material, m.p. 172–174°, 83% yield. Recrystallization from dilute ethanol or dilute methyl Cellosolve gave glistening plates melting at 173–174°.

Anal. Calcd. for $C_{19}H_{17}NO_3S$: C, 67.2; H, 5.05; N, 4.13. Found: C, 66.9; H, 4.89; N, 4.22.

4,4'-Diphenoquinone-4-*p*-tolylsulfonimide (X).—A solution of 150 mg. (0.44 mmole) of IX in 10 ml. of 2-nitropropane was added dropwise with stirring to 252 mg. (0.57 mmole) of lead tetraacetate in 50 ml. of dry chloroform. After stirring for one hour the dark-red mixture was filtered and the filtrate added slowly to 250 ml. of petroleum ether. After cooling in an ice-bath for several hours, the reddish-brown precipitate was collected, washed with petroleum ether and redissolved in 35 ml. of chloroform. The solution was filtered, the filtrate cooled in an ice-bath and the quinone monoimide precipitated by the gradual addition of petroleum ether. After standing at 4° for several hours, 50 mg. of brown, crystalline material, which melted from 195–200° with loss of color above 175°, was obtained. The compound could also be purified by recrystallization from benzene–petroleum ether; $\lambda_{max}^{CHCl_3}$ 433 mμ (ε 67,000).

Anal. Calcd. for $C_{19}H_{15}NO_3S$: C, 67.6; H, 4.48. Found: C, 67.2; H, 4.48.

The infrared spectrum of X showed no —NH— stretching vibrations in the 3 μ region. Strong bands at 6.15 and 6.50 μ, which were not present in IX, were assigned to the carbonyl absorption and the —C=N— grouping of the quinone imide, respectively. Strong bands observed in IX at 7.45 and 8.15 μ and presumably associated with the phenolic —OH group of IX were not noted in X.

Reduction of X to IX.—A solution of 109 mg. (0.32 mmole) of X in 130 ml. of anhydrous benzene was added dropwise with stirring to 350 mg. of lithium aluminum hydride in 30 ml. of anhydrous diethyl ether. The mixture was then heated under reflux for 2.75 hours after which time excess lithium aluminum hydride was decomposed with a saturated solution of ammonium chloride. The organic phase was taken to dryness under reduced pressure and the residual solid recrystallized from dilute ethanol to yield 19 mg. of IX, m.p. 170°, 18% yield. The mixed melting point with an authentic sample of IX, m.p. 172–174°, was 171–173°.

Acknowledgment.—The authors are indebted to Dr. S. W. Fenton for assistance in the interpretation of the infrared spectra and for valuable suggestions.

MINNEAPOLIS 17, MINN.

[CONTRIBUTION FROM THE GEORGE M. MOFFETT RESEARCH LABORATORIES, CORN PRODUCTS REFINING CO., AND THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO.]

The Catalyzed Condensation of Aromatic Compounds with Carbohydrates. 1-Deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol[1]

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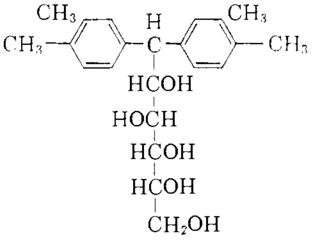
The product of the reaction of starch with *o*-xylene in liquid hydrogen fluoride, 1-deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol, was examined with regard to physical and chemical properties. In addition to behaving in a manner normal for polyhydroxy compounds, this glucitol (1) forms stable gels with bases and certain hydrocarbons, (2) forms a monoanhydro compound by spontaneous decomposition of a mono-*p*-toluenesulfonate, (3) forms a second monoanhydro compound by reaction of its 2,3,4,5-tetrabenzoate 6-*p*-toluenesulfonate with methanolic sodium hydroxide, and (4) dehydrates in the presence of acids to form the second monoanhydro compound, a dianhydro compound and 3,3',4,4'-tetramethylstilbene.

