with participation of the iodine atom, to lead initially to a 1,2-iodonium ion. This ion must then decompose to some extent to D-glucal and positive iodine (likely either as methyl hypoiodite or iodine chloride), which recombine to form a 2,3-*trans*-iodonium ion (such as II) which can lead to the formation of VII. It is of interest to note from the point of view of neighboring iodine participation (9) that the methanolysis of V afforded only a 20% yield of VII. Since VII proved highly resistant to change under the conditions of methanolysis, it could not be the main product of the reaction.

EXPERIMENTAL

Mixture of 1-O-Benzoyl-2-iodo-2-deoxy-triacetate Derivatives of β-D-Glucopyranose and α-D-Mannopyranose

D-Glucal triacetate (10), 37.5 g (0.133 mole), was added to 30 g (0.131 mole) of silver benzoate suspended in 400 ml of dry benzene. Iodine, 36 g (0.141 mole), was added to the stirred solution and the purple color which formed after the addition of each portion disappeared almost immediately. After all the iodine had been added the mixture had a faint brown coloration. The mixture was stirred for 30 minutes at room temperature, the silver iodide was collected by filtration, and the filter cake washed with benzene. The combined filtrates were washed with sodium thiosulphate and sodium bicarbonate and finally with water. The benzene was removed *in vacuo* to leave 65.4 g (96%) of a crystalline residue; m.p. 123–148°, $[\alpha]_D$ +25.9° (*c*, 2.0 in chloroform). A study of the solubility properties of the components of the mixture led to the following scheme for their separation by fractional crystallization.

1-O-Benzoyl-2-iodo-2-deoxy-β-D-glucopyranoside Triacetate (V)

The above-mentioned crystalline mixture, 50 g, was dissolved in 75 ml of acetone, and 150 ml of cyclohexane was added. There was obtained 6.13 g of crystals, $[\alpha]_D$ +7.1° (*c*, 2.1 in chloroform), and mother liquor A. After two recrystallizations from methanol there remained 4.70 g of white crystals, $[\alpha]_D$ +2.2 (*c*, 1.9 in chloroform), with a transition beginning at 145°. When the melting point was determined at a sufficiently slow rate to allow completion of the transition, the melting point was 150–151.5°. Further recrystallization from either methanol or ethanol did not change the melting point or rotation. The n.m.r. spectrum (Fig. 1B) showed the presence of only one type of anomeric hydrogen.

In the presence of onefold excess of sodium hydroxide in 50% aqueous dioxane at 0°, compound V consumed within 60 minutes 5 equiv of base per mole with the liberation of 1 mole-equiv of iodide ion.

Anal. Calc. for $C_{19}H_{21}O_9I$: C, 43.86; H, 4.07; I, 24.40. Found: C, 43.61; H, 4.34; I, 24.71.

1-O-Benzoyl-2-iodo-2-deoxy-α-D-mannopyranose Triacetate (IV)

The crystalline residue obtained after evaporation of solvent from mother liquor A was dissolved in 350 ml of benzene, and 700 ml of 30–60° petroleum ether was added. Crystals, 9.84 g, were deposited, $[\alpha]_D$ +43.1° (*c*, 1.8 in chloroform), in mother liquor B. One recrystallization from methanol gave 7.43 g of large white crystals, $[\alpha]_D$ +45.3° (*c*, 2 in chloroform), m.p. 157–160° with a transition at about 150°. After the transition was complete, the melting point was 159.5–160°. The melting point and rotation were not changed by further recrystallization either from methanol or ethanol. The n.m.r. spectrum of the product (Fig. 1) showed the presence of only one type of anomeric hydrogen.

In the presence of a onefold excess of sodium hydroxide in 50% aqueous dioxane at 0° compound IV consumed within 40 minutes 6 equiv of base per mole with the liberation of 1 mole equiv of iodide ion. It is apparent that the elimination of the iodine atom led to the formation of acidic products.

Anal. Calc. for $C_{19}H_{21}O_9I$: C, 43.86; H, 4.07; I, 24.40. Found: C, 44.13; H, 3.96; I, 24.00.

