thick sirup (1.13 g.) which was dissolved in ethanol (50 ml.) and 2*N* aqueous sodium hydroxide (20 ml.) was added. The solution was warmed to 50–60° for 1 hr., evaporated to 25 ml., diluted with water (100 ml.), and chloroform (100 ml.) was added. The chloroform layer was separated and washed with water until neutral, dried (potassium carbonate) and evaporated to give benzyl 4-*O*-(β-D-xylopyranosyl)-2,3-di-*O*-benzyl-D-xyloside as a sirup (0.44 g.).

Hydrogenation of benzyl 4-O-(β-D-xylopyranosyl)-2,3-di-O-benzyl-D-xyloside. The aforementioned sirup (0.44 g.) was dissolved in ethanol (50 ml.), and palladium-charcoal catalyst (1.4 g.) was added. The catalyst was prepared by dissolving palladium chloride (0.3 g.) in 2 *N* hydrochloric acid to which acid-washed charcoal (1.5 g.) was added and the mixture was shaken with hydrogen at atmospheric pressure until the supernatant solution was colorless (about 2 hr.). The palladium-charcoal catalyst was filtered, washed with water until the washings were free of chloride ion, then with ethanol (500 ml.), and the catalyst was used immediately. The hydrogenation apparatus and reaction flask were flushed with hydrogen and the reaction mixture was shaken for 24 hr. after which time no more hydrogen was taken up. The charcoal catalyst was removed by filtration, washed with aqueous methanol, and the combined filtrates were evaporated to a sirup (0.22 g.). Chromatographic analysis with 1-butanol-ethanol-water (4:1:5) and *p*-anisidine hydrochloride spray reagent indicated three components, xylose, xylobiose and an unknown component which had an R_F value between the other two compounds. (This unknown compound was probably a 1:1′-linked xylose disaccharide.)

Isolation of 4-O-β-D-xylopyranosyl-β-D-xylose (xylobiose). The mixture of three components described above was applied to three pieces of Whatman No. 3 MM filter paper (8 × 22 in.) and the paper was irrigated with 1-butanol-ethanol-water (4:1:5) for 3 days. Elution of the appropriate section of the paper with aqueous methanol and evaporation of the eluant provided xylobiose (67 mg.) which had $[\alpha]_D^{23}$ −15° (*c* 2.2 in water) and migrated as a single spot on a paper chromatogram and on electrophoresis with borate buffer. However, even after nucleating this material with an authentic sample it did not crystallize. Since the optical rotation {$[\alpha]_D^{23}$ −15° (*c*, 2.2 in water)} was more positive than the literature value {$[\alpha]_D$ −25.5° (equil. value)} it appeared that some of the α 1→4 linked disaccharide was present.

The xylobiose obtained above was heated at 95–100° for 2 hr. with acetic anhydride (5 ml.), sodium acetate (0.15 g.) and acetic acid (1 ml.) and evaporated to dryness under reduced pressure. Water (25 ml.) and chloroform (25 ml.) were added to the residue and after separation of the layers the aqueous layer was washed with chloroform (3 × 25 ml.). The combined chloroform extracts were dried (potassium carbonate) and evaporated to give 120 mg. of a sirup which crystallized when nucleated with an authentic sample of xylobiose hexaacetate, m.p. and mixed m.p. 155–156°, $[\alpha]_D^{22}$ −76° (*c*, 1 in chloroform) after recrystallization from ethanol.

Anal. Calcd. for $C_{22}H_{30}O_{11}$: C, 49.44; H, 5.62; Found: C, 49.57; H, 5.69.

A solution of xylobiose hexaacetate (41 mg.) in methanol (10 ml.) was treated with metallic sodium (3 mg.). After keeping overnight the solution was evaporated to dryness and the residue recrystallized from methanol. The 4-*O*-β-D-xylopyranosyl-β-D-xylose (xylobiose) thus obtained had a m.p. and mixed m.p. of 184°, $[\alpha]_D^{23}$ −23° (equil. value, *c*, 0.5 in water); lit.[6,21] m.p. 185–186°, $[\alpha]_D^{25}$ −32° to −25.5°.

