1,4-Anhydro-D-iditol.—The material eluted from Florisil with methanol (2.13 g.) was hydrolyzed in aqueous acetic acid and then in aqueous base. After deionization, 1.6 g. of material was obtained which was crystallized twice from isopropyl alcohol to give 800 mg. of material with m.p. 94–95°, $[\alpha]^{25}D$ +17.9° (*c* 3.5, water). Le Maistre[32] has reported m.p. 95–96° and $[\alpha]^{25}D$ −17.7° for the L compound.

Anal. Calcd. for $C_6H_{12}O_5$ (164.16): C, 43.90; H, 7.37. Found: C, 44.00; H, 7.60.

1,4-Anhydro-D-galactitol and 1,4-Anhydro-D-talitol.—These were prepared from D-lyxose and isolated as described for the products from D-xylose. 1,4-Anhydro-D-galactitol had m.p. 95–96°, $[\alpha]^{25}D$ −18° (*c* 2, water), and an infrared spectrum identical with that of an authentic sample.[3]

2,3:5,6-Diisopropylidene-1,4-anhydro-D-talitol was shown to have an infrared spectrum in chloroform identical with that of the known racemic compound,[29] melted at 45°, and had $[\alpha]^{26}D$ −19.4° (*c* 2.9, toluene).

Anal. Calcd. for $C_{12}H_{20}O_5$ (244.29): C, 59.00; H, 8.25. Found: C, 59.31; H, 8.46.

Hydrolysis of the isopropylidene derivative gave a sirup which has not crystallized in more than a year and which has not given a crystalline acetate, benzoate, or *p*-nitrobenzoate. The sirup shows only one component on chromatography in a variety of solvents and has $[\alpha]D$ −57.8° (*c* 2.2, water).

Periodate Oxidations.—All oxidations were carried out in unbuffered sodium metaperiodate at room temperature (22–25°). Utilization of oxidant was followed by titration of iodine released from a suitable aliquot on addition of 5 ml. each of 2 *N* sulfuric acid and 20% aqueous potassium iodide with either 0.1 *N* or 0.01 *N* thiosulfate. The possibility of iodine consumption by the products of the oxidation was checked by the addition of a standard iodine solution, sulfuric acid, and iodide to a sample of the oxidation mixture and titration of the iodine present with standard thiosulfate. No consumption of iodine was observed.

Formaldehyde was determined with chromotropic acid by an adaptation of the method of Frisell, Meech, and Mackenzie.[33] Formic acid was determined by addition of an excess of ethylene glycol to an aliquot of the reaction mixture and titration with 0.01 *N* sodium hydroxide to the methyl orange end point, after 30 min.

The Preparation of Trialdehyde from 1,4-Anhydro-DL-allitol.—To an ice-cold solution of 492 mg. (3 mmoles) of 1,4-anhydro-DL-allitol in 50 ml. of water was added 11.5 ml. (6.1 mmoles) of 0.53 *M* sodium metaperiodate. After 0.5 hr. at room temperature, the reaction was essentially complete and the volume was made up to 1500 ml. with water. If this dilution was not made, iodine was produced in the reaction mixture in about 1 hr. No iodine was observed in the diluted solution even after 5 days at 25°. The dilute solution was used to follow the increase in absorbancy and to follow the oxidation of the absorbant compound. Absorbancy was measured in a Zeiss PM II spectrophotometer using 0.2-ml aliquots of the diluted reaction mixture diluted with 5.0 ml. of water.

When the absorbancy had reached a maximum value (24 hr.), 10 ml. of 0.53 *M* sodium metaperiodate was added to 500 ml. of the solution. The consumption of oxidant and the appearance of acid and formaldehyde were followed as outlined above.

Immediately after dilution to 1.5 l., a 500-ml. aliquot was treated with 1 g. of sodium borohydride. After standing overnight, the excess hydride was destroyed with acetic acid and the solution was concentrated to a small volume. After deionizing, the residue was acetylated in pyridine. Examination of the product by vapor phase chromatography using Dow–Corning high vacuum grease on Chromosorb W at 220° showed one component with a retention time greater than that for arabitol pentaacetate.

A second 500-ml. aliquot was similarly treated when the absorbancy had reached a maximum value. The same yield of the same acetate was obtained.

(32) J. W. Le Maistre, private communication.

(33) W. R. Frisell, L. A. Meech, and C. G. Mackenzie, *J. Biol. Chem.*, **207**, 709 (1954).

The Route of Cyclic Anhydride Formation from Mono-*O*-tolylsulfonyl Glycols[1]

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In the intramolecular displacement of *p*-tolylsulfonate anions by an oxide ion it is shown that a tolylsulfonyl ester on a primary hydroxyl function is displaced by oxide ions derived from hydroxyl groups in the following order of reactivity: primary γ-OH > secondary γ-OH = secondary α-OH > primary δ-OH. A tolylsulfonyl ester on a secondary hydroxyl function is displaced most readily by an oxide ion derived from a primary α-OH; reactions with competing oxide ions derived from primary γ-hydroxyls and secondary α-hydroxyls have not been observed.

