the pH was adjusted to 7.0. Magnesium sulfate (5 λ of a 1 *M* solution) and 0.1 mg. of crystalline ribonuclease were added. The pH was adjusted from time to time as required. After 6 hr., the whole sample was streaked on Whatman 3 MM paper which was developed in solvent A. Each of the (3′→5′)-linked isomers was completely degraded to uridylic acid and the free nucleoside.

Acknowledgment.—The authors wish to thank the Cancer Chemotherapy National Service Center, U. S. Public Health Service, for a generous gift of 6-thionosine. This research was supported in part by a grant (CA-05697) from the U. S. Public Health Service.

Neighboring Group Participation in the Elimination of the Exocyclic Secondary *p*-Tolylsulfonyloxy Group in D-Glucofuranose Derivatives[1,2]

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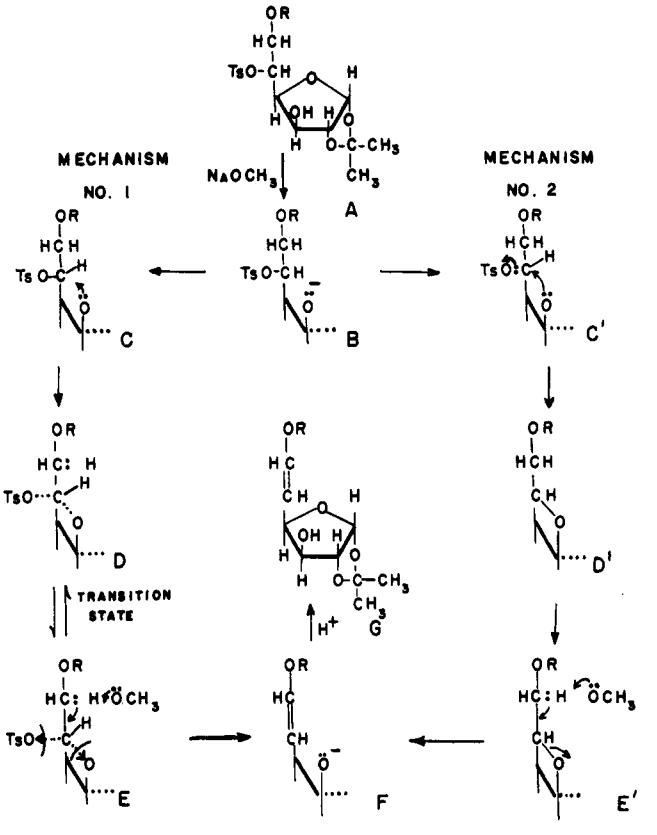
Received October 21, 1963

Base-catalyzed elimination of the exocyclic secondary tosyloxy group in a D-glucofuranose structure is dependent on the participation of a neighboring alkoxide group. Model tosylated D-glucofuranose derivatives with a stereochemical configuration similar to 6-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose are synthesized and treated with sodium methoxide to substantiate an anchimeric assistance in desulfonyloxylation. Tosyloxy elimination is always accompanied by β-proton elimination, with subsequent formation of 5-deoxy-α-D-*xylo*-hexofuran-5-enose derivatives when specific 5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose derivatives contain a free C-3 hydroxyl group. Since increased yield of olefin is observed when the sodium methoxide concentration is raised from 1 to 4 moles per mole of tosylate, it is suggested that tosyloxy elimination is dependent on the concentration of an ionized C-3 hydroxyl group, and that protonization of the β-hydrogen with subsequent formation of olefin is dependent on the concentration of methoxide ion.

Desulfonyloxylation and β-elimination of 6-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (V) in the presence of sodium methoxide, with subsequent formation of 6-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose (XI) has been recently reported.[3] This reaction reveals that, although the stereochemical configuration of V would seem to permit a 3,5-anhydro ring, olefin formation is dominant. This elimination of an exocyclic secondary tosyloxy group, as observed in a selected series of D-glucofuranose derivatives, is now examined in greater detail and two mechanisms for a β-proton elimination in the formation of olefins are proposed (see col. 2).

