

p-hydroxytetraphenylmethane; m. p. and mixed m. p. 278°.

Anal. Calcd. for C₂₈H₂₀O: C, 89.28; H, 6.66. Found: C, 88.63; H, 6.83.

Summary

Triphenylchloromethane reacts with silver hyponitrite to give benzopinacol diphenyl ether, benzophenone, triphenylmethyl peroxide, phenol,

triphenylmethyl, triphenylcarbinol and *p*-hydroxytetraphenylmethane. The interpretation rests upon the assumption that triphenylmethyl hyponitrite is first formed and then decomposes with the liberation of the triphenylmethoxyl radical.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Disaccharides in "Hydrol"

BY GEORGE H. COLEMAN, MARION A. BUCHANAN AND PHILIP T. PAUL

In the commercial production of crystalline *d*-glucose by the hydrolysis of corn starch with dilute hydrochloric acid there is obtained a mother liquor known as "hydrol."

The concentrated hydrol contains about 75% of dissolved solids of which one-third is not fermentable by yeast. Berlin¹ has identified gentiobiose as one of the constituents of the non-fermentable portion. By acetylation he obtained a yield of β -octaacetylgentiobiose corresponding to 18.3% of the non-fermentable material.

Fischer² obtained a non-fermentable product which he called "isomaltose" by allowing *d*-glucose to stand in concentrated hydrochloric acid for about fifteen hours at 10–15°. Berlin³ observed that the properties of the crude non-fermentable material from hydrol closely resembled those of isomaltose. He prepared isomaltose from *d*-glucose according to Fischer's method and from this by acetylation obtained β -octaacetylgentiobiose.

Pictet and Georg⁴ by acetylation of Fischer's product also obtained gentiobiose octaacetate but pointed out that gentiobiose represented only a small percentage of the crude material. By fractional precipitation of the acetylated material they were able to obtain in addition to gentiobiose octaacetate the octaacetate of another disaccharide which they called "isomaltose."

Zemplén and Bruckner⁵ synthesized 1- β -methyl heptamethyl-6- α -glucosidoglucose and thinking that Pictet's isomaltose might be 6- α -glucosidoglucose they repeated Pictet's work and methylated the isomaltose fraction. As a result of their

work they concluded that Pictet's isomaltose was not a pure compound but was a mixture which contained 6- α -glucosidoglucose.

The present work was undertaken for the purpose of identifying if possible other material than gentiobiose in the non-fermentable portion of hydrol. Commercial hydrol⁶ was fermented by yeast and non-fermentable material isolated by the method used by Berlin. This product was methylated using a combination of the dimethyl sulfate-sodium hydroxide method of Haworth⁷ and the methyl iodide silver oxide method of Purdie and Irvine.⁸ After several methylations there was obtained a fraction which distilled at about 200° under 1-mm. pressure. The methoxyl and molecular weight values of this product corresponded to an octamethyl disaccharide. After standing for some time partial crystallization occurred. When this partial crystallization was apparently complete the viscous sirup was separated from the crystals by centrifuge filtration. The crystalline material represented about 20% of this product and was identified as heptamethyl β -methylgentiobioside having a specific rotation of -24° . It was identified by its physical properties and by hydrolysis and isolation of the products of hydrolysis. The sirup representing about 80% of the product had a specific rotation of $+80^\circ$. Zemplén and Bruckner record a specific rotation of $+95^\circ$ for 1- β -methylheptamethyl-6- α -glucosidoglucose.

The methoxyl content and the molecular weight of this sirup agreed with the calculated values

(6) The authors wish to express their appreciation to William B. Newkirk and Arthur Pulfry of the Corn Products Refining Company for their kindness in supplying the hydrol used and for suggestions made in connection with this work.

(7) Haworth, *J. Chem. Soc.*, **107**, 8 (1915); Haworth and Leitch, *ibid.*, **113**, 188 (1918).

(8) Purdie and Irvine, *ibid.*, **83**, 1021 (1903).

(1) Berlin, *THIS JOURNAL*, **48**, 2627 (1926).

(2) Fischer, *Ber.*, **23**, 3687 (1890).

(3) Berlin, *THIS JOURNAL*, **48**, 1107 (1926).

(4) Pictet and Georg, *Helv. Chim. Acta*, **9**, 612 (1926).

(5) Zemplén and Bruckner, *Ber.*, **64**, 1852 (1931).

for an octamethyl derivative of a disaccharide. Its reducing power after hydrolysis toward Fehling's solution was approximately the same as that of crystalline heptamethyl- β -methylgentiobioside after hydrolysis. Zemlén and Braun⁹ found the reducing power of completely methylated disaccharides after hydrolysis differed very noticeably with the position of the linkage between the two hexose residues. Since gentiobiose is 6- β -glucosidoglucose, it seemed quite possible, in spite of the fact that several disaccharides having the alpha configuration are fermentable by yeast, that a large percentage of the sirup might be 1- β -methylheptamethyl-6- α -glucosidoglucose. In an effort to add further support to this assumption, portions of the sirup were hydrolyzed. 2,3,4,6-Tetramethylglucose and 2,3,4-trimethylglucose were identified as the hydrolysis products.