It previously has been shown[2] that, under basic conditions in a system containing a primary hydroxyl group γ to a *p*-tolylsulfonyl ester function and a secondary hydroxyl group α to the function, intramolecular *p*-tolylsulfonate anion displacement proceeds preferentially by attack of the oxide ion in the γ-position.

The purpose of the present investigation was to elucidate the route of base-catalyzed tolylsulfonate anion displacement in each of the following three situations involving unbranched glycols: (1) primary hydroxyl group α and γ to the ester, (2) a primary hydroxyl δ and a secondary hydroxyl α to the ester, and (3) secondary hydroxyl groups α and δ to the ester.

To examine the first two situations, the products formed when the 2- and 1-*O*-*p*-tolylsulfonyl esters of L-1,2,5-pentanetriol (I)[3] were treated with alkali were investigated.

1,5-Di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol (II) was prepared from L-glutamic acid by the following series of reactions: L-glutamic acid → L-α-hydroxyglutaric acid → dimethyl L-α-hydroxyglutarate → methyl L-α-hydroxyglutarolactonate → L-1,2,5-pentanetriol (I) → 1,5-di-*O*-benzoyl-L-1,2,5-pentanetriol → II.

Treatment of II with aqueous sodium hydroxide gave tetrahydrofurfuryl alcohol, $[\alpha]^{24}D$ +14.9 ± 0.3° (*c* 5.0, nitromethane), as the only isolable product. Kenyon, *et al.*,[4] reported $[\alpha]^{20}_{5893}$ −17.5° (*c* 5.0, nitromethane) for the levorotatory enantiomer. Since Gagnaire and Butt[5] found that the tetrahydrofurfuryl alcohol having a positive rotation is the L isomer, it is

(1) This investigation was supported in whole by Public Health Service Research Grant GM 09021 from the National Institute of General Medical Sciences.

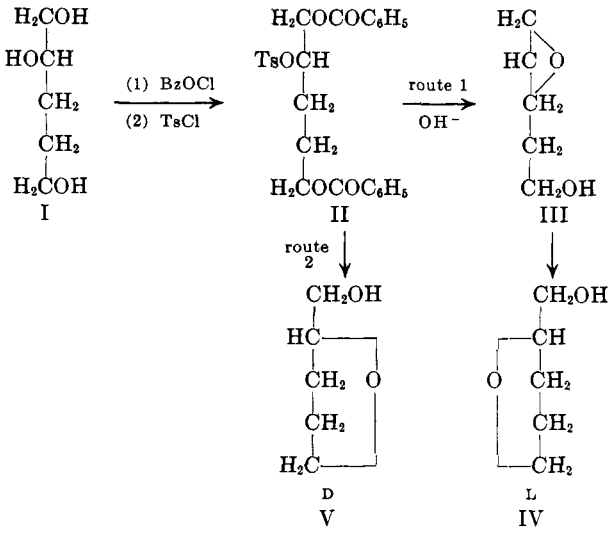
(2) F. C. Hartman and R. Barker, *J. Org. Chem.*, **28**, 1004 (1963).

(3) H. Katsura, *Nippon Kagaku Zasshi*, **77**, 1789 (1956); *Chem. Abstr.*, **53**, 5126 (1959).

(4) M. P. Balfe, M. Irwin, and J. Kenyon, *J. Chem. Soc.*, 313 (1951).

(5) D. Gagnaire and A. Butt, *Bull. soc. chim. France*, 312 (1961).

SCHEME I



concluded that the tetrahydrofurfuryl alcohol obtained is predominantly the L isomer, whose formation can be explained only by a double inversion of configuration (route 1), indicating preferential participation of the α-hydroxyl group in displacement of the tolylsulfonyl ester. Based on the previously reported rotation of tetrahydrofurfuryl alcohol, the maximum per cent of II reacting *via* route 2 is 7.5%.

An attempt was made to determine whether the difference between the observed rotation and the reported[4] rotation of tetrahydrofurfuryl alcohol is due to partial racemization resulting from initial displacement by the γ-hydroxyl group (route 2) or to the presence of optically inert impurities in the isolated product. It was felt that the rotation of the tetrahydrofurfuryl alcohol that would result if only route 1 was operative would be identical with that of the tetrahydrofurfuryl alcohol obtained by the acid-catalyzed dehydration of L-1,2,5-pentanetriol, since the acid-catalyzed reaction usually proceeds without inversion of configuration.[6] However, the tetrahydrofurfuryl alcohol obtained from L-1,2,5-pentanetriol by treating it with 2 *N* hydrochloric acid at 100° for 36 hr. had $[\alpha]^{24}D$ +10.2 (*c* 5.0, nitromethane), which indicated appreciable racemization. Gagnaire and Butt[5] have reported also racemization in the acid-catalyzed dehydration of 1,2,5-pentanetriol using more drastic conditions.