Four pairs of 5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose derivatives, all of which contain an alkali stable R group substituted for the hydrogen on the C-6 hydroxyl group, were synthesized. One derivative in each pair has its C-3 hydroxyl group protected with an alkali stable R group. Each compound was treated with sodium methoxide, and the products were characterized. A scheme for the synthesis of compounds I to VIII (Table I) is as follows. Unimolar tosylation of 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[4] gave 6-deoxy-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (I). The catalytic hydrogenation of 5,6-anhydro-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose[5] and subsequent tosylation furnished 6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (II). Treatment of 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose[6] with sodium methoxide, followed by a monotosylation of the product[7]



therefrom, furnished 1,2-*O*-isopropylidene-6-*O*-methyl-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (III). The reaction of 5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[4] with sodium methoxide and subsequent tosylation of the product obtained produced 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*O*-methyl-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (IV). A preparation for the compound which initiated the study of olefin formation, namely 6-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (V), is described in an earlier paper.[3] When 5,6-anhydro-3-*O*-benzyl-1,2-*O*-

(1) Journal Paper No. 2237 of the Purdue University Agricultural Experiment Station.

(2) Presented before the Division of Carbohydrate Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(3) R. E. Gramera, T. R. Ingle, and R. L. Whistler, *J. Org. Chem.*, **29**, 878 (1964).

(4) A. S. Meyer and T. Reichstein, *Helv. Chim. Acta*, **29**, 152 (1946).

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isopropylidene-α-D-glucofuranose[4] was treated with sodium benzyl alkoxide and the product obtained was tosylated, 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (VI) was produced. Tosylation of 3-*O*-acetyl-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-α-D-glucofuranose[8] afforded 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-6-*O*-triphenylmethyl-α-D-glucofuranose (VII). A synthesis of 3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-6-*O*-triphenylmethyl-α-D-glucofuranose (VIII) is described.[9]

Products obtained when compounds I, III, V, and VII were treated with sodium methoxide under experimental conditions usually adopted for anhydro ring formation are identified as 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose (IX), 5-deoxy-1,2-*O*-isopropylidene-6-*O*-methyl-α-D-*xylo*-hexofuran-5-enose (X), 6-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose (XI), and 5-deoxy-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-α-D-*xylo*-hexofuran-5-enose (XII), respectively (Table I).

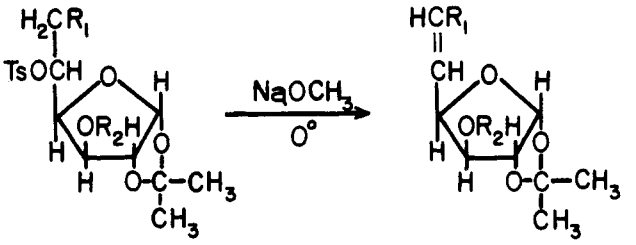
Structural identity of olefin IX was made by comparison with a known compound.[10] Isolation and identification of 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose,[11] after a reductive ozonolysis of olefins X, XI,[3] and XII, showed that the position of the double bond in the above-mentioned compounds is between C-5 and C-6.

Maximum yield of olefins IX, X, XI, and XII was obtained when the concentration of sodium methoxide in the base-catalyzed elimination reaction was increased from 1 to 4 moles per mole of tosylate. This observation suggests that a sufficiently ionized C-3 hydroxyl group is necessary to facilitate tosyloxy elimination, and that protonization of the β-hydrogen in the formation of an olefin is dependent on the concentration of methoxide ion. A decrease in the yield of olefin formation in systems containing less than 3 moles of sodium methoxide per mole of tosylate is undoubtedly due in part to a repressed ionization of the C-3 hydroxyl group in the chloroform–sodium methoxide system. For example, if dimethylformamide (DMF) is substituted for chloroform, olefin formation in near quantitative yield is complete in a very short time, even when a lower sodium methoxide concentration is employed. The results obtained in DMF can best be explained by an increased ionization of the C-3 hydroxyl group.

Compounds II, IV, VI, and VIII, when treated with sodium methoxide at 0°, gave mostly unchanged starting compound, a small amount of detosylated material, but no detectable olefin. Isolation of sodium *p*-tolylsulfinate supports a detosylation rather than desulfonyloxylation of the reacted compounds.