The specific rotation of heptamethyl- β -methylgentiobioside is -24° . The specific rotation of the non-crystallizable filtrate was $+80^\circ$. From a consideration of these values, the percentage of gentiobiose in hydrol, the amount of crystalline 2,3,4-trimethyl- β -methylglucoside obtained from the hydrolysis of the filtrate and the amount obtained from the hydrolysis of heptamethyl- β -methylgentiobioside it seems probable that the non-crystallizable filtrate contains a methylated disaccharide other than gentiobiose which forms 2,3,4,6-tetramethylglucose and 2,3,4-trimethylglucose upon hydrolysis.

Experimental

An amount of hydrol corresponding to 1500 g. of dry matter was fermented with yeast and the non-fermentable material isolated in essentially the manner described by Berlin. After thorough drying in a vacuum desiccator the product weighed 523 g.

Methylation.—The following is typical of the methylation and distillation procedure used. Two 35-g. portions of the non-fermentable product were methylated with dimethyl sulfate and sodium hydroxide. The products thus obtained were combined and treated twice with methyl iodide and silver oxide. The methylated product weighing about 50 g. was distilled¹⁰ under reduced pressure. A small fraction which distilled below 180° at 1 mm. was discarded. Two fractions boiling above this temperature and a still residue were remethylated with methyl iodide and silver oxide and the distillation repeated. Fraction 1 which weighed 19 g. and distilled at 199 – 204° at 1.1 mm. is typical of the products used in the present work; $[\alpha]^{20}_D +57.5^\circ$ in water.

(9) Zemlén and Braun, *Ber.*, **58**, 2566 (1925).

(10) A distilling flask with a 22 cm. externally heated fractionating column was used. Pressures were determined by a McLeod gage.

Anal. Calcd. for $C_{20}H_{38}O_{11}$: CH_3O , 54.6; mol. wt., 454. Found: CH_3O , 51.7; mol. wt. (freezing benzene), 464.

Heptamethyl- β -methylgentiobioside.—Partial crystallization occurred with all fractions from the last distillation on standing for a few weeks. A portion of fraction 1 was allowed to stand for several months to make sure that the crystallization was practically complete. It was then filtered by centrifuging in a glass crucible having a sintered glass bottom. The filtrate, a clear yellow viscous sirup, was collected in a glass cup arranged for this purpose. From 12.9 g. of the mixture 2.44 g. of solid was obtained. After two crystallizations from petroleum ether it melted at 107 – 108° (uncorr.); $[\alpha]^{20}_D -24.1^\circ$ in water.

Anal. Calcd. for $C_{20}H_{38}O_{11}$: CH_3O , 54.6; mol. wt., 454. Found: CH_3O , 52.4, 54.0; mol. wt. (freezing benzene), 472.

For heptamethyl- β -methylgentiobioside Zemlén¹¹ records a melting point of 109° and a specific rotation of -22.4° in water. Haworth and Wylam¹² record a melting point of 106° and a specific rotation of -33.9° in water.

The reducing power of the crystalline material after hydrolysis was determined by the method used by Zemlén and Braun⁹ except that the amount of cuprous oxide was determined by weighing as such. This was found to be 9.9% of that calculated for an equal weight of *d*-glucose. The viscous clear yellow filtrate was analyzed, $[\alpha]^{20}_D +80^\circ$ in ethyl alcohol.

Anal. Calcd. for $C_{20}H_{38}O_{11}$: CH_3O , 54.6; mol. wt., 454. Found: CH_3O , 53.6; mol. wt. (freezing benzene), 448.

The reducing power after hydrolysis was determined by the method used for the crystalline heptamethyl- β -methylgentiobioside. This was found to be 10.0% of that calculated for an equal weight of *d*-glucose.

Hydrolysis of Heptamethyl- β -methylgentiobioside.—This compound (11.04 g.) was hydrolyzed with 5% hydrochloric acid according to the procedure of Haworth and Wylam. The products of hydrolysis were separated by extraction of the aqueous solution with chloroform.¹³ The 2,3,4,6-tetramethylglucose crystallized spontaneously on removal of the solvent. The melting point after recrystallization was 86° (uncorr.). It was shown to be 2,3,4,6-tetramethylglucose by comparison with an authentic sample.

The trimethylglucose was isolated from the aqueous solution by the method described by Haworth and Wylam.¹² The sirup remaining after evaporation of the solvent under reduced pressure weighed 3.53 g. Three grams of this sirup was converted to the methylglucoside and the product distilled. Two fractions were collected. The first boiling at 135 – 140° (4 mm.) weighed 0.73 g. The second boiling at 140 – 142° (4 mm.) weighed 0.91 g. After standing for several weeks the second fraction partially crystallized. After seeding with the crystals thus obtained the first fraction crystallized readily. A total of 0.61 g. of crystalline material was obtained. After recrystallization from ligroin the melting point was 93° (uncorr.).