In a further effort to determine whether route 2 is operative, the tetrahydrofurfuryl alcohol ($[\alpha]^{25}D$ + 14.9°) obtained from II was converted to its 3,5-dinitrobenzoyl ester which was recrystallized to constant melting point and rotation and then converted back to the alcohol. The alcohol obtained in this fashion had $[\alpha]^{25}D$ +15.5 ± 0.3° (*c* 5.0, nitromethane), a value only slightly different from the rotation of the starting alcohol. Examination of the alcohol preparations by gas chromatography indicated the presence of a small proportion of material with a very short retention time relative to tetrahydrofurfuryl alcohol which we feel is a contaminant due to the method of isolating the alcohol. On this basis we conclude that, in the base-catalyzed displacement of the tolylsulfonyl group from II, route 2 is followed by less than 5% of the sample.

(6) L. F. Wiggins, *Advan. Carbohydrate Chem.*, **5**, 191 (1950).

The initial formation of III is substantiated by the demonstration that treatment of II with sodium methoxide results in the formation of an epoxide in 95% yield. Unless the method used to determine the presence of an epoxide in the reaction mixture[7] gives positive results with *ortho* esters, this finding rules out anchimeric assistance by the benzoyloxy group with the intermediate formation of an *ortho* ester, as Baker and Haines[8] demonstrated in the displacement of mesyloxy groups in the alditols. Since both benzoyl groups are primary, they should be removed at approximately the same rate, thereby allowing approximately equal opportunity for the two hydroxyl groups to assist in the displacement. The electron-withdrawing tendency of the neighboring sulfonate ester might potentiate the release of the α-hydroxyl group, although this effect would be counteracted by steric hindrance due to the same group.

1-*O*-*p*-Tolylsulfonyl-L-1,2,5-pentanetriol (X) was prepared as follows: I → 1,2-*O*-isopropylidene-L-1,2,5-pentanetriol (VI) → 5-*O*-benzyl-1,2-*O*-isopropylidene-L-1,2,5-pentanetriol (VII) → 5-*O*-benzyl-L-1,2,5-pentanetriol (VIII) → 5-*O*-benzyl-1-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol (IX) → X. (See Scheme II.)

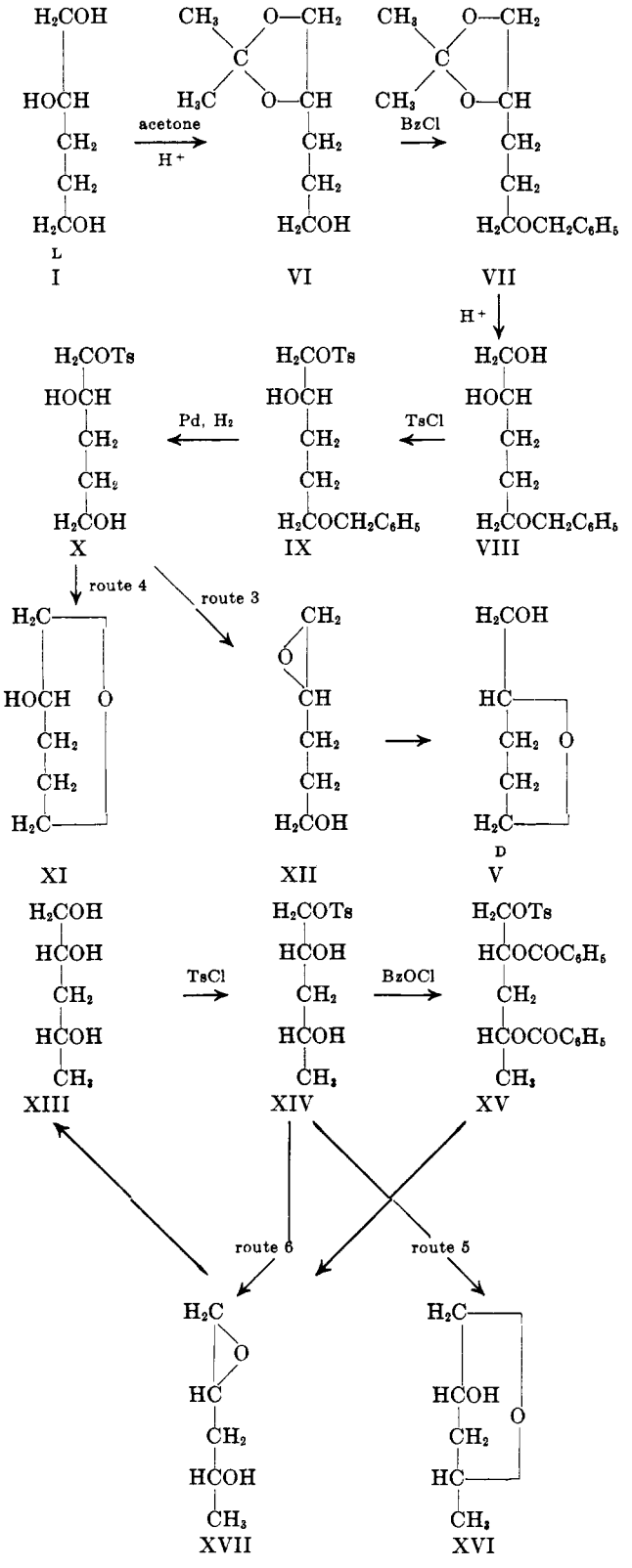
Treatment of X with aqueous base results in a mixture which was shown by gas chromatography to be 92.5% tetrahydrofurfuryl alcohol (V) and 7.5% 3-hydroxytetrahydropyran (XI). The tetrahydrofurfuryl alcohol is the D isomer (V) since the specific rotation of its 3,5-dinitrobenzoyl ester is equal in magnitude and opposite in direction to the corresponding derivative obtained from IV. The possibility of the formation of XI by rearrangement of the epoxide (XII) is excluded on the basis that no XI results from the rearrangement of epoxide III, which is formed when II is treated with base. Thus, the formation of V and XI from X on treatment with base shows that routes 3 and 4 are operative.