A practical method has been described recently for the synthesis of 1,1-diaryl-1-deoxy-D-glucitols in which carbohydrates such as starch, cellulose and glucose are condensed with aromatic compounds in the presence of liquid hydrogen fluoride.[2] With this development it became of interest to study some of the properties and reactions of these glucitols. Most of the work reported here describes the compound 1-deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol (I), which was isolated from the reaction of starch with *o*-xylene in liquid hydrogen fluoride. Occasional reference is made to 1-deoxy-1,1-bis-(4-methylphenyl)-D-glucitol.

Two oxidation methods were used to help establish the structure of I. Permanganate oxidation gave excellent yields of the known,[3] crystalline 3,3',4,4'-tetramethylbenzophenone (II), which was further characterized as the known, crystalline oxime. Isolation of this ketone showed that in the original glucitol both aryl groups are attached to the same carbon atom. Periodate oxidation resulted in the consumption of four moles of periodate with formation of three moles of formic acid and one mole of formaldehyde per mole of glucitol. Such results show the presence of five vicinal hydroxyl groups, one of which is primary. Further evidence on these points was obtained by analysis for hydroxyl groups and the formation of a trityl ether.



I

Periodate oxidations of I originally were made in aqueous ethanol. In such a solvent the appearance of an iodine color indicated overoxidation had occurred.[4] Analytically, periodate consumption was very close to theoretical (four moles per mole of I). However, when attempts were made to isolate the expected diarylacetaldehyde, Ar_2CHCHO (III), only the crystalline ketone, Ar_2CO (II), could be found. Compound III was eventually isolated as a sirup by oxidation of either a very dilute aqueous solution (0.05%) or an aqueous

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(1) Presented in part before the Division of Petroleum Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.

(2) (a) C. B. Linn, Abstr. 132nd Meeting of the American Chemical Society, New York, p. 5R (1957); (b) C. B. Linn, U. S. Patent 2,798,098, July 2, 1957.

(3) A. Bistrzycki and E. Reintke, *Ber.*, **38**, 839 (1905).

(4) J. M. Bobbitt, *Adv. in Carbohydrate Chem.*, **11**, 1 (1956).

slurry of I.[5] When the sirupy aldehyde was treated with acetic anhydride and sodium acetate in an effort to obtain the acetate of the corresponding vinyl alcohol[6] the ketone II again was isolated.[7]

The retention of the *gluco* configuration is based on the fact that the product obtained in the hydrogen fluoride system with toluene is identical to that obtained by the aluminum chloride-catalyzed glucosylation of toluene.[8] Hurd and Bonner[9] have argued satisfactorily that configuration is maintained in such a reaction.

Certain physical properties of I were observed. The compound is not very soluble in aromatic hydrocarbons and forms a stable gel in *o*-xylene. When treated with an excess of hot sodium hydroxide I is changed to a glass which, when treated with water or ethanol, forms a very stable gel. Treatment of this gel with acid produces starting material. Compound I is fairly stable to heat under neutral conditions. The compound can be distilled at 1 mm. using a free flame as heat source. From the distillate compound I can be isolated with about 60% recovery. Hydroxyl analysis on mother liquors from which such recovery is made indicates some dehydration takes place during distillation.

The acid-catalyzed dehydration of I produces a series of products, three of which have been obtained crystalline. The crystalline compounds are a monoanhydro-I, a dianhydro-I and 3,3′,4,4′-tetramethylstilbene. The monoanhydro derivative is the same as that obtained by alkaline treatment of the 2,3,4,5-tetrabenzoate 6-*p*-toluenesulfonate of I. When treated with acids this monoanhydro compound is, in turn, converted to the same dianhydro-I and substituted stilbene as are obtained by acid treating I itself. Unequivocal structure proof has not been obtained for either of the anhydro compounds.[10]