Acknowledgment. The authors thank Professor J. K. N. Jones for a specimen of xylobiose and Professor R. L. Whistler for a specimen of xylobiose hexaacetate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Synthesis of Quaternary Ammonium Salts by Displacement of Benzenesulfonate Esters with Trimethylamine

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Received April 24, 1961

Quaternary salts have been prepared directly by the reaction of trimethylamine with 1,6-di-*O*-benzenesulfonyl-D-mannitol, 1,6-di-*O*-benzenesulfonyl-3,4-*O*-isopropylidene-D-mannitol, 1,6-di-*O*-benzenesulfonyl-2,5-anhydro-D-glucitol, and pentaerythritol tetrabenzenesulfonate.

The syntheses of certain bis- and other quaternary ammonium salts were undertaken as a result of our interest in compounds with ganglionic blocking activity. Bisquaternary salts have been prepared by reaction of ditosylates with secondary amines followed by reaction with methyl iodide.[2] Diepoxides were converted into bistertiary amines by reaction with secondary amines.[3] Quaternization was effected with methyl iodide or dimethyl sulfate. In the work described herein, the direct formation of quaternary salts was realized by the nucleophilic displacement of benzenesulfonate esters with trimethylamine.

Quaternary salts of pyridine have been obtained by refluxing sulfonic acid esters of primary alcohols with anhydrous pyridine. 2,3-*O*-Isopropylidene-1-*O*-tosyl-D,L-glyceritol,[4] 2,3:4,5-di-*O*-isopropyli-

(1) The portion of this paper by Donald L. Schmidt constitutes a part of a dissertation to be presented to the faculty of the University of Utah in candidacy for the degree of Doctor of Philosophy.

(2) A. C. Cope and E. E. Schweizer, *J. Am. Chem. Soc.*, 81, 4577 (1959).

(3) L. Vargha and E. Kasztreiner, *Chem. Ber.*, 92, 2506 (1959).

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dene-1,6-di-*O*-tosylgalactitol,[5] and 1,2,3,4-tetra-*O*-acetyl-6-*O*-mesyl-β-D-glucopyranose[6] have yielded the corresponding pyridinium salts, but the sulfonate ester groups of secondary alcohols in 2,5-di-*O*-tosyl-1,3:4,6-di-*O*-benzylidenegalactitol did not react under the same conditions.[5]

Esters of benzenesulfonic acid were selected instead of the more thoroughly investigated derivatives of *p*-toluenesulfonic acid first because of their ease of preparation and secondly because of their higher reactivity toward nucleophilic reagents. In an investigation[7] on the reaction of polyvinyl sulfonates with tertiary amines, the apparent rates of quaternization by pyridine decreased in the order: polyvinyl benzenesulfonate, polyvinyl *p*-toluenesulfonate. Tertiary amines with one or more alkyl groups were found to be less reactive than pyridine and its homologs.

The selective esterification of the primary hydroxyl groups of D-mannitol with benzenesulfonyl chloride in pyridine has been described.[8] Acetonation of the resulting 1,6-di-*O*-benzenesulfonyl-D-mannitol gave the 3,4-*O*-isopropylidene derivative. The structure of the latter was demonstrated by an independent synthesis in which authentic 3,4-*O*-isopropylidene-D-mannitol[9] gave the same di-*O*-benzenesulfonate by reaction with benzenesulfonyl chloride and pyridine at a temperature near 0°.

2,5-Anhydro-D-glucitol, hitherto reported[10,11] as a colorless semisolid, was obtained in crystalline form. Reaction with benzenesulfonyl chloride, under conditions providing for reaction at primary hydroxyl groups only as in the above two examples, gave a di-*O*-benzenesulfonate presumed to be 1,6-di-*O*-benzenesulfonyl-2,5-anhydro-D-glucitol.

Compounds having analyses corresponding to the di-*O*-benzenesulfonates of 1,4:3,6-dianhydro-D mannitol and 1,4:3,6-dianhydro-D-glucitol were obtained by effecting sulfonation under the same conditions as previously described but at a higher temperature.