The route of displacement when the third situation exists was demonstrated by examination of the products formed when the 1-*O*-*p*-tolylsulfonyl ester of 1,2,4-pentanetriol (XIV) was treated with alkali. The tolylsulfonyl ester was not isolated from the reaction in which it was formed. An excess of aqueous base was added to the reaction mixture and the amount of triol (XIII) formed was determined by periodate oxidation. The amount of triol formed was 42% of the theoretical, indicating that 58% of the ester had been converted to 2-methyl-4 hydroxytetrahydrofuran (XVI). These findings indicate that secondary α- and γ-hydroxyl functions participate with approximately equal ease in the displacement of a primary tolylsulfonate anion. The amount of triol formed is a measure of the amount of 1,2-epoxy-4-hydroxypentane (XVII) formed (route 6), since previous work has shown that a 4-hydroxyl group cannot attack the 1-position of a 1,2-epoxide.[2] The amount of XVI formed is a measure of the extent of γ-hydroxyl group participation (route 5).

The assumption that the tolylsulfonyl ester utilized in the above experiments was 1-*O*-*p*-tolylsulfonyl-1,2,4-pentanetriol (XIV) was validated by converting a sample of it to the dibenzoyl ester (XV) and refluxing

(7) W. C. J. Ross, *J. Chem. Soc*, 2257 (1950).
(8) B. R. Baker and A. H. Haines, *J. Org. Chem.*, **28**, 438 (1963).

SCHEME II



the latter in acetone containing potassium iodide for 2 hr.; 95% of the theoretical amount of sodium *p*-tolylsulfonylate was obtained indicating that XV was a primary tolylsulfonyl ester.[9]

Upon treating XV with aqueous base, 38% of the tolysulfonyloxy function is displaced by the γ-hydroxyl group giving rise to 2-methyl-4-hydroxytetrahydrofuran (XVI), and 62% is displaced by the α-hydroxyl group forming the epoxide (XVII) which rearranges to give the triol (XIII). The amount of XVI formed was determined by isolation. The amount of XIII formed was measured by periodate oxidation of the aqueous solution after XVI had been extracted. These findings indicate that, although the rate of removal of the benzoyl groups may influence the proportion of reaction which occurs *via* route 5 or 6, it does not exercise complete control over the route taken.

Our results are in accord with the finding that treatment of 6-*O*-*p*-tolylsulfonyl-D-fructose phenylosotriazole with sodium methylate yields 60% of the corresponding 5,6-epoxide.[10]

The base-catalyzed displacement of a *p*-tolylsulfonate anion is described as follows.

(1) In a secondary *p*-tolylsulfonyl ester containing primary hydroxyl groups α and γ to the ester function, the oxide ion derived from the α-hydroxyl group is involved. The epoxide which is formed rearranges to the more stable tetrahydrofuran ring.

(2) In a primary *p*-tolylsulfonyl ester containing a secondary hydroxyl group α and a primary hydroxyl group δ to the ester, the ion from the α-hydroxyl group is involved primarily. Displacement by the δ-oxide occurs to only a slight degree. The epoxide ring formed by displacement by the α-hydroxyl group rearranges to a five-membered ring.

(3) In a primary tolylsulfonyl ester with secondary hydroxyl groups α and γ to the ester, the displacement proceeds with approximately equal participation of the two hydroxyl groups. The epoxide formed by attack of the α-hydroxyl group is opened to the *vic* glycol.

These findings indicate that the extent to which various hydroxyl groups participate in the displacement of tolylsulfonate anions depends upon their position and on whether they are primary or secondary. As would be expected from their greater acidity,[11] primary hydroxyl groups are more reactive than secondary. It is also probable that a hydroxyl group α to the ester function is more acidic due to electron withdrawal by the sulfonic ester group.[12]

The ratio of products found in the various cases examined is dependent then upon the specific rate of cyclization, which is probably greatest for the five-membered ring, and upon the acidity of the hydroxyl function, which is greater for primary hydroxyl functions and which is enhanced when the hydroxyl is adjacent to the ester being displaced.