The hydrocarbon, 3,3′,4,4′-tetramethylstilbene, which is formed by acid treating either I or monoanhydro-I, is a new stilbene; the known analog was also prepared from 1-deoxy-1,1-bis-(4-methylphenyl)-D-glucitol. Structure was proved by ultraviolet and infrared absorption spectra of the stilbene as well as elemental analysis. In the formation of such a compound a Wagner rearrangement probably occurred.[11]

Several crystalline derivatives were prepared from I. These included the pentabenzoate, monobenzoate, 6-*p*-toluenesulfonate tetrabenzoate, 6-trityl ether and dibenzylidene acetal. A number of attempts to prepare a crystalline pentaacetate gave only sirups. No attempt has been made to establish the structure of the dibenzylidene acetal. The very low yield of crystalline acetal indicated it is not the main product of the reaction.

The tetrabenzoate 6-*p*-toluenesulfonate was easily convertible by standard methods to a monoanhydro-I. This anhydro derivative is the same as that isolated when I is treated with mineral acids, organic acids or—in excellent yield—by fusing in vacuum with potassium acid sulfate. This anhydro compound (m.p. 211–213°) contains three hydroxyl groups and consumes one mole of periodate per mole. While attempting to prepare the 6-*p*-toluenesulfonate of *I*, a second monoanhydro compound (m.p. 160°) was isolated. Such a spontaneous conversion of a toluenesulfonate to an anhydro derivative is reminiscent of the experience reported by Forrest, Mason and Todd[12] with the 5′-*p*-toluenesulfonate of riboflavin.

In general, the behavior of I is that expected of a polyhydric alcohol. Outstanding characteristics which have been noted are (1) gelling properties of I in base and certain hydrocarbons, (2) dehydration of I to give a stilbene as an end product and (3) formation from I of an anhydro compound when monotoluenesulfonation is attempted.

Experimental

1-Deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol (I).—Compound I was prepared in 85% crude yield by treating starch with *o*-xylene in liquid HF according to the procedure of Linn.[13] Highly purified I was obtained by recrystallization from ethanol to constant m.p. and rotation. Such a purified material has m.p. 146.5–147°; $[\alpha]^{26}\text{D}$ +40.2° (*c* 1, C_2H_5OH), +32.8 (*c* 1, HOAc), +61.5 (*c* 1, C_5H_5N).

Anal.[14] Calcd. for $C_{22}H_{30}O_5$: C, 70.54; H, 8.08; OH,[15] 22.72. Found: C, 70.52, 70.73; H, 7.95, 8.00; OH, 22.5.

Permanganate Oxidation.—One gram of powdered I was dissolved in 1000 ml. of boiling water containing 5 ml. of 10% sodium hydroxide. To the homogeneous solution was added 25 ml. of a hot aqueous solution of $KMnO_4$ (4 g.) in 5-ml. aliquots. The solution was cooled immediately and extracted with three 200-ml. portions of benzene. On evaporation of the benzene there was recovered 0.5 g. (78.5%) of crude 3,3′,4,4′-tetramethylbenzophenone. Recrystallization from 5 ml. of benzene gave 0.3 g. of ketone, m.p. 142–143°; literature value[5] for 3,3′,4,4′-tetramethylbenzophenone is 140°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.66; H, 7.62. Found: C, 86.15, 86.06; H, 7.54, 7.62.

The oxime prepared from the ketone had m.p. 150–151°, literature value[5] 147°.

Periodate Oxidation.—Compound I (25 mg.) and 125 mg. of $NaIO_4$ were dissolved in 50 ml. of 50% (v./v.) aqueous ethanol and 5-ml. aliquots were removed periodically for analysis. The use of aqueous ethanol and analysis for

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[5] C. F. Huebner, R. Lohmar, R. J. Dimler, S. Moore and K. P. Link, *J. Biol. Chem.*, **159**, 503 (1945), report the successful preparation of 2-benzimidazolecarboxaldehyde by sodium periodate oxidation of an aqueous slurry of D-*arabo*-benzimidazole.