Reaction of the several benzenesulfonate esters with trimethylamine gave quaternary salts, demonstrating that the amine was an effective nucleophilic reagent. 1,6-Di-*O*-benzenesulfonyl-D-mannitol, 1,6-di-*O*-benzenesulfonyl-2,5-anhydro-D-glucitol, and 1,6-di-*O*-benzenesulfonyl-3,4-*O*-isopropylidene-D-mannitol were found to react with anhydrous trimethylamine at room temperature to give the bisquaternary salts. The reactions were carried out conveniently in carbonated beverage bottles. Cyclic ethers, formed by internal displacement, if obtained were not detected. The reactivity of pentaerythritol tetrabenzenesulfonate toward trimethylamine was appreciably depressed as would be expected as a consequence of the neopentyl type of structural grouping. Indeed the demonstration of displacement of all four functions by trimethylamine with good yield of product was not expected. In all of these examples the sulfonic ester group is that formed from primary alcohols. Benzenesulfonate ester groups derived from secondary alcohols were also reactive toward trimethylamine but required a somewhat higher reaction temperature. 1,4:3,6-Dianhydro-D-mannitol dibenzenesulfonate and 1,4:3,6-dianhydro-D-glucitol dibenzenesulfonate reacted with trimethylamine to give crystalline products. Analytical samples of the bisquaternary salts were difficult to obtain and, as syntheses of very closely related compounds were reported in the literature,[12] additional work on these compounds was abandoned.

Purification of the quaternary ammonium salts was found to be difficult to effect by the usual recrystallization procedure. Ion-exchange chromatography proved to be a much more efficient method. Fractions containing organic material were readily located by testing aliquots with alkaline permanganate. The method also served to exchange anions associated with the quaternary salts.

EXPERIMENTAL[13,14]

1,6-Di-O-benzenesulfonyl-3,4-O-isopropylidene-D-mannitol. 3,4-*O*-Isopropylidene-D-mannitol[9] (12 g.) was dissolved in 80 g. of anhydrous pyridine and the resulting solution cooled to 0°. Redistilled benzenesulfonyl chloride (12 g.) was added slowly and the reaction mixture was maintained at 0° for 12 hr. Water was then added in small portions while stirring and keeping the temperature from rising. The resulting solution was poured into ice and water. 1-6-Di-*O*-benzenesulfonyl-3,4-*O*-isopropylidene-D-mannitol (10 g., 59%) crystallized, m.p. 114–115°. An analytical sample, m.p. 115–115.5°, $[\alpha]_D^{25}$ +47° (*c*, 3.5 chloroform), was obtained after five recrystallizations from ethanol-water. As the compound was found to be unstable at elevated temperatures, drying was effected at room temperature for 14 hr. at 2 mm.

Anal. Calcd. for $C_{21}H_{26}O_{10}S_2$: C, 50.20; H, 5:19. Found: C, 50.21; H, 5.48.

Anhydrous hydrogen chloride (14 g.) was dissolved in 500 ml. of anhydrous acetone. 1,6-Di-*O*-benzenesulfonyl-D-mannitol[8] (40 g.) was added and the resulting solution was allowed to stand overnight. Basic lead carbonate (200 g.) was added and the suspension was mechanically stirred for 24 hr. The solid was filtered and more (100 g.) basic lead carbonate added. The resulting suspension was mechanically stirred for 3 days. The solid was filtered and the filtrate evaporated to a sirup. The latter was dissolved in ethanol and

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(6) B. M. Iselin and J. C. Sowden, *J. Am. Chem. Soc.*, 73, 4984 (1951).

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(9) P. Brigl and H. Grüner, *Ber.*, 67, 1969 (1934).

(10) R. C. Hockett, M. Zief, and R. M. Goepp, Jr., *J. Am. Chem. Soc.*, 68, 935 (1946).

(11) P. Brigl and H. Grüner, *Ber.*, 66, 1945 (1933); 67, 1582 (1934).

(12) A. C. Cope and T. Y. Shen, *J. Am. Chem. Soc.*, 78, 3177 (1956).

(13) Melting points are uncorrected.

(14) Elemental analysis by K. W. Zimmermann, Australian Microanalytical Service, University of Melbourne.

water added to the clouding point. After refrigeration of the resulting mixture for 24 hr., 24 g. (55%) of 1,6-di-*O*-benzenesulfonyl-3,4-*O*-isopropylidene-D-mannitol, m.p. 113–114°, was obtained. A mixture of the product synthesized by this route and the compound formed by reaction of benzenesulfonyl chloride with 3,4-*O*-isopropylidene-D-mannitol melted at 113–115°. The infrared spectra of the compounds prepared by the two routes were identical.