Experimental[13]

Dimethyl L-α-Hydroxyglutarate.[3]—Nitrogen trioxide[14] was bubbled intermittently into a gently stirred suspension of 500 g. of L-glutamic acid in 1200 ml. of water. The temperature was maintained between 10–15° with an ice bath. When the evolution of nitrogen became vigorous, the addition of nitrogen trioxide was stopped until the evolution of nitrogen subsided. The

(9) R. S. Tipson, *Advan. Carbohydrate Chem.*, **8**, 107 (1953).

(10) E. Hardegger and E. Schreier, *Helv. Chim. Acta*, **35**, 623 (1952).

(11) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(12) H. W. Heine and W. Seigfried, *ibid.*, **76**, 489 (1954).

(13) Melting points are corrected. Evaporations were carried out at water-aspirator pressure on a rotary evaporator. Aerograph gas chromatographic apparatus, Model A90-S, was used for the vapor phase separations on a 10% Carbowax 20M on Chromosorb W column. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(14) P. R. Shildneck, U. S. Patent 2,461,701 (1949); *Chem. Abstr.*, **43**, 3841 (1949).

process was continued until a homogeneous solution was obtained (approximately 7 hr.). Filtration of the solution through a layer of Celite and concentration of the filtrate at 50° gave 519 g. of α-hydroxy-L-glutaric acid as a thick, slightly yellow sirup. After drying the acid at 50° under 1-mm. pressure for 25 hr., a 100-g. portion was converted to the dimethyl ester by refluxing for 12 hr. with 500 ml. of methanol containing 10 ml. of concentrated sulfuric acid. The solution was cooled to 0°, neutralized with 120 ml. of cold 3 *N* methanolic potassium hydroxide, and concentrated at 40° to remove the methanol. The residue was taken up in 300 ml. of water and extracted with six 200-ml. portions of chloroform. Concentration of the chloroform extracts gave 82 g. of material which on vacuum distillation gave 73 g. (61%) of product, b.p. 85–92° (0.1 mm.). Katsura[3] reported b.p. 82–90° (0.13 mm.).

Methyl L-α-Hydroxyglutarolactonate.—Dimethyl L-α-hydroxyglutarate (30 g.) was heated in an open beaker for 16 hr. at 200°. Crystallization from 50 ml. of isopropyl alcohol gave 19.2 g. (78%) of crystals, m.p. 48–50°. Four recrystallizations from the same solvent gave a material with m.p. 58–60° and $[\alpha]^{24}D$ +3.1° (*c* 4.5, water).

Anal. Calcd. for $C_6H_8O_4$ (144.1): C, 50.01; H, 5.59. Found: C, 50.15; H, 5.46.

L-1,2,5-Pentanetriol.[3]—To a well-stirred, refluxing suspension of 5 g. of powdered lithium aluminum hydride in 150 ml. of dioxane was added dropwise during 1 hr. a solution of 10 g. of L-α-hydroxyglutarolactone in 100 ml. of dioxane. After the addition was complete, the mixture was refluxed for 1 hr. and then cooled to 0°. The excess lithium aluminum hydride was destroyed by the dropwise addition of ethyl acetate. Isolation of the product was accomplished in the following manner.[15] Hydrolysis of the alcoholate was effected by the addition of 20 ml. of saturated aqueous sodium sulfate solution followed by boiling for 15 min. After removal of the water with anhydrous magnesium sulfate (35 g.), the mixture was filtered and the residue was washed thoroughly with dioxane. Concentration of the combined filtrate and washings gave 7.7 g. (93%) of the triol with $[\alpha]^{24}D$ −19.6° (*c* 5.0, ethanol). Katsura[3] reported $[\alpha]^{29}D$ −11.6° (94% ethanol). The triol gave an 84% yield of a tri-*O*-*p*-nitrobenzoyl ester, which after two recrystallizations from ethanol–acetone (1:1) melted at 130–132° and had $[\alpha]^{24}D$ +8.6 (*c* 5.0, methylene chloride).

Anal. Calcd. for $C_{26}H_{21}N_3O_{12}$ (567.47): C, 55.03; H, 3.73. Found: C, 55.29; H, 3.95.

1,5-Di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol.—To a solution of 10.8 g. of L-1,2,5-pentanetriol in 150 ml. of pyridine was added dropwise with stirring 22 ml. of benzoyl chloride. The temperature was maintained below −10° with a Dry Ice bath. After the addition of the benzoyl chloride was complete, the reaction mixture was left at room temperature for 3 hr., and then 200 ml. of methylene chloride was added. The methylene chloride solution was extracted successively with cold water, 1 *N* sulfuric acid, saturated sodium bicarbonate solution, and water; it was dried over sodium sulfate and concentrated to give 29 g. (100%) of a slightly viscous sirup. The sirup was dissolved in 200 ml. of pyridine and 25 g. of *p*-toluenesulfonyl chloride was added. After remaining 48 hr. at room temperature, the reaction mixture was washed as described above. Crystallization of the product from 200 ml. of ethanol gave 23 g. (53%) of crystals which after two recrystallizations melted at 85–87° and had $[\alpha]^{24}D$ +6.2 (*c* 9.0, methylene chloride).

