Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; neut. equiv., 178. Found: C, 73.94; H, 8.02; neut. equiv., 178.

The *p*-phenylphenacyl ester of VIII (m. p. 59.5–60°) was prepared in the usual manner.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50. Found: C, 80.75; H, 6.38.

Oxidation of VIII with dilute permanganate according to the directions for the oxidation of VII and subsequent similar treatment yielded suberic acid (m. p. 139–141°; neut. equiv., 88; m. p. of *p*-bromophenacyl ester 146–146.5°).

Summary

The synthesis of 1-decyne-1,10-dicarboxylic acid, 1,9-decadiyne-1,10-dicarboxylic acid and *cis*-traumatic acid has been described.

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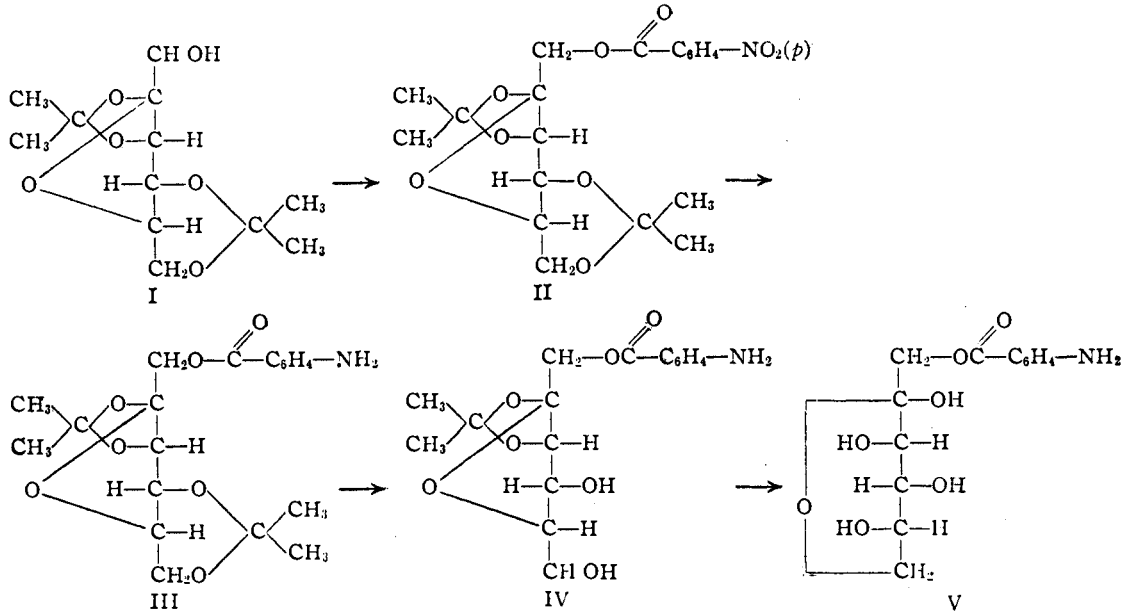
[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MERCK & CO., INC.]

Synthesis of 1-(*p*-Aminobenzoyl)-*l*-sorbose

BY JACOB FINKELSTEIN[1] AND ERIC T. STILLER[2]

Many nitrobenzoyl esters of sugars are known, but so far, no analogous amino compound has been recorded. As a possible substance for measuring the rate of glomerular filtration,[3] we have prepared 1-(*p*-aminobenzoyl)-*l*-sorbose, the first of this class of sugar derivatives, by the following series of reactions



This procedure, with certain modifications, may be applied as a general method for such types of compounds.

The preparation of 1-(*p*-nitrobenzoyl)-2,3-4,6-diacetone-*l*-sorbose was easily accomplished. The removal of both acetone groups, however, proved rather difficult and the yield of the final compound was poor.

When the diacetone compound was warmed with 50% acetic acid, it was converted into the monoacetone derivative (IV), whose structure is so formulated in accordance with the results obtained by Freudenburg and co-workers[4] from their studies on acetone sugars. This formulation was upheld by the fact that (IV) did not reduce Fehling solution while the completely hydrolyzed product did so quite readily. The method of hydrolysis used to obtain (V), as outlined below, was the only one, of the many tried, which produced small amounts of the desired product.

Experimental

2,3-4,6-Diacetone-*l*-sorbose (I).—This compound was prepared according to the method of Reichstein and Grussner.[5]

1-(*p*-Nitrobenzoyl)-2,3-4,6-diacetone-*l*-sorbose (II).—A solution of 45 g. of diacetone-*l*-sorbose was prepared in 200 cc. of dry pyridine and stirred while immersed in an ice–salt mixture. To this solution 35 g. of *p*-nitrobenzoyl

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(3) The authors wish to express their thanks to Dr. Homer W. Smith of the Department of Physiology, New York University, College of Medicine for helpful suggestions in regard to the type of compounds which would be of use in the measurement of kidney function.

(4) Freudenburg, *et al.*, *Ber.*, **61**, 1735 (1928).

(5) Reichstein and Grussner, *Helv. Chim. Acta*, **17**, 311 (1934).

chloride was added in small portions and after all had been added, the reaction mixture was allowed to stand at room temperature for sixteen hours. The solution was poured onto excess ice and carefully acidified with concentrated hydrochloric acid. The white, viscous product which separated was stirred mechanically until it became solid. It was then filtered, washed with water and recrystallized from 95% alcohol; after drying at 80° *in vacuo*, it had a m. p. 130°.

