acid was obtained by carbonation of the reaction mixtures, although 2-dibenzofurancarboxylic acid was isolated in similar reactions with dibenzofuran.[8]

Summary

New procedures are given for the preparation of some aminodibenzothiophenes and aminodibenzothiophene-5-dioxides. Additional proof is presented for the structure of 2,8-diacetyldibenzothiophene.

Ames, Iowa Received July 26, 1948

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[8] Gilman and Haubein, *ibid.*, **67**, 1033 (1945).

[Contribution from the Department of Chemistry, State University of Iowa]

The Alcoholysis of Sugar Derivatives

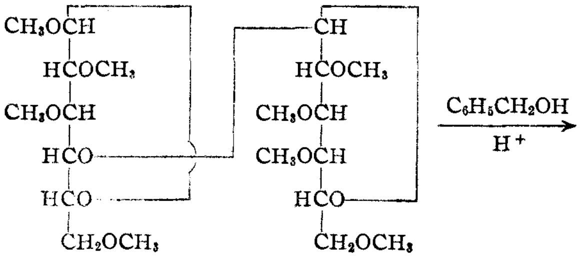
By Elmer E. Combs,[1] Chester M. McCloskey, Robert L. Sundberg and George H. Coleman[2]

The study of the alcoholysis reaction was undertaken in this Laboratory with the object of developing a method for the preparation of 2,3,6-trimethylglucose. The method was found to be satisfactory enough to warrant investigation of a larger field than originally planned with the object of obtaining a practical method of separation of the alcoholysis products of methylated disaccharides.

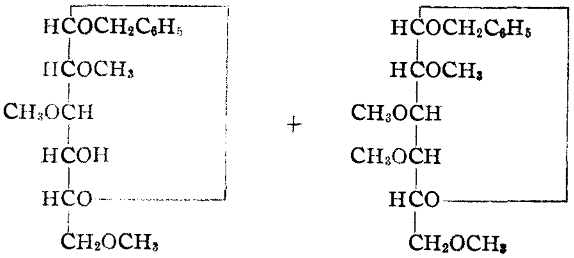
Berner[3] investigated the methyl alcoholysis of sucrose and other carbohydrates. From sucrose he obtained glucose and methyl fructofuranoside. Voss and Wachs[4] investigated the reaction rates of alcoholysis, acetolysis and hydrolysis of phenyl glucosides and found that the length of time required for completion of the reaction increased in the order mentioned with the reaction constant for methyl alcoholysis being over one-hundred times as great as that for hydrolysis. Methyl alcohol was used by the above workers and by others[5]; however, the use of methyl alcohol had the disadvantage that the hydrolysis rate of the methyl glycoside approximated that of the original compound. Considerable decomposition of the free sugars sometimes resulted during hydrolysis making it difficult to obtain crystalline compounds.

Richtmyer[6] studied the conditions under which benzyl glycosides are cleaved by catalytic hydrogenation. He found that palladium catalysts in glacial acetic acid, at room temperature and atmospheric pressure were capable of cleaving benzyl glycosides giving a quantitative yield of the free sugar. Methylated benzyl glycosides have been shown to be capable of distillation under high vacuum.[7,8] Studies of the benzyl alcoholysis of methyl α-fructofuranoside and of fructose have been described.[9] In view of these findings benzyl alcohol was selected for use in this investigation of the alcoholysis reaction.

The general procedure of benzyl alcoholysis is illustrated using methyl heptamethyl-β-lactoside.



Methyl heptamethyl-β-lactoside



Benzyl 2,3,6-trimethyl-D-glucoside

Benzyl 2,3,4,6-tetramethyl-D-galactoside

The benzyl glycosides obtained were distilled under vacuum and the separate fractions redistilled. In eleven runs the yield of the benzyl tetramethylglycoside averaged 87.7% and the yield of the benzyl trimethylglycoside averaged 46.1%. The lower yield of the trimethyl fraction was probably due to its higher boiling point and to the fact that it was subjected to high temperatures of distillation for a longer period of time. For this reason smaller runs generally gave better percentage yields than did larger runs. After separation the benzyl glycosides were catalytically reduced to the free sugar using palladium–charcoal catalyst in glacial acetic acid. In every case a nearly quantitative yield of the free sugar was obtained.

