recrystallized. From alcohol–acetone it crystallized in colorless needles; yield, 0.76 g. (86%); m. p. 71–72°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.2.

The picrate crystallized from alcohol in clusters of orange needles; m. p. 141–142°.

Anal. Calcd. for $C_{19}H_{18}\cdot C_6H_3N_3O_7$: N, 8.84. Found: N, 8.85.

5-Methylchrysene (X).—A mixture of 0.5 g. of the tetrahydro derivative and 0.05 g. of palladium–charcoal catalyst was heated at 300–320° for forty-five minutes. The mixture was digested with hot benzene and filtered, and the benzene evaporated. From alcohol–acetone the 5-methylchrysene crystallized in colorless needles; yield, 0.42 g. (85%); m. p. 116–117°. After a second recrystallization it melted at 118–118.8° (cor.). The hydrocarbon shows strong blue-violet fluorescence in ultraviolet light. The picrate crystallized from alcohol in red needles; m. p. 141–142° (reported: 142.6–143° cor.[5]; 141.6–142.4° cor.[6]). The *s*-trinitrobenzene derivative crystallized from benzene–alcohol in orange needles; m. p. 171–173° (reported: 172.6–173.6° cor.[5]).

Summary

4-Methylphenanthrene reacts with succinic anhydride in the Friedel–Crafts reaction in the 1- and 6-positions.

From the products of this reaction 1′-methyl-1,2-benzanthracene and 5-methylchrysene were synthesized.

ANN ARBOR, MICHIGAN RECEIVED JULY 18, 1940

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

Melibiotol and Maltitol

BY M. L. WOLFROM AND THOMAS S. GARDNER

The classical method of preparing sugar alcohols by the sodium amalgam reduction of the reducing sugars was tedious, gave low yields and was unsatisfactory in general. The electrolytic reduction of *d*-glucose,[1] now carried out on an industrial scale in this country, has made sorbitol and *d*-mannitol commercially available. From a laboratory standpoint, the high pressure catalytic reduction methods pioneered by Ipatieff, now make the reduction of sugars to the corresponding alcohols a comparatively simple procedure when the proper equipment is available. By such methods, Levene and Kuna[2] obtained the disaccharide alcohol cellobiotol in crystalline form and Levene and Tipson[3] crystallized 6-(β-glucosido)-dulcitol by the reduction of the synthetic 6-(β-glucosido)-*d*-galactose of Freudenberg and co-workers.[4] Senderens[5] previously had reduced lactose by high pressure catalytic methods and although he obtained some hydrolytic splitting to dulcitol, he was able to isolate a hydrated form of lactitol.

From this Laboratory, we have reported the crystallization of the anhydrous form of lactitol[6] (lactositol) and we wish now to record crystalline melibiotol and its crystalline nonabenzoate. The structure of our reduced product was verified by its lack of Fehling reduction and by hydrolysis to its components, sorbitol and *d*-galactose, each of which was identified through a crystalline characteristic derivative. The derivative used to characterize *d*-galactose was its diethyl mercaptal, a readily obtainable and easily crystallizable substance. A sirupy melibiotol had been reported by Scheibler and Mittelmeier[7] by the sodium amalgam reduction of an early melibiose preparation.

Karrer and Büchi[8] reduced maltose by high pressure, catalytic methods but were unable to crystallize the product. We have repeated the work of Karrer and Büchi, and while we were likewise unable to crystallize the maltitol, we obtained a definitely crystalline nonaacetate of this substance. Karrer and Büchi also prepared maltitol nonaacetate and characterized it as a "nicht deutlich krystallines Pulver." A comparison of the properties recorded by these workers for their preparation with those of our distinctly crystalline product, would make it appear probable that the maltitol nonaacetate of Karrer and Büchi was microcrystalline. Karrer and Büchi identified the reduced portion of the maltitol by hydrolysis and identification as tribenzylidenesorbitol. We have further characterized the glucose liberated

(1) H. J. Creighton, *Trans. Electrochem. Soc.*, **75**, 289 (1939).

(2) P. A. Levene and M. Kuna, *Science*, **85**, 550 (1937); *J. Biol. Chem.*, **127**, 49 (1939).

(3) P. A. Levene and R. S. Tipson, *ibid.*, **125**, 355 (1938).

(4) K. Freudenberg, A. Noë and E. Knopf, *Ber.*, **60**, 238 (1927).

(5) J. B. Senderens, *Compt. rend.*, **170**, 47 (1920).

(6) M. L. Wolfrom, W. J. Burke, K. R. Brown and R. S. Rose, Jr., THIS JOURNAL, **60**, 571 (1938).

(7) C. Scheibler and H. Mittelmeier, *Ber.*, **22**, 3118 (1889).

(8) P. Karrer and J. Büchi, *Helv. Chim. Acta*, **20**, 86 (1937).

on hydrolysis by the isolation of its crystalline diethyl mercaptal.