Two mechanisms, both of which indicate that desulfonyloxylation is facilitated by a neighboring C-3 alkoxy anion, can explain β-proton elimination with the formation of olefin. Mechanism 1 suggests that ionization of the C-3 hydroxyl group is necessary to facilitate an anchimeric assistance in tosyloxy elimination. The stereochemistry and nucleophilicity of the alkoxy anion

TABLE I



MODEL COMPOUNDS		OLEFINS
I	R_1 = H, R_2 = H	IX
II	R_1 = H, R_2 = CH_3	No Olefin
III	R_1 = OCH_3, R_2 = H	X
IV	R_1 = OCH_3, R_2 = $CH_2Ø$	No Olefin
V	R_1 = $OCH_2Ø$, R_2 = H	XI
VI	R_1 = $OCH_2Ø$, R_2 = $CH_2Ø$	No Olefin
VII	R_1 = $OC(Ø)_3$, R_2 = CO CH_3	XII
VIII	R_1 = $OC(Ø)_3$, R_2 = $CH_2Ø$	No Olefin

B allows an intramolecular approach of the latter, illustrated in C, to displace the tosyloxy group. However, prior to displacement, delocalization of electron density between the tosyloxy group and C-5 would be necessary, since partial bond breaking (TsO. . . .C_5) and partial bond forming (C-3. . . .O. . . .C-5) are visualized in the transition state of an S_N2 reaction.[12] It is quite conceivable that at the moment the tosyloxy bond is weakening and the 3,5-anhydro ring is forming, a β-proton is eliminated *via* an E2 mechanism. A transition state D ⇋ E in all probability is of such a nature that an anchimeric-assisted desulfonyloxylation and β-proton elimination occur in a synchronous process. The olefinic anion F picks up a proton and gives olefin G.

If mechanism 1 is operative, protonization of the β-hydrogen occurs, or is facilitated to a greater extent, while the tosyloxy carbon bond is weakening and the 3,5-anhydro ring is forming. If D ⇋ E is an acceptable transition state, it can be postulated that greater stabilization of the system may be achieved when a β-proton is eliminated rather than combined; for, if recombination of the β-proton and subsequent formation of a 3,5-anhydro ring requires more energy, or is a less stable system than transition state D ⇋ E, olefin formation would predominate.

The possibility of an initial desulfonyloxylation followed by the formation of a 3,5-anhydro intermediate,

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(10) T. E. Whiteley (Ohio State University, Columbus), University Microfilms, Ann Arbor, Mich., L. C. Card No. Mic. 60-6419, 122 pp.; *Dissertation Abstr.*, **21**, 2121 (1961).

(11) K. Iwadare, *Bull. Chem. Soc. Japan*, **16**, 40 (1941).

(12) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

which in turn loses a β-proton to give the respective olefin, is suggested in mechanism 2. Here again, as in mechanism 1, formation of the alkoxy anion B is necessary in order to initiate the reaction. In contrast to mechanism 1, however, mechanism 2 shows that the alkoxy anion C′ actually displaces the tosyloxy group to give the 3,5-anhydro intermediate D′. Elimination of a β-proton in E′ results in the formation of anion F. Anion F picks up a proton to give olefin G.

Formation of a 3,5-anhydro intermediate illustrated in mechanism 2 is suggested, since the products obtained after hydrazinolysis[13] and subsequent hydrogenolysis of V are identified as 5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose and two amino sugars, none of which are identical with 5-amino-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose.[8] Isolation of the deoxy sugar as the major product proves that olefin formation during hydrazinolysis of V is the dominant reaction. The significant observation that two different amino sugars are produced suggests that a 3,5-anhydro ring is formed during hydrazinolysis, and nucleophilic substitution on the ring at C-3 or C-5 by hydrazine takes place.

One of the amino sugars obtained in higher yields is identified as 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose,[14] while the other sugar is thought to be the 3-amino-3-deoxy-L-talose derivative. Since the solvent, hydrazine, acts as the proton acceptor as well as the nucleophile, it is not surprising that substitution of an anhydro intermediate occurs.