The methylated disaccharides used in this in-

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[1] Abstract of a portion of the dissertation submitted to the Graduate College of the State University of Iowa by Elmer E. Combs in partial fulfillment of the requirement for the degree of Doctor of Philosophy. Deceased Nov. 13, 1948.

[2] Present address, Institute of Textile Technology, Charlottesville, Virginia.

[3] Berner, *Ber.*, **66B**, 1076 (1933).

[4] Voss and Wachs, *Ann.*, **522**, 240 (1936).

[5] Coleman, Rees, Sundberg and McCloskey, This Journal, **67**, 381 (1945).

[6] Richtmyer, *ibid.*, **56**, 1633 (1934).

[7] Hess and Hwang, *Ber.*, **72B**, 1906 (1939).

[8] Hess and Gramberg, *ibid.*, **72B**, 1898 (1939).

[9] Purves and Hudson, This Journal, **59**, 49–56, 1170–1174 (1937).

TABLE I

PHYSICAL CONSTANTS OF BENZYL GLYCOSIDES

		Boiling point,			$[\alpha]^{25}D$ in $CHCl_3$	Analyses, %			
						Calculated		Found	
		°C.	Mm.	$n^{25}D$	(c, 2)	C	H	C	H
1	Benzyl 2,3,4,6-tetramethyl-D-galactoside	114–116	0.020	1.4980	80.3	62.6	8.0	62.79	8.23
2	Benzyl 2,3,4,6-tetramethyl-D-glucoside	110–111	.014	1.4936	76.1	62.6	8.0	63.05	8.01
3	Benzyl 2,3,4-trimethyl-D-glucoside	133–134	.025	1.5080	173	61.5	7.7	61.31	8.07
4	Benzyl 2,3,6-trimethyl-D-glucoside	127–128	.020	1.5110	74.9	61.5	7.7	63.30	7.89
5	Benzyl 2,4,6-trimethyl-D-glucoside	132–133	.014	1.5110	92.5	61.5	7.7	62.13	8.31

vestigation and the benzyl glycosides obtained therefrom were as follows: methyl heptamethyl-β-lactoside → benzyl 2,3,6-trimethylglucoside + benzyl 2,3,4,6-tetramethylgalactoside. Methyl heptamethylmaltoside → benzyl 2,3,6-trimethylglucoside + benzyl 2,3,4,6-tetramethylglucoside. Methylheptamethyl-β-cellobioside→benzyl 2,3,6-trimethylglucoside + benzyl 2,3,4,6-tetramethylglucoside. Methyl heptamethyl-β-melibioside→ benzyl 2,3,4-trimethylglucoside + benzyl 2,3,4,6-tetramethylgalactoside.

Of these four benzyl glycosides none has been previously reported.[10] The physical constants of the four glycosides were determined. The effect of temperature on the rate of the reaction was investigated over the range of 25 to 150°. The higher temperatures were found to cause decomposition and side reactions; 100° was selected as the optimum temperature. It was found that the reaction would not occur in the absence of an acid catalyst and that the rate of the reaction was dependent on the acid concentration. However, high acid concentrations (5% and greater) were to be avoided as causing decomposition and side reactions. The optimum concentration was found to be 2.5%.

p-Toluenesulfonic acid monohydrate was the catalyzing acid used in this investigation. It was sufficiently strong for the purpose and was easily removed by extraction with aqueous ammonia. It was found to cause no harmful side reaction. Dibenzyl ether was usually formed under the reaction conditions, but this did no harm. Hydrochloric acid was first used as the catalyst, but was discontinued as it reacted quickly with the benzyl alcohol to give benzyl chloride, making it difficult to determine the length of effective reaction. The benzyl alcoholysis of methyl heptamethyl-β-lactoside was completed in two hours as compared to twenty-two hours for the hydrolysis.

The benzyl alcoholysis procedure was applied to several monosaccharides for reference purposes, these being trimethyllevoglucosan, 2,3,4,6-tetramethylglucose and 2,4,6-trimethylglucose. In general the reaction conditions and the reaction rates were the same as for the dissacharides.