Evaporation of mother liquor B left a crystalline residue with a composition approximately that of the original reaction product. The fractional crystallization was continued until 9.28 g of mixture remained. It was not possible to obtain a further yield from this residue. The total yields of 1-*O*-benzoyl-2-iodo-2-deoxy-β-D-glucopyranose triacetate and 1-*O*-benzoyl-2-iodo-2-deoxy-α-D-mannopyranose triacetate were 14.3 and 20.9 g, respectively.

Methyl-2-iodo-2-deoxy-β-D-glucopyranoside (VII)

A solution of 10 g (0.0192 mole) of 1-*O*-benzoyl-2-iodo-2-deoxy-β-D-glucopyranose triacetate in 400 ml of 2% methanolic hydrogen chloride was allowed to stand at room temperature until it had attained constant rotation (6 hours). The solution was then neutralized with silver carbonate and, after filtration, hydrogen sulphide was used to remove silver ion. After removal of the methanol, an aqueous solution of the residue was decolorized using charcoal and then evaporated to 5.61 g of viscous oil. Crystallization from ethyl acetate gave 1.19 g (20%) of a crystalline solid, m.p. 189–189.5°, $[\alpha]_D$ +6.9° (*c*, 2.1 in methanol).

Anal. Calc. for $C_7H_{13}O_5I$: C, 27.65; H, 4.31; I, 41.74. Found: C, 27.74; H, 4.53; I, 41.22.

All attempts to isolate crystalline methyl 2-iodo-2-deoxy-α-D-glucopyranoside from the mother liquors were unsuccessful.

Acetylation of VII in the usual manner using acetic anhydride and pyridine provided a near-quantitative yield of methyl 2-iodo-2-deoxy-β-D-glucopyranoside triacetate (IX), m.p. 85–86°, $[\alpha]_D$ +6.2° (*c*, 1.3 in chloroform).

Anal. Calc. for $C_{13}H_{19}O_8I$: C, 36.29; H, 4.45; I, 29.50. Found: C, 36.18; H, 4.69; I, 29.18.

In the presence of a 50% excess of aqueous sodium hydroxide at room temperature, compound VII consumed within 20 hours 1.88 milliequiv of base per mole with the liberation of 1 mole equiv of iodide ion.

Methyl 2-Iodo-2-deoxy-α-D-mannopyranoside (VIII)

Treatment of 1-*O*-benzoyl-2-iodo-2-deoxy-α-D-mannopyranose triacetate (IV) under the same conditions mentioned above for the gluco isomer led to the isolation of a compound, m.p. 145–146°, $[\alpha]_D$ +49.2° (*c*, 1 in methanol).

Calc. for $C_7H_{13}O_5I$: C, 43.86; H, 4.07; I, 24.40%. Found: C, 44.13; H, 3.96; I, 24.00%.

Acetylation of VIII in the usual manner using acetic anhydride and pyridine gave a product (X), $[\alpha]_D$ +44.9° in chloroform, which failed to crystallize. The nuclear magnetic spectrum left no doubt that the compound was essentially pure.

In the presence of a 50% excess of aqueous sodium hydroxide, compound VIII consumed within 40 hours at room temperature 3 equiv per mole with the liberation of 1 mole equiv of iodide ion.

2-Iodo-2-deoxy-α-D-glucopyranose Tetraacetate (VI)

A solution of 0.269 g (0.5 mmole) 1-*O*-benzoyl-2-iodo-2-deoxy-β-D-glucopyranose triacetate in 2 ml of 1:1 acetic anhydride – acetic acid was added to 0.256 g of 95.5% sulphuric acid in 2 ml of the acetic anhydride – acetic acid. After mixing, the volume was adjusted to 5 ml with the 1:1 acetic acid – acetic anhydride mixture to yield a solution 0.5 *M* in sulphuric acid and 0.1 *M* in the glucose derivative. The observed optical rotation in a 2-dm tube of the solution reached a constant value of 13.5° after 15 minutes at room temperature. After standing for 25 minutes, the product was isolated in the usual manner. An oil, 0.20 g (87%), was obtained which crystallized after trituration with 30–60° petroleum ether. Recrystallization from benzene – petroleum ether gave 0.12 g of material; m.p. 109.5–111.5° $[\alpha]_D$ +125° (*c*, 1.7 in chloroform).