[6] R. C. Fuson and T.-L. Tan, THIS JOURNAL, **70**, 602 (1948).

[7] The oxidation of III to II probably takes place through the enol form (corresponding vinyl alcohol) of III; R. C. Fuson, D. J. Byers and N. Rabjohn, THIS JOURNAL, **63**, 2639 (1941), report a similar spontaneous oxidation of an analogous vinyl alcohol.

[8] C. D. Hurd and W. A. Bonner, *ibid.*, **67**, 1664, 1759, 1977 (1945).

[9] C. D. Hurd and W. A. Bonner, *ibid.*, **67**, 1972 (1945).

[10] F. García González, *Adv. in Carbohydrate Chem.*, **11**, 97 (1956), reviews proofs of structure for anhydro compounds derived from heterocyclics containing tetrahydroxybutyl side chains. The side chain of such compounds passes through a two-stage dehydration to produce a furan structure. While this is a reasonable path for I to follow, the elemental analysis of dianhydro-I does not allow a furan structure.

[11] *Cf.* M. S. Kharasch and H. G. Clapp, *J. Org. Chem.*, **3**, 355 (1938); B. M. Benjamin and C. J. Collins, THIS JOURNAL, **75**, 402 (1953); and C. J. Collins, L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **75**, 405 (1953), who showed the facile formation of stilbenes by Wagner rearrangement of 2,2-diarylethanols.

[12] H. S. Forrest, H. S. Mason and A. R. Todd, *J. Chem. Soc.*, 2530 (1952), isolated a non-sulfur-containing solid on treatment of riboflavin with *p*-toluenesulfonyl chloride. The structure of this compound was not proved but was tentatively proposed as 4′,5′-anhydroriboflavin.

[13] C. B. Linn, Preprints of papers presented before the Division of Petroleum Chemistry at the 132nd Meeting of the American Chemical Society, New York, p. 173 (1957).

[14] Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

[15] Hydroxyl determinations were made by the method of A. G. Hamlin, *J. Textile Inst.*, **48**, T81 (1957).

periodate were according to Hough, *et al.*[16] Periodate consumption in moles per mole of I was 3.74 in 15 minutes and 3.78 after 2 hours (theory 4.0). Formic acid produced was measured according to Wolff, *et al.*,[17] and rose gradually from 1.89 in 15 minutes to 2.95 (theory 3.0) after 3 hours. Formaldehyde analysis[18] showed the presence of 0.94 mole of formaldehyde per mole of I after 30 minutes oxidation (theory 1.0).

Oxidation in this medium (aqueous ethanol) gave rise to an iodine color within an hour. This was taken as an indication of overoxidation and when a carbonyl compound was isolated from the reaction mixture it proved to be 3,3′,4,4′-tetramethylbenzophenone rather than the expected 2,2-bis-(3,4-dimethylphenyl)-acetaldehyde. In an attempt to avoid overoxidation, Compound I was oxidized with periodate in aqueous acetic acid according to the method given by Siggia.[19] In this case, 80 mg. of I and 594 mg. of H_5IO_6 were dissolved in 100 ml. of 80% aqueous acetic acid; 25-ml. aliquots were analyzed for periodate consumption. After 1 hour 4.2 moles (theory 4.0) of periodate had been consumed per mole of I. This value was unchanged after 3 hours. Again, the attempt to isolate the diarylacetaldehyde from the reaction mixture was unsuccessful.

The 2,2-bis-(3,4-dimethylphenyl)-acetaldehyde was eventually isolated by suspending 3.74 g. of I in 600 ml. of water containing 8.6 g. of $NaIO_4$. With occasional stirring the solid glucitol was replaced with a sirup. After 24 hours standing at room temperature the sirup was extracted with benzene and removal of benzene left a theoretical amount of the sirupy diarylacetaldehyde. This material was characterized as the crystalline 2,4-dinitrophenylhydrazone, m.p. 182–183°.