Anal. Calcd. for $C_{26}H_{26}O_7S$ (482.49): C, 64.72; H, 5.43. Found: C, 64.58; H, 5.42.

L-Tetrahydrofurfuryl Alcohol.—A solution of 1 g. of L-1,2,5-pentanetriol in 10 ml. of 2 *N* hydrochloric acid was heated in a stoppered tube at 100° for 36 hr. and then continuously extracted with ether for 12 hr. The ether extract was concentrated, and the residue was taken up in methylene chloride, dried over sodium sulfate, and filtered. Concentration of the filtrate gave 0.77 g. (90%) of product with $[\alpha]^{24}D$ +10.2 (*c* 5.0, nitromethane). Conversion of 0.42 g. of this alcohol to the 3,5-dinitrobenzoyl ester gave 1.0 g. (82%) of sirup which from solution in 20 ml. ethanol gave 0.62 g. (51%) of crystals, m.p. 74–76°. After three recrystallizations, the material melted at 74–76° and had $[\alpha]^{24}D$ +16.4 (*c* 2.0, methylene chloride).

Anal. Calcd. for $C_{12}H_{12}N_2O_7$ (296.2): C, 48.65; H, 4.08. Found: C, 48.43; H, 4.17.

(15) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLemore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).

Action of Aqueous Alkali on 1,5-Di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol.—To a solution of 5.29 g. of 1,5-di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol in 100 ml. of acetone was added 40 ml. of 1 *N* sodium hydroxide. After the reaction mixture had remained at room temperature for 24 hr., the acetone was removed by concentration and the remaining aqueous solution continuously was extracted with ether for 12 hr. The ether extract contained 1.01 g. (92%) of material, $[\alpha]^{24}D$ +14.9° (*c* 5.0, nitromethane), which was demonstrated by gas chromatography to be predominantly a compound whose retention time was identical with that of tetrahydrofurfuryl alcohol.

3,5-Dinitrobenzoyl-L-tetrahydrofurfuryl Alcohol and Its Saponification.—A portion of the tetrahydrofurfuryl alcohol (0.6 g.) was converted to the 3,5-dinitrobenzoyl ester in the usual manner to give 1.46 g. (84%) of sirup, $[\alpha]^{24}D$ +18.6° (*c* 4.0, methylene chloride), from which was obtained by crystallization from 28 ml. of ethanol 1.05 g. of crystals, m.p. 76–77°, $[\alpha]^{24}D$ +20.5 (*c* 5.0, methylene chloride). Three recrystallizations from 25 ml. of ethanol gave 0.5 g. of crystals whose melting point was raised to 77.5–78.5° and specific rotation was unchanged. The ester (0.5 g.) was dissolved in 20 ml. of acetone and 4 ml. of 1 *N* sodium hydroxide was added. After leaving the reaction mixture at room temperature for 24 hr., the acetone was removed by evaporation and 20 ml. of water was added. The reaction mixture was left at room temperature for 3 additional days at which time the tetrahydrofurfuryl alcohol was extracted from the aqueous mixture with ether as described previously. The tetrahydrofurfuryl alcohol (120 mg., 65%) obtained had $[\alpha]^{24}D$ +15.5° (*c* 5.0, nitromethane).

Action of Sodium Methoxide on 1,5-Di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-L-1,2-5-pentanetriol.—To a solution of 4.82 g. of 1,5-di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol was added 10 ml. of 1.92 *N* sodium methoxide, and the resulting solution was diluted to 50 ml. with chloroform. A 5-ml. aliquot of the reaction mixture was removed 10 min. after the sodium methoxide had been added. The aliquot was immediately neutralized to the phenolphthalein end point with 2 *N* acetic acid and its epoxide content was determined by the thiosulfate method.[7] To the neutralized aliquot was added 10 ml. of acetone and 10 ml. of 0.2 *M* sodium thiosulfate. The solution was heated at 60° with constant stirring and the pH was maintained at the phenolphthalein end point with 0.17 *N* acetic acid. After 25 min., the reaction was complete and 0.95 mequiv. (95%) of hydroxyl ions had been released, demonstrating the presence of 0.95 mequiv. (95%) of epoxide in the original aliquot. Subsequent samples showed the presence of decreasing amounts of epoxide.

5-*O*-Benzyl-1,2,-*O*-isopropylidene-L-1,2,5-pentanetriol.—A solution of 15 g. of L-1,2,5-pentanetriol in 500 ml. of dry acetone containing 1.2 ml. of concentrated sulfuric acid was stirred at room temperature for 15 hr. and then passed through a column of 50 ml. of IR 45 (OH^-).[16] Concentration of the eluent gave 25.0 g. of a sirup from which, on distillation at atmospheric pressure, was obtained 9 g. of acetone condensation products (b.p. 95–100°) and 15 g. (75%) of 1,2,-*O*-isopropylidene-D-1,2,5-pentanetriol (b.p. 225–228°). To a solution of 7.0 g. of this compounds in 100 ml. of benzene were added 11.5 g. of powdered potassium hydroxide and 12.5 ml. of benzyl chloride. After refluxing the mixture for 3.5 hr., the solids were removed by filtering through a layer of Celite and the filtrate was concentrated. Distillation of the residue gave 5.8 g. of dibenzyl ether (b.p. 80–110° at 15 mm.) and 10.3 g. (99%) of the desired product, b.p. 176–185° (15 mm.). Redistillation gave 9.7 g. of colorless, nonviscous liquid, b.p. 180–184° (15 mm.), $[\alpha]^{24}D$ +8.5° (*c* 3.0, dioxane).