When an attempt was made to trap the proposed oxetane intermediate by treating V with sodium azide in boiling methanol, unchanged starting material was recovered. This indicates that, although the nucleophilicity of the azide ion would have been sufficient to open an oxetane ring, the basicity of the reaction medium is insufficient to promote significant ionization of the C-3 hydroxyl group, the latter of which is necessary in facilitating desulfonyloxylation. This experiment supports the theory that an ionized C-3 hydroxyl group is necessary to initiate the olefin-forming reaction.

If mechanism 2 is operative, elimination of a β-proton from intermediate D′ with subsequent formation of an olefin, rather than a nucleophilic substitution on the ring of D′ by methoxide ion, can be explained by consideration of the experimental conditions used in this work for base catalysis. It is known[15] that bimolecular elimination is usually facilitated at the expense of substitution, especially when there is extensive branching at either α- or β-carbons (as would be the case of a 3,5-anhydro intermediate D′), using strong bases at high concentrations, and when the reaction is conducted in an aprotic, nonpolar solvent. Since these conditions would exist in a chloroform–sodium methoxide system, β-elimination is not unexpected. On the other hand, if intermediate D′ is in a high energy state or strained, elimination of a β-proton may reduce the energy, or increase stability of the system by formation of an olefin.

Although mechanisms 1 and 2 illustrate slightly different views in the elimination of a β-proton, the experimental facts prove that desulfonyloxylation of the D-glucofuranose structures studied requires the assistance of a neighboring C-3 alkoxy anion.

(13) R. E. Gramera and R. L. Whistler, unpublished results.

(14) R. L. Whistler and R. E. Gramera, *J. Org. Chem.*, in press.

(15) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 472.

Experimental

Analytical Methods.—Variance in the proportion of products formed during the course of the base-catalyzed elimination reaction was followed by thin layer chromatography on 1 × 3 in. silica gel G[16] coated glass plates, irrigated with A, chloroform–acetone (1:1 v./v.), and B, 1-butanol saturated with water. Plates were sprayed with a dilute ethanolic solution containing 5% sulfuric acid and charred at 110° until permanent spots developed. Chromatographic separations and identification of sugar derivatives were performed at 25° on Whatman No. 1 filter paper developed in irrigants C, 1-butanol–ethanol–water (40:11:19 v./v.), and D, ethyl acetate–pyridine–water (10:4:3 v./v.). Indicators consisted of E, potassium permanganate–periodate spray reagent, and F, iodine vapor. Evaporations were done at reduced pressure and reported melting points were obtained on a calibrated Fisher-Johns apparatus.

5,6-Dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose (IX).—A solution containing 3 g. of 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[4] dissolved in 10 ml. of pyridine was cooled with stirring to −5°. A one-half portion of 3.0 g. of tosyl chloride (*p*-toluenesulfonyl chloride) was added to the solution over a period of 2 hr. After maintaining the solution at 25° for 5 hr., it was cooled again to −5°, and the remaining half portion of tosyl chloride was added as before. After an additional 10 hr. at 25°, the reaction mixture was treated with ice and stirred for 0.5 hr., after which 10 ml. of chloroform was added and the total mixture was poured into ice–water. The chloroform layer was washed sequentially with water, an ice-cold solution of dilute hydrochloric acid until slightly acidic (pH 4.0), and an aqueous solution of sodium bicarbonate until neutral. After several washings with water, the chloroform layer was dried over anhydrous sodium sulfate, filtered, and evaporated below 40° to a sirup (3.7 g.) which contained 6-deoxy-5-*O*-*p*-tolylsulfonyl-1,2-*O*-isopropylidene-α-D-glucofuranose (I). A 2-g. portion of the sirupy product containing I was dissolved in 15 ml. of alcohol-free chloroform, The mixture was cooled to 0°, and 8 ml. of a methanolic solution containing 12.5% of sodium methylate was added. The solution was stirred at 0° for 1 hr. and then at 25° for an additional 16 hr. After the addition of a saturated solution of potassium bicarbonate, the mixture was evaporated to remove methanol. The residue was extracted six times with 25-ml. portions of chloroform; the latter was dried over anhydrous sodium sulfate and evaporated to a sirup which absorbed bromine from a bromine–carbon tetrachloride solution and instantaneously decolorized a solution of potassium permanganate. Examination of this sirup by thin layer chromatography in irrigants A and B revealed that the major component, IX, migrated the same as the known compound recorded in the literature.[10] After compound IX was isolated from paper chromatograms, it crystallized from petroleum either (b.p. 40–60°), m.p. 64°, $[\alpha]^{25}D$ −60.5° (*c* 2.0, water); the melting point remained undepressed when admixed with an authentic sample.