Anal. Calcd. for $C_{24}H_{24}O_4N_4$: C, 66.64; H, 5.60; N, 12.96. Found: C, 66.99, 66.73; H, 5.77, 5.69; N, 12.97, 12.96.

1-Deoxy-6-*O*-trityl-1,1-bis-(3,4-dimethylphenyl)-D-glucitol.—Ten grams of I was dissolved in 20 ml. of warm pyridine and 7.45 g. of chlorotriphenylmethane in 5 ml. of pyridine was added. The mixture was heated on the steam-bath for 2 hours. After cooling, a small amount of water was added to hydrolyze any excess reagent after which the reaction mixture was poured with stirring into ice-water and the solids rubbed to a firm condition. Solids were separated by filtration, dissolved in chloroform, and the chloroform solution washed successively with dil. HCl, satd. $NaHCO_3$ solution and water. Solids remaining upon removal of chloroform weighed 7.46 g. (45%). The crude was recrystallized from ethanol to constant m.p. and rotation. The pure product (5.24 g. 31.7%) had m.p. 157° and $[\alpha]^{25}\mathrm{D}$ +26.7° (*c* 2, C_2H_5OH).

Anal. Calcd. for $C_{41}H_{44}O_5$: C, 79.87; H, 7.14. Found: C, 79.80; H, 7.01.

1-Deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol Dibenzylidene Acetal.—According to a standard procedure[20] 10 g. of I, 3.68 g. of powdered, anhydrous zinc chloride and 20 ml. of benzaldehyde were placed in a glass stoppered bottle and shaken for 24 hours at room temperature. The resulting homogeneous solution was poured into an aqueous sodium bisulfite solution with stirring. The solids that separated were removed by filtration and dissolved in chloroform. The chloroform solution was extracted twice with aqueous sodium bisulfite solution, then water, then was dried over anhyd. sodium sulfate, filtered and evaporated to give 11.4 g. of crude acetal mixture. The crude was dissolved in isopropyl alcohol from which a crystalline product separated (1.2 g. in two crops). This solid material was recrystallized from isopropyl alcohol to constant m.p. and rotation to yield 0.5 g. (3.4%) of a dibenzylidene acetal, m.p. 172–174°, $[\alpha]^{25}\mathrm{D}$ +8.2° (*c* 1, $CHCl_3$).

Anal. Calcd. for $C_{36}H_{38}O_5$: C, 78.54; H, 6.91. Found: C, 78.80, 78.80; H, 7.12, 7.08.

The mother liquors from which the crystalline acetal was removed were chromatographed on alumina. Separation into two fractions was obtained. Both fractions were sirups and were not investigated further.

2,3,4,5,6-Penta-*O*-benzoyl-1-deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol.—Ten grams of I was dissolved in 75 ml. of pyridine at 60°, 31.2 ml. of benzoyl chloride was added and the mixture heated at 60° for 45 minutes. The mixture was poured into 600 ml. of stirred ice-water and the water decanted from the resulting solids. The solids were dissolved in chloroform and the chloroform solution washed successively with dil. HCl, satd. sodium bicarbonate solution and water. The chloroform solution was then dried over Drierite, filtered and chloroform removed by evaporation to give 19.7 g. (82.5%) of crude solids. The crude was recrystallized from glacial acetic acid to constant m.p. 113–113.5° and specific rotation $[\alpha]^{25}\mathrm{D}$ +27.8° (*c* 2, $CHCl_3$). The yield of purified product was 9.95 g. (41.6%).

Anal. Calcd. for $C_{57}H_{50}O_{10}$: C, 76.51; H, 5.59. Found: C, 76.84; H, 5.91.