Anal. Calcd. for $C_{15}H_{22}O_3$ (250.3): C, 71.98; H, 8.85. Found: C, 72.28; H, 8.94.

5-*O*-Benzyl-D-1,2,5-pentanetriol.—To a solution of 9 g. of 5-*O*-benzyl-1,2-*O*-isopropylidene-L-1,2,5-pentanetriol in 200 ml. of dioxane was added 50 ml. of 0.1 *N* hydrochloric acid, and the resulting solution was boiled (approximately 1 hr.) until no acetone could be detected in the distillate with 2,4-dinitrophenylhydrazine reagent. After concentration, the residue was dissolved in 50 ml. of ethanol and the resulting solution was passed through a column containing 10 ml. of IR 45 (OH^-).[16] Concentration of the eluent gave 7.3 g. of a slightly yellow viscous sirup which was distilled at 1 mm. The product (6.1 g., 81%) was obtained as a colorless viscous sirup, b.p. 158–163°, $[\alpha]^{24}D$ −11.3° (*c* 2.3, ethanol).

(16) Rohm and Haas Co., Philadelphia, Pa.

Anal. Calcd. for $C_{12}H_{18}O_3$ (210.3): C, 68.54; H, 8.63. Found: C, 68.38; H, 8.41.

5-O-Benzyl-1-O-p-tolylsulfonyl-L-1,2,5-pentanetriol.—A solution of 3.4 g. of *p*-toluenesulfonylchloride in 20 ml. of pyridine was added to a solution of 3.6 g. of 5-*O*-benzyl-L-1,2,5-pentanetriol in 20 ml. of pyridine, with both solutions at 0°. The reaction mixture was left at 0° for 24 hr. and then the product was isolated by taking up the reaction mixture in methylene chloride and washing as described previously. The sirup (5.7 g., 90%) obtained was characterized as the 2-*O*-*p*-nitrobenzoyl ester (78% from the sirup) which melted at 54.5–55.5°, $[\alpha]^{24}D$ +3.5 (*c* 2.0, methylene chloride).

Anal. Calcd. for $C_{26}H_{27}NO_8S$ (513.5): C, 60.81; H, 5.30. Found: C, 60.56; H, 5.45.

1-O-p-Tolylsulfonyl-L-1,2,5-pentanetriol.—Palladium chloride (2 g. of 10% palladium chloride on charcoal) in 25 ml. of ethyl acetate was hydrogenated at room temperature and atmospheric pressure for 1 hr. at which time it was filtered and thoroughly washed with ethyl acetate to remove hydrogen chloride. The catalyst then was rehydrogenated in 25 ml. of ethyl acetate, and 2.6 g. of 5-*O*-benzyl-1-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol in 25 ml. of ethyl acetate was added. After 10 min. the hydrogenation was complete with the consumption of 151 ml. of hydrogen (95%). The catalyst was removed by filtering the mixture through Celite, and the filtrate was concentrated to give 1.9 g. (100%) of the product as a sirup, from which an 88% yield of the crystalline 2,5-di-*O*-*p*-nitrobenzoyl ester, m.p. 133–135°, $[\alpha]^{24}D$ +3.6° (*c* 4.5, methylene chloride), could be obtained.

Anal. Calcd. for $C_{26}H_{24}N_2O_{11}S$ (572.4): C, 54.55; H, 4.22. Found: C, 54.44; H, 4.20.

Action of Aqueous Alkali on 1-O-p-Tolylsulfonyl-L-1,2,5-pentanetriol.—To a solution of 1.9 g. of 1-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol in 10 ml. of methanol was added 10 ml. of aqueous 1 *N* sodium hydroxide. After heating the solution at 50° for 0.5 hr., it was neutralized with 2 *N* hydrochloric acid, concentrated until no methanol remained, decolorized with charcoal, and filtered through Celite. The filtrate was extracted continuously with ether for 24 hr. and the ether extract was concentrated. The residue was taken up in 20 ml. of methylene chloride and the solution was dried with sodium sulfate, filtered, and concentrated. Analysis of the product (0.56 g., 79%) by gas chromatography showed it to be approximately 7.5% of a compound with the same retention time as 3-hydroxytetrahydrofuran,[17] in addition to tetrahydrofurfuryl alcohol. The tetrahydrofurfuryl alcohol was the D isomer as was shown by $[\alpha]^{24}D$ −20.7 ± 0.8° (*c* 1.0, methylene chloride) of the 3,5-dinitrobenzoyl ester obtained in 41% yield from the mixture.