2,5-Anhydro-D-glucitol. 2,5-Anhydro-1,6-di-*O*-benzoyl-D-glucitol (16 g.), prepared by the procedure of Brigl and Grüner,[11] was dissolved in 350 ml. of absolute methanol and the resulting solution cooled to 0°. To this, 35 ml. of 0.5*M* barium methoxide was added and the mixture was allowed to react at 4° for 15 hr. The barium methoxide was neutralized with aqueous sulfuric acid, and the barium sulfate removed by filtration. The filtrate was evaporated to a sirup under reduced pressure and dissolved in chloroform. Upon adding a few drops of petroleum ether (b.p. 30–60°) to this solution, crystallization was initiated. 2,5-Anhydro-D-glucitol was obtained in an amount of 2 g. (34%), m.p. 130–131°. An analytical sample, m.p. 130–131°, $[\alpha]_D^{25}$ −53° (*c*, 4.1 water), was obtained by recrystallization from ethanol-chloroform. The compound was previously obtained as a colorless semisolid.[10]

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 43.26; H, 7.31.

1,6-Di-O-benzenesulfonyl-2,5-anhydro-D-glucitol. 2,5-Anhydro-D-glucitol (2 g.) was dissolved in 30 ml. of anhydrous pyridine and the resulting solution was cooled to 0°. Redistilled benzenesulfonyl chloride (10 ml.) was added in portions, and the reaction mixture was allowed to stand at 4° for 24 hr. It was then poured into 150 g. of ice containing 9 ml. of sulfuric acid. The resulting mixture was extracted with 75 ml. of chloroform. The organic phase was washed three times with cold water and then dried over anhydrous sodium sulfate. Addition of petroleum ether (b.p. 30–60°) to the chloroform solution yielded 3.4 g. (57.5%) of crystalline 1,6-di-*O*-benzenesulfonyl-2,5-anhydro-D-glucitol, m.p. 108–110°. An analytical sample, m.p. 109–109.5° and $[\alpha]_D^{25}$ + 21° (*c*, 1.8 chloroform), was obtained by repeated recrystallization from chloroform-petroleum ether.

Anal. Calcd. for $C_{18}H_{20}O_9S_2$: C, 48.64; H, 4.54. Found: C, 49.15; H, 4.82.

2,5-Di-O-benzenesulfonyl-1,4:3,6-dianhydro-D-mannitol. 1,4:3,6-Dianhydro-D-mannitol[15] (6.5 g.) was converted into the 2,5-di-*O*-benzenesulfonyl derivative, 10.5 g. (55%), m.p. 106–107°, $[\alpha]_D^{25}$ + 196° (*c*, 11.3 chloroform), by the same procedure as used in the synthesis of 1,6-di-*O*-benzenesulfonyl-2,5-anhydro-D-glucitol except for an increase in reaction temperature to 30° and recrystallized from ethanol.

Anal. Calcd. for $C_{18}H_{18}O_8S_2$: C, 50.69; H, 4.25. Found: C, 51.22; H, 4.33.

2,5-Di-O-benzenesulfonyl-1,4:3,6-dianhydro-D-glucitol. The compound was prepared by the same method as described above from 1,4:3,6-dianhydro-D-glucitol,[16] m.p. 59–60°, 53%, $[\alpha]_D^{25}$ + 113° (*c*, 10.0 chloroform).

Anal. Calcd. for $C_{18}H_{18}O_8S_2$: C, 50.69; H, 4.25. Found: C, 51.04; H, 4.38.

1,6-Dideoxy-1,6-bis(dimethylamino)-D-mannitol dimethobenezenesulfonate. 1,6-Di-*O*-benzenesulfonyl-D-mannitol[3] (50 g.) was placed in a 16 ounce carbonated beverage bottle. A calcium chloride drying tube was inserted in the top, and the bottle was thoroughly cooled by immersion in a mass of chopped Dry Ice. Anhydrous trimethylamine (100 g.) previously cooled in a bath of acetone–Dry Ice was added to the bottle. The bottle was closed using a commercial cap which was crimped on the top in the usual fashion. The bottle was removed from the cooling bath and allowed to warm to room temperature and retained at that temperature for 10 hr. The bottle was then immersed in an ice-salt bath and opened. A tube leading into an aqueous hydrochloric acid solution was attached, and the excess trimethylamine was allowed to escape at room temperature. After all visible liquid was lost, the bottle was immersed in a boiling water bath and residual trimethylamine removed under decreased pressure (aspirator). Ethyl acetate was added to the bottle, and the white solid was broken with a glass rod and collected on a filter. The product was dissolved in a minimum of hot absolute ethanol and a sufficient amount of ethyl acetate added to initiate crystallization. An amount of 60 g. (96%) of 1,6-dideoxy-1,6-bis(dimethylamino)-D-mannitol dimethobenzenesulfonate, m.p. 190–195°, was obtained. An analytical sample, m.p. 196–196.3°, was prepared by recrystallizing eight times from absolute ethanol–ethyl acetate and then drying the sample at 136° for 3 days at 0.5 mm.