Mono-*O*-benzoyl-1-deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol.—Ten grams of I was dissolved in 100 ml. of pyridine and the solution cooled to 5° in an ice-bath. Benzoyl chloride (3.1 ml.) was added dropwise with stirring and the mixture was allowed to cool to room temperature and stand for 24 hours. The mixture then was poured into 600 ml. of water and the oil that separated gradually solidified. The solids were removed by filtration, dissolved in 150 ml. of chloroform and the chloroform solution washed successively with 50-ml. portions of 0.5 *N* HCl, satd. $NaHCO_3$ solution and water. The chloroform phase was dried over anhydrous sodium sulfate, filtered and chloroform removed to leave 10 g. (78.6%) of crude product. The crude was dissolved in 60 ml. of *n*-butyl alcohol and 7.0 g. of crystals was harvested in four crops. The crystals were fractionally recrystallized to give about 2.4 g. of product melting in the range 138–141°. This material was recrystallized from methanol, with severe loss, until constant m.p. and specific rotation were reached. This pure monobenzoate had m.p. 140–141° and $[\alpha]^{26}\mathrm{D}$ +28.9° (*c* 1, $CHCl_3$).

Anal. Calcd. for $C_{29}H_{34}O_6$: C, 72.76; H, 7.16. Found: C, 72.68, 72.41; H, 7.28, 7.21.

2,3,4,5-Tetra-*O*-benzoyl-1-deoxy-6-*O*-tosyl-1,1-bis-(3,4-dimethylphenyl)-D-glucitol.—Twenty grams of anhydrous I was dissolved in 50 ml. of anhydrous pyridine and 11 g. of freshly purified *p*-toluenesulfonyl chloride dissolved in 25 ml. of anhydrous chloroform was then added with stirring. The mixture was allowed to stand for 2 hours at 0° and for 4 hours at room temperature. The solution again was cooled to 0° and 27 ml. of benzoyl chloride was added dropwise with stirring. The mixture was allowed to stand at room temperature overnight, cooled to 0°, and 5 ml. of water was added dropwise with stirring. Temperature was raised to that of the room and 20 ml. more of water was added. Chloroform (150 ml.) was added to the mixture and the chloroform solution was washed successively with dil. HCl, satd. bicarbonate solution, water and then dried over anhydrous sodium sulfate. After filtration, chloroform was removed under reduced pressure and the residue was triturated with hot ethanol. The ethanol-insoluble product was filtered (30 g., 60%) and recrystallized by dissolving in a minimum of acetone and adding hot ethanol to incipient crystallization. The yield of pure compound was 23.7 g. (47%), m.p. 153–155°, $[\alpha]^{25}\mathrm{D}$ +30.2° (*c* 2, $CHCl_3$).

Anal. Calcd. for $C_{57}H_{52}O_{11}S$: C, 72.42; H, 5.55; S, 3.39. Found: C, 72.26, 72.46; H, 5.58, 5.61; S, 3.38, 3.42.

On treatment of this ester with sodium iodide in acetone the theoretical amount of sodium *p*-toluenesulfonate was isolated. The iodo product was found as a sirup.

Anhydro-1-deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol (High Melting Form). (a) **From 2,3,4,5-Tetra-*O*-benzoyl-1-deoxy-6-*O*-tosyl-1,1-bis-(3,4-dimethylphenyl)-D-glucitol.**—Four grams of the tetrabenzoate *p*-toluenesulfonate was dissolved in 200 ml. of methanol. Methanolic sodium hydroxide (46.8 ml. of 0.4925 *N*) then was added and the mixture was refluxed for two hours; 40 ml. of water was added and refluxing was continued for an additional hour. The mixture was cooled and neutralized to phenolphthalein with 0.1 *N* HCl after which it was concentrated until a white solid separated. The product was removed by filtration, washed with water and dried to give 1.9 g. of crude anhydro com-

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(16) L. Hough, D. B. Powell and B. M. Woods, *J. Chem. Soc.*, 4799 (1956).

(17) I. A. Wolff, B. T. Hofreiter, P. R. Watson, W. L. Deatherage and M. M. MacMasters, THIS JOURNAL, **77**, 1654 (1955).