1,2,4-Pentanetriol.—To a well-stirred solution of 43 g. of 1-penten-4-ol in 453 g. of 90% formic acid was added during a 30-min. period 59 g. of 30% hydrogen perioxide, the temperature being maintained below 40° with an ice bath. After the addition was complete, the reaction mixture was left at room temperature for 24 hr. and then concentrated at 50°. To remove the formic acid, the residue was taken up in 200 ml. of water and concentrated; this process was repeated three times. The formate ester was saponified then by boiling with 300 ml. of 2 *N* sodium hydroxide for 1 hr., at which time the solution was passed successively through columns containing 500 ml. of IR 120 (H^+)[16] and 500 ml. of IR 45 (OH^-).[16] The eluent was concentrated and the residue was distilled to give 41 g. (68%) of product, b.p. 149–153° (0.03 mm.), which after redistillation appeared pure by paper chromatography and gas chromatography and which consumed 1 molar equiv. of sodium metaperiodate.

Anal. Calcd. for $C_5H_{12}O_3$ (120.1): C, 49.98; H, 10.06. Found: C, 48.71; H, 10.08.

2,4-Di-O-benzoyl-1-O-p-tolylsulfonyl-1,2,4-pentanetriol.—A solution of 8.0 g. of *p*-toluenesulfonyl chloride in 25 ml. of pyridine was added to a solution of 4.8 g. of 1,2,4-pentanetriol in 25 ml. of pyridine, both solutions at 0°. The resulting mixture was left for 2 hr. at 0°, then warmed to room temperature, and left for 4 hr. The reaction mixture was then cooled to 0°, and 13 ml. of benzoyl chloride was added dropwise to keep the temperature below 20°. Two hours after the addition was complete the reaction mixture was worked up in the usual fashion and 19 g. (95%) of product was obtained as a thick slightly yellow sirup.

Action of Sodium Iodide on 2,4-Di-O-benzoyl-1-O-p-tolylsulfonyl-1,2,4-pentanetriol.—A solution of the tolylsulfonyl ester (3.57 g.) in 25 ml. of acetone containing 4.3 g. of sodium iodide was refluxed for 2 hr. and then cooled to 0°. The sodium *p*-toluenesulfonate (1.23 g., 95%) was removed by filtration. No sodium *p*-toluenesulfonate was formed when 1,5-di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-L-1,2,5-pentanetriol was treated with sodium iodide under the same conditions.

2-Methyl-4-hydroxytetrahydrofuran.—A solution of 1. g. of 1,2,4-pentanetriol in 10 ml. of 2 *N* hydrochloric acid was hea ted in a stoppered tube for 36 hr. at 100°. The product (0.81 g., 95%) was isolated in the manner described for the isolation of L-tetrahydrofurfuryl alcohol prepared by the anhydrization of L-1,2,5-pentanetriol.

Action of Sodium Methoxide on 2,4-Di-O-benzoyl-1-O-p-tolylsulfonyl-1,2,4-pentanetriol.—Freshly prepared sodium methoxide (1 ml., 2.3 *N*) was added to a solution of 4.26 g. (0.88 mequiv.) of the *p*-tolylsulfonyl ester in 75 ml. of chloroform at 0°, and the resulting mixture was diluted to 100 ml. with cold chloroform. After 30 min., a 10-ml. aliquot was removed and its epoxide content, determined as described previously, was found to be 0.38 mequiv. (43%). The epoxide content was the same after 70 min.

Action of Aqueous Alkali on 2,4-Di-O-benzoyl-1-O-p-tolylsulfonyl-1,2,4-pentanetriol.—To a solution of 2,4-di-*O*-benzoyl-1-*O*-*p*-tolylsulfonyl-1,2,4-pentanetriol in 100 ml. of acetone was added 40 ml. of aqueous 1 *N* sodium hydroxide. After remaining at room temperature for 3 days, the reaction mixture was titrated with 1 *N* hydrochloric acid; 32.8 mequiv. (97%) of base had been consumed. The neutral solution was extracted continuously with ether for 24 hr. From this ether solution 0.43 g. (38%) of material was isolated which by gas chromatography could not be separated from the 3-methyl-3-hydroxytetrahydrofuran obtained from the dehydration of 1,2,4-pentanetriol. The aqueous solution was diluted to 100 ml. Periodate consumption of aliquots indicated the presence of 840 mg. (62%) of triol in the aqueous layer.

Action of Aqueous Alkali on 1-O-p-Tolylsulfonyl-1,2,4-pentanetriol.—To a solution of 0.75 g. of 1,2,4-pentanetriol in 25 ml. of pyridine at 0° was added a solution of 1.2 g. of *p*-toluenesulfonyl chloride in 15 ml. of pyridine at 0°. After the reaction mixture had remained for 12 hr. at 0°, 20 ml. of 1 *N* sodium hydroxide was added and the solution was left at room temperature for 3 days at which time it was neutralized with 2 *N* sulfuric acid. By periodate oxidation it was determined that the solution contained 0.32 g. (42%) of 1,2,4-pentanetriol.

(17) D. Gagnaire and A. Butt, *Bull. soc. chim. France*, 309 (1961).