The synthesis of maltitol nonaacetate adds another member to the list of maltose acetates containing an acyclic structure in the non-glucosidic portion of this disaccharide. We have been struck by the remarkable similarity exhibited by the rotations of these derivatives in chloroform solution, as shown in Table I. It would appear that the lactol carbon of the glucosidic portion in these α-glucosides may be making the major contribution to their rotations.

TABLE I

ROTATIONS OF ACYCLIC MALTOSE ACETATES

Substance	Spec. rot., $CHCl_3$, 25°	Mol. rot.
Maltitol nonaacetate	+84°	+61,000
Maltose diethyl mercaptal octaacetate[9]	+88	+69,000
aldehydo-Maltose octaacetate[10]	+93.5	+63,000
aldehydo-Maltose octaacetate monoethyl alcoholate[10]	+85	+62,000

Experimental

Melibiotol.—A solution of 100 g. of melibiose dihydrate in 200 cc. of water containing 50 g. of a nickel catalyst supported on kieselguhr was reduced in a steel shaking autoclave (American Instrument Company) at an initial hydrogen pressure of 2350 lb. per sq. in. (160 atm.) at 40°. A maximum temperature of 150° at a pressure of 2800 lb. per sq. in. (190 atm.) was attained in one hour and maintained for an additional four hours. The cooled mixture was filtered, heated short of boiling, and treated with hydrogen sulfide until precipitation was complete. The filtered solution was clarified further by boiling for one hour with activated charcoal (5 g.), filtered hot and concentrated (37°) to a thick sirup under reduced pressure. The resultant sirup was extracted five times with boiling absolute ethanol and the white residue crystallized within three days on standing under absolute ethanol; yield approximately 80%. Pure material was obtained by recrystallizations effected by solution in a small quantity of water, addition of an excess of ethanol and standing at ice-box temperature overnight; m. p. 173°, spec. rot. +116° (24°, *c* 1.4, H_2O).[11] The substance crystallized as needles and was unaffected by heating at 100° for eight hours under reduced pressure. It reduced Fehling solution only after acid hydrolysis. It was readily soluble in water but was practically insoluble in other common solvents.

Anal. Calcd. for $C_{12}H_{24}O_{11}$: C, 41.84; H, 7.03. Found: C, 41.98; H, 6.94.

Melibiotol Nonabenzoate.—The crystalline melibiotol was benzoylated in dry pyridine with an excess of benzoyl chloride. The reaction, which was exothermic and required initial cooling, was completed by two hours of refluxing. The cooled solution was poured into an excess of water, the separated oil removed by chloroform extraction and the extract washed with aqueous sodium bicarbonate and with water. The sirup obtained on solvent removal from the dried extract was crystallized from ethanol (95%) and purified by recrystallization from a mixture of 5 parts of pyridine and 95 parts of ethanol (95%); m. p. 157°, spec. rot. +123° (25°, *c* 3, U. S. P. $CHCl_3$). The substance crystallized as small prisms. It was very soluble in chloroform, acetone and benzene; moderately so in ether; slightly soluble in hot alcohol; practically insoluble in water.

Anal. Calcd. for $C_{12}H_{15}O_{11}(C_6H_5CO)_9$: C, 70.29; H, 4.72; C_6H_5CO, 7.03 cc. 0.1 *N* NaOH per 100 mg. Found: C, 70.43; H, 4.58; C_6H_5CO, 7.0 cc.

Identification of the Hydrolytic Products of Melibiotol.—A solution of 3 g. of crystalline melibiotol in 60 cc. of 5% hydrochloric acid was heated at 90° for two hours. The hydrolysate was divided into two equal parts and the solvent removed from each under reduced pressure. The resultant sirup from one part was treated with benzaldehyde and concentrated hydrochloric acid according to the procedure of Karrer and Büchi.[8] The purified reaction product was characterized by melting point (190–191°) and mixed melting point as tribenzylidenesorbitol, for which Karrer and Büchi record the melting point of 190–191°.

The sirup from the second half of the hydrolysate was dissolved in 2.5 cc. of concentrated hydrochloric acid (d. 1.19) and shaken with 1 cc. of ethyl mercaptan. A crystalline product began to separate after fifteen minutes and crystallization was completed in an ice–salt-bath. The filtered product was washed with cold water and recrystallized thrice from water. The product was identified by melting point (140–141°) and mixed melting point as *d*-galactose diethyl mercaptal, for which Fischer[12] recorded the melting point of 140–142°.

Maltitol.—Maltose monohydrate, purified through the octaacetate, was reduced as described above for the synthesis of crystalline melibiotol and the reduction product was isolated in the same manner. The maltitol was obtained only in the form of an amorphous, white, hygroscopic solid which reduced Fehling solution only after acid hydrolysis. After drying under reduced pressure for ten hours at 90°, the substance showed a specific rotation of +102° (22°, *c* 2.7, H_2O). Karrer and Büchi[8] record a specific rotation of approximately +90° for their reduced maltose. A portion of the maltitol was hydrolyzed as described previously for melibiotol and the hydrolytic products were identified in the same manner as tribenzylidenesorbitol (m. p. 190°; mixed m. p. unchanged) and *d*-glucose diethyl mercaptal (m. p. 126°; mixed m. p. unchanged), for which Fischer[12] recorded the melting point of 127–128°.