6-Deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (II).—Three grams of 6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose[5] was dissolved in 10 ml. of dry pyridine to which was added 8 ml. of alcohol-free chloroform containing 3 g. of tosyl chloride. After the reaction mixture was maintained at 37° for 3 days, it was cooled to 0° and 2 ml. of water were added to hydrolyze excess tosyl chloride. Within 0.5 hr. the solution was poured into 100 ml. of ice–water and 20 ml. of chloroform then was added. The aqueous layer was drawn off, extracted twice with chloroform, and the combined organic layer was washed free of pyridine with several portions of a cold dilute solution of hydrochloric acid to pH 4.0. The organic extract was neutralized with a dilute solution of sodium bicarbonate, washed free of salts, and dried over anhydrous magnesium sulfate. After filtration and evaporation a light yellow sirup (4.93 g.) was obtained, $[\alpha]^{25}D$ −25.1° (*c* 1.84, chloroform). Thin layer chromatograms of II showed the material was essentially pure. A 500-mg. portion of II was chromatographed on alumina and sequentially eluted with a mixture of benzene–petroleum ether of increasing benzene concentration. A main

(16) Brinkman Instruments, Inc., Great Neck, L. I., N. Y.

fraction (376 mg.) was chromatographically pure but could not be induced to crystallize, $[\alpha]^{25}D$ −21.5° (*c* 2.0, chloroform).

Anal. Calcd. for $C_{17}H_{24}O_7S$ (372.41): OCH_3, 11.56; S, 8.61. Found: OCH_3, 11.28; S, 8.47.

5-Deoxy-1,2-*O*-isopropylidene-6-*O*-methyl-α-D-*xylo*-hexofuran-5-enose (X).—Unimolar tosylation of 10.6 g. of pure distilled 1,2-*O*-isopropylidene-6-*O*-methyl-α-D-glucofuranose,[7] b.p. 148–150° (0.04 mm.), $[\alpha]^{25}D$ −6.0° (*c* 2.3, chloroform), was performed by the method described for I. A sirupy product (12 g.) obtained after tosylation, containing 1,2-*O*-isopropylidene-6-*O*-methyl-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (III), was treated with sodium methoxide by the procedure given for I. A crystalline product obtained from the base catalysis of II was identified as X, 2.3-g. yield, m.p. 112.5°, $[\alpha]^{25}D$ −171° (*c* 0.75 g., chloroform). Chromatography of X in irrigants C and D when sprayed with indicator E or subjected to indicator F revealed a single component. Compound X instantaneously decolorized a solution of potassium permanganate and absorbed bromine from a bromine–carbon tetrachloride solution.

Anal. Calcd. for $C_{10}H_{16}O_5$ (216.23): C, 55.53; H, 7.45; OCH_3, 14.35. Found: C, 55.30; H, 7.34; OCH_3, 14.24.

3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-methyl-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (IV).—Eight grams of 5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[4] was dissolved in 125 ml. of absolute methanol containing 0.75 g. of sodium. After 3 days at 30°, the reaction mixture was cooled to 5°, neutralized with a dilute solution of sulfuric acid, filtered, and evaporated to remove methanol. The remaining residue was extracted with chloroform; the latter was washed with water and concentrated to a sirup which was subjected to high vacuum distillation. Pure distilled 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*O*-methyl-α-D-glucofuranose [3.55 g., b.p. 170–172° (0.02 mm.), $[\alpha]^{25}D$ −40.4° (*c* 2.0, chloroform), methoxyl, 9.46%] was obtained and 3 g. was tosylated by the conditions described for II. Compound IV was obtained as a light yellow sirup which on thin layer chromatography in irrigants A or B migrated as a single component to yield 4.36 g., $[\alpha]^{25}D$ −14.5° (*c* 2.0, in chloroform).