(11) Zemlén, *Ber.*, **57**, 698 (1924).

(12) Haworth and Wylam, *J. Chem. Soc.*, **123**, 3120 (1923).

(13) Irvine and Black, *ibid.*, 862 (1926).

Hydrolysis of the Filtrate.—The non-crystallizable filtrate (10.14 g.) was hydrolyzed and the products isolated as described for methylated gentiobiose. The crude tetramethylglucose weighed 5.44 g. After recrystallization from ligroin the melting point was 86° (uncorr.). A mixed melting point with an authentic sample of 2,3,4,6-tetramethylglucose showed no depression.

From the aqueous solution 3.31 g. of a thick sirup was obtained. Two and eight-tenths grams of this sirup was converted to the methylglucoside and the product distilled. A fraction weighing 1.53 g. and boiling at 139–143° (4 mm.) was collected. Upon seeding with crystals of 2,3,4-trimethyl- β -methylglucoside it crystallized readily.

A total of 0.27 g. of crystalline material was obtained. It was shown to be 2,3,4-trimethyl- β -methylglucoside by comparison with an authentic sample.

Summary

1. The non-fermentable material in "hydrol" has been methylated and heptamethyl- β -methylgentiobioside isolated and identified.

2. Evidence for the presence of 6- α -glucosidoglucose in the non-fermentable material has been obtained.

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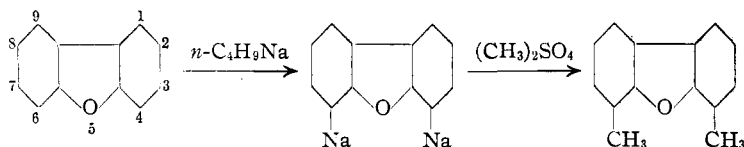
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. V. Dimetalation

BY HENRY GILMAN AND RICHARD V. YOUNG

Introduction

It was previously demonstrated that metalation of dibenzofuran proceeds anomalously to introduce a metal (lithium, sodium, potassium, mercury) in the 4-position.¹ Two of the most important positions, from a biological viewpoint, are 4 and 6. Dibenzofuran undergoes dimetalation to give a 4,6-dimetalated product. The constitution of the 4,6-disiododibenzofuran was established by the following sequence of reactions.



The 4,6-dimethyldibenzofuran was shown to be identical with an authentic specimen prepared by ring closure.²

The disodium compound undergoes the usual replacement reactions, yielding 4,6-diiododibenzofuran with iodine, 4,6-dibenzofurandicarboxylic acid on carbonation, 4,6-dihydroxydibenzofuran on oxidation, and 4,6-dibenzofurandisulfonic acid on oxidation of the disulfonic acid obtained by the action of sulfur dioxide on the disodium compound.

4-Methyldibenzofuran is metalated in the 6-position. The position of the metal was established by carbonating to a 4-methylcarboxylic acid, which on oxidation gave 4,6-dibenzofuran-

(1) THIS JOURNAL, 56, 1415 (1934).

(2) Sugii and Shindo, *J. Pharm. Soc. Japan*, 54, 149 (1934). The authors are grateful to Professor Sugii for a specimen of their 4,6-dimethyldibenzofuran.

dicarboxylic acid. 4-Methoxydibenzofuran is likewise metalated in the 6-position, the organometallic compound being oxidized to a 4-methoxyhydroxydibenzofuran, which on hydrogen iodide cleavage gave 4,6-dihydroxydibenzofuran. These two nuclear substitution reactions are significant from the point of view of orientation for, like dimetalation, they emphasize the essential independence of the benzenoid nuclei, and the highly developed acidities of the 4- and 6-hydrogens. On the basis of the activating effects of a methyl and a methoxyl group, one might have expected some homonuclear substitution, but in every case so far examined metalation takes place predominantly heteronuclearly if a 4-position be occupied.

Experimental Part

Mono- and Dimetalation.—Monometalation of dibenzofuran is effected satisfactorily by a miscellany of organoalkali compounds, all preparations being carried out in a three-necked flask (in an inert atmosphere, preferably nitrogen) provided with a stirrer, condenser and dropping funnel. (a) *From n-butyl-lithium.*—The *n*-butyl-lithium solution in ether (prepared from 0.5 mole of *n*-butyl bromide) is filtered through a loose plug of glass wool directly into a flask containing 0.4 mole of dibenzofuran in ether. The resulting solution is then refluxed with stirring for four to five hours. (b) *From n-butylsodium.*—To a solution of 0.1 mole of dibenzofuran in 60 cc. of ether is added 0.032 mole of di-*n*-butylmercury and 2.3 g. or 0.1 atom of sodium. Reaction sets in almost immediately and is allowed to proceed with stirring for sixteen hours.

Dimetalation is best realized with *n*-butylsodium. To a solution of 0.032 mole of dibenzofuran in 75 cc. of ether