Deacetylation of the crystalline maltitol nonaacetate described below produced an amorphous maltitol (spec. rot. +102°, H_2O) which also was not amenable to crystallization.

Maltitol Nonaacetate.—A portion of the amorphous maltitol was acetylated with hot acetic anhydride and fused sodium acetate. The sirup obtained on pouring the cooled acetylation mixture into an excess of water was dis-

(9) M. L. Wolfrom and E. E. Stahly, THIS JOURNAL, **53**, 4379 (1931).

(10) M. L. Wolfrom and M. Konigsberg, *ibid.*, **62**, 1153 (1940).

(11) All rotations are recorded to the D-line of sodium light, 24° is the temperature, *c* is the concentration in g. per 100 cc. soln.

(12) E. Fischer, *Ber.*, **27**, 673 (1894).

solved in chloroform and the extract washed free of acid. The sirup obtained on solvent removal from the dried extract was crystallized from absolute ethanol, from which it separated as long, distinct needles. Pure material was obtained on further recrystallization from the same solvent; m. p. 86–87°, spec. rot. +84° (20°, *c* 3.3, U. S. P. $CHCl_3$). Karrer and Büchi[8] record an analysis and a melting point of approximately 86° for a product which they characterized as a "nicht deutlich krystallines Pulver." Our preparation was very soluble in chloroform and acetone; soluble in benzene; moderately soluble in hot ethanol; very moderately so in ether; practically insoluble in water.

Anal. Calcd. for $C_{12}H_{15}O_{11}(CH_3CO)_9$: C, 49.86; H, 5.86; CH_3CO, 12.45 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.76; H, 5.78; CH_3CO, 12.2 cc.

We are indebted to Mr. S. H. Nichols, Jr., for the preparation of the melibiose used in this work.

Summary

1. Melibiotol has been synthesized in crystalline form by the high pressure catalytic reduction of melibiose and further characterized as a crystalline nonabenzoate.

2. The structure of melibiotol was demonstrated by its lack of reduction and by its hydrolysis to sorbitol and *d*-galactose, both of which were characterized as crystalline derivatives.

3. The work of Karrer and Büchi on the reduction of maltose has been repeated and the amorphous maltitol produced has been characterized as a crystalline nonaacetate and both hydrolytic components (sorbitol and *d*-glucose) of the maltitol preparation have been identified by crystalline derivatives.

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[CONTRIBUTION NO. 229 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Partial Reduction of Acetylenes to Olefins Using an Iron Catalyst

BY A. F. THOMPSON, JR., AND S. B. WYATT[1]

The problem of reduction of acetylenic compounds to the corresponding olefins has engaged the attention of many workers. Palladium has come to be accepted as a catalyst whose selective action can be utilized for this type of partial reduction. Recently, Campbell and O'Connor[2] have reported that Raney nickel exhibits similar selective properties, and have used it as a catalytic agent in the preparation of numerous olefins from the corresponding acetylenes.

Both palladium and Raney nickel are unsatisfactory, however, to the extent that both are excellent catalysts for the reduction of olefins, and the reduction must therefore be watched constantly and stopped at the proper moment. Therefore, the announcement by Paul and Hilly[3] of an iron catalyst, similar to Raney nickel, but unable to effect the reduction of olefins, was of considerable importance. It was decided to investigate the properties of this catalyst in this Laboratory, since certain synthetic studies being carried on here involve reduction of triple bonds to double bonds, in the presence of conjugated systems of carbon–carbon double bonds. Moreover, Paul and Hilly[3] worked exclusively with liquids and it was considered desirable to work with solid substances in order to be able to characterize the reaction products more effectively.

Diphenylacetylene was chosen as the first substance to be investigated. It proved to be an unfortunate choice, since it behaved abnormally, being reduced quantitatively to diphenylethane by hydrogen and the iron catalyst at 100° and 1000 lb. per sq. in. This happened in each of three separate experiments. It was especially surprising in view of the results of Campbell and O'Connor,[2] who obtained isostilbene by persistent reduction of diphenylacetylene with Raney nickel.

To avoid any special effect of phenyl groups, an aliphatic acetylene with appropriate properties was sought, and 2,5-dimethylhexyne-3-diol-2,5 was chosen. It proved more resistant to reduction, but at 150° and 1400 lb. per sq. in. it was reduced nearly quantitatively to the beta form of the olefin, m. p. 67–69°. The corresponding acetylene and ethane both melt above 90°. The unsaturation of the product was confirmed by quantitative

(1) From the thesis submitted by S. B. Wyatt in partial fulfilment of the requirements for the degree of Bachelor of Science.

(2) Campbell and O'Connor, THIS JOURNAL, **61**, 2897 (1939). This paper includes numerous references to earlier investigations of partial hydrogenation.

(3) Paul and Hilly, *Bull. soc. chim.*, [5] **6**, 218 (1939).