Anal. Calcd. for $C_{24}H_{30}O_8S$ (478.33): OCH_3, 6.48; S, 6.70. Found: OCH_3, 6.21; S, 6.53.

6-*O*-Benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose (XI).—Preparation of XI by base catalysis of 6-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (V) was described in an earlier paper.[3]

3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-glucofuranose (VI).—In 200 ml. of a cooled, continuously stirred solution of benzyl alcohol which contained 1.7 g. of sodium, 15 g. of 5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[4] was dissolved. After the reaction was maintained at 25° for 3 days, it was slowly neutralized with a chilled dilute solution of sulfuric acid. Sodium sulfate was filtered from solution and washed with two 10-ml. portions of benzyl alcohol. The combined washings and filtrate were extracted with two 25-ml. portions of water and then dried over anhydrous magnesium sulfate. After filtration, the excess benzyl alcohol was removed by high vacuum distillation. A 5-g. portion of the remaining residue was subjected to high vacuum distillation from which 3.2 g. of a colorless sirup, namely, 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose, was obtained, b.p. 170–175° (0.02 mm.), $[\alpha]^{25}D$ −42.6° (*c* 1.5, chloroform). After 3 g. of the benzylated derivative was tosylated by the method described for II, compound VI was obtained as a light yellowish sirup in a 3.95-g. yield, $[\alpha]^{25}D$ −14.1° (*c* 2.0, chloroform). A 250-mg. portion of VI was chromatographed on alumina by the procedure described for II. The main fraction (186 mg.) migrated as a single component when examined by thin layer chromatography in irrigants A or B, but could not be induced to crystallize.

Anal. Calcd. for $C_{30}H_{34}O_8S$ (554.63): S, 5.78. Found: S, 5.64.

5-Deoxy-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-α-D-*xylo*-hexofuran-5-enose (XII).—Tosylation of 12 g. of 3-*O*-acetyl-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-α-D-glucofuranose[8] by the usual method gave amorphous 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-6-*O*-triphenylmethyl-α-D-glucofuranose (VII) in 14.7-g. yield, $[\alpha]^{25}D$ −21.4° (*c* 1.8 g., chloroform). When 2 g. of VII was treated with sodium methoxide by the method described for I, a crystalline product identified as XII was obtained from a mixture of benzene and petroleum ether in a 1.86-g. yield, m.p. 83°, $[\alpha]^{25}D$ −15.4° (*c* 1.4 g., chloroform). Chromatography of XII in irrigants C and D revealed a single component. Compound XII decolorized a solution of potassium permanganate and absorbed bromine from a bromine–carbon tetrachloride solution.

Anal. Calcd. for $C_{28}H_{28}O_5$ (444.30): C, 75.66; H, 6.34. Found: C, 75.38; H, 6.42.

3-*O*-Benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-6-*O*-triphenylmethyl-α-D-glucofuranose (VIII).—A procedure for the preparation of VII has been described in an earlier paper.[14]

Reaction of II, IV, VI, and VIII with Sodium Methoxide.—Experimental conditions employed for the base catalysis of compounds I, III, V, and VII were applied to compounds II, IV, VI, and VIII. Thin layer chromatography of the reaction products indicated that mostly starting compound and some detosylated product were produced. Olefin was not detected in any of the reaction products when the usual tests for unsaturation were employed. A small amount of sodium *p*-tolylsulfinate was isolated as a by-product in these reactions.

Reductive Ozonolysis of X and XII.—Compounds X and XII, when subjected to reductive ozonolysis by a specific procedure described in a recent paper,[3] gave sirupy 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose,[11] which was converted to its crystalline hydrazone,[11,17] m.p. 141°, $[\alpha]^{25}D$ −42° (*c* 2.0, chloroform). Nucleation of aged sirupy 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose with an authentic sample of it's crystalline dimer[18] gave bis(1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose)-5,5′:3′,5 cyclic acetal, m.p. 183°.

Acknowledgment.—The authors wish to thank Robert Schaffer of the National Bureau of Standards for seed crystals of bis(1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose)-5,5′:3′,5 cyclic acetal. This work was supported in part by a grant from the U. S. Department of Health, Education, and Welfare.

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