Anal. Calcd. for $C_{24}H_{40}O_{10}N_2S_2$: C, 49.64; H, 6.94; N, 4.82. Found: C, 49.98; H, 7.05; N, 4.54.

1,6-Dideoxy-1,6-bis(dimethylamino)-D-mannitol dimethiodide, m.p. 257–259°, was previously reported.[3]

1,6-Dideoxy-1,6-bis(dimethylamino)-D-mannitol dimethochloride. 1,6-Dideoxy-1,6-bis(dimethylamino)-D-mannitol dimethobenzenesulfonate (30 g.) was dissolved in a solution of 250 ml. of methanol and 100 ml. of chloroform. The resulting solution was cooled in an ice bath and saturated with anhydrous hydrogen chloride. The yield of white crystals, m.p. 300° dec., was 15 g. (86%). The dimethochloride was recrystallized by dissolving in a minimum of hot water, addition of ethanol to the saturation point, and then dropwise incorporation of ethyl acetate to induce crystallization. An analytical sample was prepared by recrystallizing eleven times and drying at 136° at 0.5 mm. for 3 days.

Anal. Calcd. for $C_{12}H_{30}O_4N_2Cl_2$: C, 42.73; H, 8.97; Cl, 21.02. Found: C, 42.69; H, 8.91; Cl, 21.06.

Ion-exchange chromatography of 1,6-dideoxy-1,6-bis(dimethylamino)-3,4-O-isopropylidene-D-mannitol dimethobenzenesulfonate. 1,6-Dideoxy-1,6-bis(dimethylamino)-3,4-*O*-isopropylidene-D-mannitol dimethobenzenesulfonate was prepared from 1,6-di-*O*-benzenesulfonyl-3,4-*O*-isopropylidene-D-mannitol (5 g.) in the same manner as described for 1,6-dideoxy-1,6-bis(dimethylamino)-D-mannitol dimethobenzenesulfonate. The sirup obtained was chromatographed on a Dowex (50–150)[17] column using the general procedure of Calmon and Kressman,[18] applying 1*M* sodium sulfate as the developer and locating organic material by spot testing with a solution of 1% potassium permanganate in 2.5*N* sodium hydroxide. 1,6-Dideoxy-1,6-bis(dimethylamino)-3,4-*O*-isopropylidene-D-mannitol dimethobisulfate (1.1 g., 23%; m.p. 210–214° dec.) was isolated from appropriate fractions by evaporation of solvent. The disulfate salt was passed through an anion resin (Dowex 1-X8)[17] charged with iodide. The solution from the column gave a white crystalline solid in essentially quantitative yield after evaporation of solvent. 1,6-Dideoxy-1,6-bis(dimethylamino)-3,4-*O*-isopropylidene-D-mannitol dimethiodide, m.p. 285–290° dec. (reported[3] m.p., 272° dec.), was recrystallized from ethanol-water.

Anal. Calcd. for $C_{15}H_{34}O_4N_2I_2$: C, 32.16; H, 6.12. Found: C, 32.22; H, 6.03.

1,6-Dideoxy-1,6-bis(dimethylamino)-2,5-anhydro-D-glucitol dimethobenzenesulfonate. The compound was synthesized from 1,6-di-*O*-benzenesulfonyl-2,5-anhydro-D-glucitol by the same method as described for 1,6-dideoxy-1,6-bis(dimethylamino)-D-mannitol dimethobenzenesulfonate. The sirup originally obtained crystallized, m.p. 194.5–196°, from a chloroform solution after standing for 6 months.

Anal. Calcd. for $C_{24}H_{38}O_9N_2S_2$: C, 51.23; H, 6.81. Found: C, 51.39; H, 6.75.

Tetrakis(dimethylaminomethyl)methane tetramethobenzene-

(15) P. Brigl and H. Grüner, *Ber.*, **65**, 641 (1932).

(16) R. C. Hockett, H. G. Fletcher, Jr., E. L. Sheffield, and R. M. Goepp, Jr., *J. Am. Chem. Soc.*, **68**, 927 (1946).

(17) A product of the Dow Chemical Co., Midland, Mich.