(18) M. Lambert and A. C. Neish, *Can. J. Res.*, **B28**, 83 (1950).

(19) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949.

(20) F. J. Bates and Assocs., "Polarimetry, Saccharimetry and the Sugars," U. S. Govt. Printing Office, Washington, D. C., 1942, p. 484.

pound. The crude was recrystallized from methanol to give 0.77 g. (51%) of pure product of constant m.p. 211–212.5° and specific rotation $[\alpha]^{25}\text{D}$ +53.2° (*c* 1, C_2H_5OH).

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.11; H, 7.92. Found: C, 74.32, 74.34; H, 7.94, 7.83; hydroxyl analysis by the method of Hamlin[15] was 14.60% (theory for three hydroxyls, 14.31%); periodate consumption[19] became constant at 0.94 mole per mole of anhydro compound indicating that 2 of the 3 hydroxyl groups present are vicinal; this particular oxidation was very slow, showing periodate consumption in moles per mole of compound of 0.45 at 6 hours, 0.9 at 24 hours and 0.94 at 44 hours.

(b) **By Fusion of I with Potassium Hydrogen Sulfate.**—Ten grams of I was fused *in vacuo* (40–50 μ) and 1 g. of $KHSO_4$ was added to the fused mass. The mixture was then fused at 40–50 μ for 5 minutes, cooled, fused for 5 minutes, cooled and finally fused for 10 minutes. The light green glass (9.6 g.) was dissolved in methanol and, by fractional crystallization from this solvent, over 4 g. of crude anhydro compound was isolated. Recrystallization from methanol gave the pure anhydro compound, m.p. 210–212°. By concentration of the original mother liquor and treatment with chloroform, chloroform–hexane and benzene a total of 3.6 g. of starting glucitol was recovered as well as an additional 0.5 g. of anhydro derivative. The yield of anhydro compound, based on glucitol converted, was 60%.

The same anhydro compound was isolated in about 7% yield by refluxing I in 6 *N* HCl for 4 hours.

Anhydro-1-deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol (Low Melting Form).—Four grams of I was dissolved in 10 ml. of anhydrous pyridine, the solution cooled to 0° and 2.2 g. of pure *p*-toluenesulfonyl chloride dissolved in 20 ml. of anhydrous chloroform was then added dropwise with rapid stirring. The solution was allowed to stand for 2 hours at 0° and then 4 hours at room temperature. The mixture was again cooled to 0° and 1 ml. of water added dropwise with stirring followed by 4 ml. of water at room temperature. The mixture was taken up in 50 ml. of chloroform and the chloroform solution washed with dil. HCl, satd. sodium bicarbonate solution, water and then dried over anhydrous sodium sulfate. The chloroform, on evaporation, left a white solid which was crystallized from methanol to give 1.4 g. (37%) of crude product. The anhydro compound was recrystallized from methanol to constant m.p. 159–160° and specific rotation $[\alpha]^{25}\text{D}$ +37.8° (*c* 1, $CHCl_3$), +76.9° (*c* 0.4, C_2H_5OH).

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.11; H, 7.92; OH, 14.31. Found: C, 74.22, 74.08; H, 7.66, 7.74; OH, 14.30.

Periodate oxidation[19] showed the consumption of 1.03 moles of periodate per mole of anhydro compound indicating that two of the hydroxyl groups in the molecule are vicinal. In contrast to the periodate oxidation of the anhydro compound, m.p. 211–213°, the oxidation of this compound was very rapid, reaching 1.03 moles within a half-hour.