Anal. Calc. for $C_{14}H_{19}O_9I$: C, 36.69; H, 4.18; I, 27.70. Found: C, 36.50; H, 3.99; I, 27.82.

Acetolysis of 1-O-Benzoyl-2-iodo-2-deoxy-α-D-mannopyranose Triacetate

The acetolysis was carried out in exactly the same manner as for 1-*O*-benzoyl-2-iodo-2-deoxy-β-D-glucopyranose triacetate. The specific rotation of the solution reached a minimum observed value of 1.47° (using a 2-dm tube) after standing the solution 9 minutes at room temperature and remained at this value for about 42 minutes. The observed rotation of the solution then rose to a constant value of 4.5°. The product, 0.21 g (91%) of a viscous oil, $[\alpha]_D$ +41.5° (*c*, 1.7 in chloroform), was isolated in the usual manner. The nuclear magnetic resonance spectrum showed two signals of about equal intensity in the region characteristic of anomeric hydrogens for this type of compound. One signal was in the form of a singlet at 6.74 p.p.m. and the other a doublet at 6.30 p.p.m. with a spacing of 8.5 c.p.s. The intensities of these signals were considerably lower than expected and it seems likely, therefore, that the reaction was not restricted to replacement of the benzoyloxy group by acetoxy group.

Methyl 3-Acetamido-3-deoxy-β-D-altropyranoside Triacetate

Methyl 2-iodo-2-deoxy-β-D-glucopyranoside, 0.20 g (0.66 mmole), was dissolved in 2.5 ml of dry methanol saturated with ammonia and the solution, in a sealed tube, was heated for 6 hours at 120°. The methanol and ammonia were removed and the residue was dissolved in water. After treatment with silver carbonate and then with hydrogen sulphide, the aqueous solution was decolorized with charcoal. Evaporation of the water *in vacuo* left 0.11 g of a deliquescent white powder, which was acetylated using 1 ml of pyridine and 0.7 ml of acetic anhydride for 22 hours. The product, 0.19 g of a light yellow oil, was isolated in the usual manner and dissolved in a small amount of absolute ethanol. After standing at 4° for 19 hours there was deposited 0.16 g (65%) of a crystalline material, m.p. 189.5–190°, $[\alpha]_D$ −123° (*c*, 1.1 in chloroform), −149° (*c*, 1.2 in methanol). The reported (5–7) physical constants for methyl 3-acetamido-3-deoxy-β-D-altropyranoside triacetate are: m.p. 188°, $[\alpha]_D$ −119° (chloroform).

Anal. Calc. for $C_{15}H_{23}O_9N$: C, 49.86; H, 6.42. Found: C, 50.04; H, 6.51.

Methyl 2-Deoxy-β-D-glucopyranoside

A solution of 0.303 g (1 mmole) of methyl 2-iodo-2-deoxy-β-D-glucopyranoside (VII) and 0.148 (2.04 mmoles) of diethylamine in 10 ml of water was hydrogenated at room temperature and pressure using 0.035 g of palladium on charcoal as catalyst. The theoretical amount of hydrogen was taken up in 16 minutes. After 30 minutes, the catalyst was removed by filtration and the filtrate was treated with silver carbonate to remove iodide ion and then with hydrogen sulphide to remove silver ion. After evaporation of the water and diethylamine *in vacuo* an aqueous solution of the residue was decolorized with charcoal. Evaporation of the water left 0.15 g (84%) of crystalline material which, after recrystallization from ethyl acetate, melted at 121.5–122°, $[\alpha]_D$ −46.9° (*c*, 1.0 water). The physical constants reported (11) for methyl 2-deoxy-β-D-glucopyranoside are: m.p. 122–123°, $[\alpha]_D$ −48.4° (water).