(18) C. Calmon and T. R. E. Kressman, *Ion Exchangers in Organic and Biochemistry*, Interscience, New York, 1957, pp. 157–175.

sulfonate. Pentaerythritol tetrabenzenesulfonate[19] (1.5 g.), 15 ml. of anhydrous tetrahydrofuran, and 35 ml. of anhydrous trimethylamine were sealed in a Carius bomb tube. The reaction container was immersed in an oil bath and maintained at a temperature of 115° for 5 days during which time the product precipitated. The tube was opened and volatile compounds removed to yield tetrakis(dimethylaminomethyl)methane tetramethobenzenesulfonate. Recrystallization from ethanol–ethyl acetate gave 0.40 g. (20%); m.p. 300° dec. An analytical sample was prepared by repeated recrystallizations from the same solvent.

(19) E. R. Buchman, U. S. Patent **2,703,808** (March 8, 1955).

Anal. Calcd. for $C_{41}H_{64}O_{12}N_4S_4$: C, 52.77; H, 6.91. Found: C, 52.40; H, 7.12.

Other quaternary salts of tetrakis(dimethylaminomethyl)-methane have been reported.[20]

Acknowledgment. We are very grateful to the Strasenburgh Laboratories for financial support and for their interest, encouragement, and advice.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Synthesis of 1,5-Di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose from D-Arabitol[1,2]

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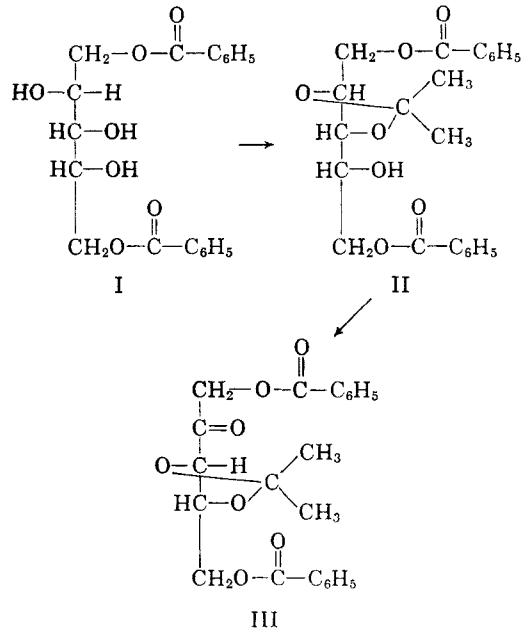
Received May 2, 1961

The pentitol derivative, 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol, has been prepared and the position of the acetone group established. Oxidation with chromium trioxide gave 1,5-di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose. This confirms the general applicability of this oxidative route to the synthesis of derivatives of the rare ketopentoses.

Although D-xylulose-5-phosphate was shown in 1956 to be an intermediate in the carbohydrate metabolism of both plants and animals,[4] there exists as yet no chemical method for its synthesis. In exploratory studies directed toward this end, we have prepared 1,5-di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose (III) by a route which may be applicable to other xylulose esters. This general method[5] was previously employed in the synthesis of a derivative of another rare ketopentose, D-ribulose.

In the work herein described, D-arabitol, a readily available starting material, was benzoylated using a modification of the published method.[6] The 1,5-di-*O*-benzoyl-D-arabitol (I) so obtained was acetonated giving 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol (II). The position of the acetone group in II was established as C-2–C-3 by comparing the tribenzoate, prepared by benzoylation and subsequent deacetonation, with the tribenzoate prepared by debenzalation of the known 1,4,5-tri-*O*-benzoyl-2,3-*O*-benzylidene-D-arabitol.[6] The two tribenzoates



were identical with respect to optical rotation and infrared spectra. Interestingly, the tribenzoate derived from the benzylidene tribenzoate melted at 104° while that derived from the isopropylidene tribenzoate melted at 93–94°. However, infrared spectra and cross-seeding established that the two tribenzoates were dimorphic. The structure assigned to the isopropylidene tribenzoate is consistent with the finding that one mole of periodate was consumed by the acetone compound produced on saponification. Compound II was oxidized using chromium

(1) This report is based on a portion of the thesis submitted by David H. Rammler to the Graduate School of the University of California, Berkeley, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) This work was supported in part by a grant from the American Cancer Society.

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(5) D. H. Rammler and D. L. MacDonald, *Arch. Biochem. Biophys.*, **78**, 359 (1958).

(6) W. T. Haskins, R. M. Hann and C. S. Hudson, *J. Am. Chem. Soc.*, **65**, 1663 (1943).