Dianhydro-1-deoxy-1,1-bis-(3,4-dimethylphenyl)-D-glucitol. (a) **From I.**—One gram of I was fused with 0.03 g. of benzenesulfonic acid at 150–170° for 45 minutes. After cooling, the resulting dark glass (0.86 g.) was dissolved in 10 ml. of benzene. A 5-ml. aliquot, containing an estimated 0.43 g. of product, was put on a column of alumina (0.75 in. × 7 in.). The column was then eluted successively with 250-ml. portions of hexane, benzene, ether and ethanol; 50-ml. fractions were collected. From the hexane fractions was isolated 70 mg. of solids which proved to be 3,3′,4,4′-tetramethylstilbene (see below). The product eluted with ether and ethanol (217 mg.) crystallized spontaneously on removal of solvent, m.p. 112.5–114°. The product was recrystallized from ether–hexane to give pure dianhydro compound, m.p. 112.5–114°, $[\alpha]^{25}\text{D}$ +234° (*c* 1, $CHCl_3$).

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.06; H, 7.75; OH, 5.03. Found: C, 77.91, 78.12; H, 7.98, 7.87; OH, 5.23.

It should be noted here that any I remaining in such a reaction mixture as that cited above will be very tenaciously absorbed on alumina. Of the many solvents used in attempting to remove the glucitol from a column of alumina only glacial acetic acid was effective, although much inorganic material was removed at the same time.

(b) **From the Anhydro Compound, M.p. 211–213°.**—The anhydro compound (740 mg.) was treated with benzenesulfonic acid in the same fashion as in part (a). Chromatography of 500 mg. of crude product gave 130 mg. of substituted stilbene and 220 mg. of dianhydro compound.

3,3′,4,4′-Tetramethylstilbene.—This hydrocarbon was, as shown above, isolated from reaction mixtures resulting from the fusion of either I or the monoanhydro compound (m.p. 211–213°) in the presence of benzenesulfonic acid. It was also isolated in 3.5% yield by vacuum distillation of the fusion mixture of I with $KHSO_4$. The latter fusion mixture, in the absence of distillation, gave exclusively the high melting monoanhydro compound (*q.v.*). The stilbene was also formed when compound I was heated with HCl in the following manner: 5 g. of glucitol was refluxed in 6 *N* HCl for 4 hours. The solution was cooled, neutralized and evaporated to dryness. Methanol was added to the residue, inorganic material filtered off and the filtrate refrigerated. About 200 mg. of crystals, m.p. 138–140°, separated. Recrystallization from ethanol gave 3,3′,4,4′-tetramethylstilbene, m.p. 140–141°.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.46; H, 8.54. Found: C, 90.74, 90.47; H, 8.49, 8.41.

Solvent was removed from the mother liquor and the residue was slurried in chloroform. The chloroform-insoluble material was removed by filtration to give 350 mg. of product which, when recrystallized from methanol, melted at 211–213°. This compound gave no m.p. depression with the monoanhydro compound of m.p. 211–213°.

When Compound I was heated at 100° in a sealed tube with concd. HCl, the stilbene could be isolated by chromatography of the crude product. No anhydro compound was isolated in this case.

Using the same technique, 1-deoxy-1,1-bis-(4-methylphenyl)-D-glucitol when heated with concd. HCl in a sealed tube for 2 hours at 100° gave a 5.5% yield of the known 4,4′-dimethylstilbene, m.p. 181–182°, literature value[21] 179°. The dibromo derivative had m.p. 208–210°.

Ultraviolet absorption spectra on both hydrocarbons showed the presence of stilbene-like structures. The infrared spectra confirmed the presence of symmetrically disubstituted olefins: with 4,4′-dimethylstilbene the *p*-disubstituted aromatic was indicated, and with 3,3′,4,4′-tetramethylstilbene the 1,2,4-trisubstituted aromatic was indicated. For the α,α'-dibromo-4,4′-dimethylbibenzyl, the ultraviolet spectrum showed complete disappearance of the stilbene-like structure while the infrared spectrum showed removal of the band due to symmetrically disubstituted olefin and retention of the band due to *p*-disubstituted aromatics.

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[21] K. Brand, *Ber.*, **46**, 2935 (1913).