Methyl 2-Deoxy-β-D-glucopyranoside Triacetate

A solution of 0.10 g of methyl 2-deoxy-β-D-glucopyranoside in 0.7 ml of pyridine and 0.5 ml of acetic anhydride was allowed to stand for 18 hours at 4°. The product, 0.17 g of crystalline material, was isolated in the usual manner. After recrystallization from ether – 30–60° petroleum ether, the material melted at 97–99°, $[\alpha]_D$ −34.8° (*c*, 0.9 in chloroform). Methyl 2-deoxy-β-D-glucopyranoside triacetate is reported (5) to melt at 96–97°, $[\alpha]_D$ −30.2° (tetrachloroethane).

Methyl 2-Deoxy-α-D-glucopyranoside

Hydrogenation of 0.303 g (1 mmole) of methyl 2-iodo-2-deoxy-α-D-mannopyranoside (VIII) and purification of the product in the same manner as described above for the β-anomer gave 0.16 g (89%) of material which was recrystallized from ethyl acetate. The substance melted at 93.5–94.5°, $[\alpha]_D$ +143° (*c*, 0.9 in methanol). Methyl 2-deoxy-α-D-glucopyranoside is reported (11) to melt at 92–93°, $[\alpha]_D$ +145° (*c*, 0.8 in methanol). The tri-*O*-acetyl derivative failed to crystallize.

Reductions with Zinc–Copper Couple

1-*O*-Benzoyl-2-iodo-2-deoxy-β-D-glucose triacetate (0.15 g) was dissolved in 6.5 ml of absolute methanol, and 0.7 g of zinc–copper couple (8) was added. The mixture was stirred for 8 hours at room temperature. After filtration, the filtrate was evaporated to dryness *in vacuo* and the residue was taken up in chloroform. Evaporation of the clarified chloroform solution left 0.15 g of a white, semicrystalline, waxy solid which gave a strong positive test for zinc. The material, which was partially soluble in water and gave an immediate precipitate with silver nitrate, was suspended in water and titrated with aqueous sodium hydroxide. One equivalent of base per molecular weight of starting material was rapidly consumed. A further equivalent of base was consumed slightly less rapidly. A non-combustible precipitate was formed, which likely was zinc oxide. Filtration and evaporation *in vacuo* left a residue which was acetylated with pyridine and acetic anhydride. A 74% yield of a substance characterized as D-glucal triacetate (mixed melting point and infrared spectra) was obtained.

A similar reduction of 1-*O*-benzoyl-2-iodo-2-deoxy-α-D-mannopyranose triacetate gave a 79% yield of D-glucal triacetate.

ACKNOWLEDGMENTS

The authors wish to thank the Bristol Laboratories Incorporated and the National Research Council of Canada for the financial support of this research through grants to R. U. L. The nuclear magnetic resonance spectra were determined by Mrs. A. Westland and the microanalyses were conducted by Miss E. Busk of these laboratories.

REFERENCES

1. J. Stanek and V. Schwarz. Collection Czechoslov. Chem. Communs. **20**, 42 (1955).
2. R. U. Lemieux and G. Huber. J. Am. Chem. Soc. **78**, 4117 (1956).
3. C. Prevost. Compt. rend. **196**, 1129 (1933).
4. R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider. J. Am. Chem. Soc. **80**, 6098 (1958).
5. E. Fischer, M. Bergmann, and H. Schotte. Ber. B, **53**, 509 (1920).
6. E. W. Bodycote, W. N. Haworth, and E. L. Hirst. J. Chem. Soc. 151 (1934).
7. W. N. Haworth, W. H. G. Lake, and S. Peat. J. Chem. Soc. 271 (1939).
8. R. S. Shank and H. Schechter. J. Org. Chem. **24**, 1825 (1959).
9. S. Winstein, E. Grunwald, and L. L. Ingraham. J. Am. Chem. Soc. **70**, 821 (1948).
10. W. W. Pigman and H. S. Isbell. J. Research Natl. Bur. Standards, **19**, 204 (1937).
11. F. Shafizadeh and M. Stacey. J. Chem. Soc. 3609 (1952).