Experimental

Alcoholysis of Methyl Heptamethyl-β-lactoside.—A mixture of 30 g. of methyl heptamethyl-β-lactoside and 9 g. of *p*-toluenesulfonic acid monohydrate was dissolved in 300 ml. of benzyl alcohol contained in a 500-ml. round-bottomed flask. The flask was heated in an oil-bath at 100° for two hours at atmospheric pressure followed by two hours at aspirator pressure. The solution was cooled and 1 l. of chloroform added. The resulting solution was extracted with 250 ml. of water containing 30 ml. of concd. ammonium hydroxide followed by two extractions with 250 ml. of water. The chloroform layer was dried over potassium carbonate and the solvent distilled off at 0.5 to 1.0 mm. pressure. The amber colored oil was fractionated under reduced pressure through a 10-inch externally heated column packed with platinum gauze, giving two principal fractions. Each fraction was then redistilled separately. The physical constants given are for the redistilled fractions.

Fraction 1: Benzyl 2,3,4,6-tetramethyl-D-galactoside, yield 26 g. (80%), b. p. 114–116° at 0.02 mm., $n^{25}D$ 1.4980, $[\alpha]^{25}D$ 80.3 in chloroform (*c*, 2). *Anal.* Calcd. for $C_{17}H_{26}O_6$; C, 62.6; H, 8.0. Found: C, 62.7; H, 8.23. Catalytic hydrogenation, using palladium-charcoal as the catalyst, gave a quantitative yield of sirupy 2,3,4,6-tetramethyl-D-galactose. On standing at 0° for several days, about 25% of the material crystallized out; m. p. 70.2° (cor.)

Fraction 2: Benzyl 2,3,6-trimethyl-D-glucoside, yield 17.5 g. (51%), b. p. 127–128° at 0.02 mm., $n^{25}D$ 1.5110, $[\alpha]^{25}D$ 74.9 in chloroform (*c*, 2). *Anal.* Calcd. for $C_{16}H_{24}O_6$: C, 61.5; H, 7.7. Found: C, 63.30; H, 7.89. Catalytic hydrogenation of 12.9 g. of this compound in glacial acetic acid gave 6.7 g. of crystalline 2,3,6-trimethyl-D-glucose (73%).

Alcoholysis of Other Methylated Sugars.—All other methylated disaccharides and monosaccharides mentioned above were subjected to the same benzyl alcoholysis procedure as described for octamethyl lactose. The properties of the benzyl glycosides obtained are summarized in Table I.

Compounds 3 and 5 in Table I were obtained in crystalline form from their respective sirupy distillates in approximately 75% yield. Compound 3, m. p. 79–80.2 cor.; compound 5, m. p. 90.6–91.1° cor. Compounds 1, 2, and 4, being sirups, are probably mixtures of the α- and β-forms, with considerable α as evidenced by the positive rotation. Compound 3, being crystalline, seems to be definitely an α-form. Compound 5 should also be an α-form, the β-form having been described by Richtmyer.[11]

Catalytic Reduction of Benzyl Glycosides.—The general procedure used in reduction of the glycosides is illustrated by the following example. A solution of 12.9 g. of benzyl 2,3,6-trimethyl-D-glucoside in 50 ml. of glacial acetic acid with palladium–charcoal catalyst (0.5 g. of palladium chloride and 3 g. of charcoal) absorbed the theoretical amount of hydrogen overnight (hydrogen pressure 3–4 atm.). The catalyst was filtered off and the reaction flask and catalyst washed with water. The combined filtrate and washings were evaporated under reduced pressure to a sirup. Toluene (250 ml.) was added and removed under reduced pressure. Ether was added to

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(10) The benzyl glycoside which had been reported by Hess and Gramberg (ref. 8) was a benzyl 2,3,6-trimethyl-β-D-glucoside; it was quite impure, with a methoxyl content 3.5% too high due to the presence of some trimethylglucose. Its rotation of $[\alpha]^{20}D$ +8.3° is quite different from the value +74.9° reported by the present authors.

(11) Richtmyer, THIS JOURNAL, 61, 1831 (1939).

the residue which crystallized. Crystallization was completed on standing for several days at 0°; yield 6.7 g. (73%).

In addition to reduction of benzyl glycosides this method was successfully applied to the reduction of the benzyl group from 3-benzyl 2,4,6-trimethyl-D-glucose without reduction of the aldehydic group. The 2,4,6-trimethyl-D-glucose was crystallized from carbon tetrachloride, m. p. 126°. When mixed with an authentic sample of 2,4,6-trimethyl-D-glucose, the melting point was not depressed.

Summary

1. A new method of separation of the cleavage products of methylated disaccharides has been developed. This involves conversion of the methylated disaccharide to two benzyl glycosides, treatment with benzyl alcohol in the presence of an acid, separation of the glycosides by fractionation under high vacuum, and reduction of the benzyl glycosides to give the methylated monosaccharides.

2. This method gives good yields (85%) of the tetramethyl monosaccharides and fair yields (50%) of the trimethyl monosaccharides.

3. Two new crystalline benzyl glycosides, (presumably α-forms) have been prepared; benzyl 2,3,4-trimethyl-D-glucoside, and benzyl 2,4,6-trimethyl-D-glucoside. Three new sirupy benzyl glycosides (presumably mixtures of the α- and β-forms) have been prepared: benzyl 2,3,4,6-tetramethyl-D-galactoside, benzyl 2,3,4,6-tetramethyl-D-glucoside, and benzyl 2,3,6-trimethyl-D-glucoside.

IOWA CITY, IOWA RECEIVED JUNE 28, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, CALIFORNIA]

Aluminum Monolaurate and Proposed Structures for Aluminum Soaps[1]

BY CHARLES G. MCGEE[2]

The chemistry of aluminum soaps has long been in confusion. It has been stated: that only mono soaps exist,[3,4] that only a basic compound intermediate between mono- and di-soaps exists together with various sorption products,[5] and that the mono- as well as the di- and tri-soaps all exist.[6] Di-soaps have been prepared by several authors,[7,8,9] while efforts to prepare tri-soaps[10,11] failed.

It is the purpose of this paper to present evidence concerning the existence of aluminum mono-soaps. In the course of this work, no compounds were prepared having a ratio of exactly one molecule of fatty acid per atom of aluminum, but the preparations obtained had approximately one to one ratios and were stable under a wide variety of conditions. It is believed that these are true compounds, of the nature of copolymers, and that as a result exact stoichiometric composition is not necessarily to be expected. Products containing from 1.2–0.8 molecules of fatty acid per aluminum atom will be referred to as aluminum mono-soaps.

The materials used in this study are those used in the previously reported work.[9] Analysis was carried out by ashing or by a split analysis in which the aluminum was determined by a standard procedure using 8-hydroxyquinoline and the fatty acid determined by precipitation and weighing.

Aluminum Mono-Soaps

Preparation from Aluminum Di-soaps, Accompanied by Alcoholysis.—In the course of an investigation on the free acid content of commercial aluminum soaps, it was noted that the use of hot methanol for extraction gave much higher results than when acetone was employed. Analysis of these residues indicated that they approximated the composition then expected for a compound of the formula $Al(OH)_2$-fatty acid.

However, this reaction was repeated on samples of aluminum dilaurate prepared by Smith, *et al.*[9] Exhaustive treatment with hot methanol gave products containing 1.2–1.0 molecules of fatty acid per aluminum atom. The initial reaction is always accompanied by a marked physical change in the soap from a powder to a plastic mass. The reaction required several minutes at the boiling point of the methanol, and many days at room temperature. The plastic product contained large amounts of methanol and much free fatty acid. It gradually hardened over a period of several days, after which it was ground up and retreated with the methanol. During later treatments, it frequently reconsolidated.

To examine this assumed reaction, a weighed sample of aluminum dilaurate was treated with methanol, and the weight of fatty acid liberated and the loss in weight of the soap were determined. It was found that after drying *in vacuo*

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[1] Study conducted under Contract OEMsr-1057 between Stanford University and the Office of Emergency Management, recommended by Division 11.3 of the National Defense Research Council, and supervised by Prof. J. W. McBain.

[2] Present address: Stanford Research Institute, Stanford, California.

[3] Alexander, reports to Div. 11.3, NDRC.

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[5] Eigenberger and Eigenberger-Bittner, *Kolloid Z.*, **91**, 287 (1940).

[6] Lawrence, *J. Inst. Petroleum*, **31**, 312 (1945). British Petroleum Warfare Board Memo No. 368.

[7] Ostwald and Rideal, *Kolloid Z.*, **69**, 185 (1934).

[8] Markowicz, *Färber Ztg.*, **34**, 326 (1928).

[9] Smith, Pomeroy, McGee and Mysels, THIS JOURNAL, **70**, 1053 (1948).

[10] McBain and McClatchie, *ibid.*, **54**, 3226 (1932).

[11] Licata, *Drugs, Oils & Paints*, **51**, 148 (1936).