Anal. Calcd. for $C_{18}H_{23}O_9N$: C, 55.74; H, 5.66; N, 3.42. Found: C, 55.98; H, 5.69; N, 3.39.

1-(*p*-Aminobenzoyl)-2,3-4,6-diacetone-*l*-sorbose (III).—A suspension of 25 g. of 1-(*p*-nitrobenzoyl)-2,3-4,6-diacetone-*l*-sorbose in 450 cc. of absolute alcohol was reduced by hydrogen in the presence of Adams catalyst. The reduction was complete in ten minutes at 30-lb. pressure. The solution was then filtered and evaporated to a small volume when the crystalline product separated. After crystallization was complete, the product was recrystallized from absolute alcohol. It was dried at 100° in vacuum and had a m. p. 168 to 169°.

Anal. Calcd. for $C_{19}H_{25}O_7N$: C, 60.15; H, 6.64; N, 3.69. Found: C, 60.03; H, 6.58; N, 3.79.

1-(*p*-Aminobenzoyl)-2,3-monoacetone-*l*-sorbose (IV).—A suspension of 1.1 g. of 1-(*p*-aminobenzoyl)-2,3-4,6-diacetone-*l*-sorbose in 14 cc. of 50% acetic acid was warmed on the steam-bath for one hour. During this time, the crystalline compound slowly went into solution. The solution was then concentrated in vacuum at 60° to about 4 cc. and cooled. Upon neutralization with sodium hydroxide a solid was precipitated. This was filtered, washed with water and then twice recrystallized from boiling water to yield a colorless crystalline compound upon cooling. The filtered substance was washed and dried at 100° *in vacuo* over phosphorus pentoxide; m. p. 171 to 172°. The compound does not reduce Fehling solution.

Anal. Calcd. for $C_{16}H_{21}O_7N$: C, 56.61; H, 6.24; N, 4.13. Found: C, 56.61; H, 6.48; N, 4.18.

1-(*p*-Aminobenzoyl)-*l*-sorbose (V).—Ten grams of the *p*-aminobenzoyl diacetone-*l*-sorbose was suspended in 150 cc. of 0.1 *N* sulfuric acid and heated on the steam-bath for three hours. The solution was then cooled and stirred with an excess of moist barium carbonate for about thirty minutes. The precipitate which formed was removed by centrifugation. The aqueous solution was concentrated *in vacuo* at 25 to 30° to about 20 cc. when a small amount of a crystalline product (the monoacetone derivative) separated. After separating these few crystals, the solution was again concentrated and the small volume obtained was dissolved in a benzene–alcohol solution and again evaporated. This procedure was repeated until a dry, amorphous residue was obtained. The amorphous compound was dissolved in methanol and the solution treated dropwise with dry ether until a faint turbidity appeared. The solution was then set in the refrigerator when a small amount of an oil was deposited. This procedure was continued until crystals began to separate from the solution. At this point, the clear liquid was decanted from the oil and when treated with dry ether, as previously described, a solid precipitate was obtained. This product was then recrystallized from a mixture of 95% alcohol and absolute alcohol and after standing in the refrigerator for several days, gave a crop of small crystals. These crystals were collected, washed with absolute alcohol and ether and dried in a vacuum desiccator over phosphorus pentoxide. The m. p. was 159 to 160°; $[\alpha]^{20}D$ −5.0° (*C*, 2.52%; water).

Anal. Calcd. for $C_{13}H_{17}O_7N$: C, 52.17; H, 5.74; N, 4.68. Found: C, 52.17; H, 5.78; N, 4.85.

The insoluble material obtained from the barium carbonate treatment contains a great deal of the monoacetone derivative. Therefore, the entire residue was refluxed with alcohol and the alcohol evaporated to dryness. The monoacetone derivative so obtained was then hydrolyzed as above. This recovery process was continued until all of the monoacetone compound was hydrolyzed.

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Summary

A series of reactions for the synthesis of 1-(*p*-aminobenzoyl)-*l*-sorbose has been described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Indirect Phenol–Aldehyde Condensations[1]

BY JOSEPH B. NIEDERL AND IRVING W. RUDERMAN[2]

Introduction

In an effort further to elucidate the mechanism of the phenol–formaldehyde condensation, the study of the condensation of *p*-alkylated phenol dialcohols with both *p*-alkylated and *o,p*-dialkylated phenols was continued.

Since an *o,p*-dialkylated phenol, or "blocked" phenol, has only one open reactive position, its condensation with a *p*-alkylated phenol dialcohol can only yield a tri-nuclear linear compound. The condensation of a *p*-alkylated phenol with a *p*-alkylated phenol dialcohol may, however, theoretically at least, proceed beyond the tri-nuclear stage. Morgan,[3] Megson and Drummond[4] and Koebner[5] have reported the isolation in high yield of a tri-nuclear linear compound from the condensation of *p*-cresol and *p*-cresol dialcohol, but there is no report in the literature of how other *p*-alkylated phenols react under similar conditions.

Accordingly, in this investigation 4-*tt*-octyl-

(1) Abstracted in part from the thesis of I. W. Ruderman presented to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, June, 1944. This paper was presented before the Division of Paint, Varnish and Plastics Chemistry at the 108th meeting of the American Chemical Society in New York, N. Y., September, 1944.

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(3) J. Morgan, *J. Soc. Chem. Ind.*, **49**, 245T (1930).

(4) Megson and Drummond, *ibid.*, **49**, 251T (1930).

(5) M. Koebner, *Chem. Ztg.*, **54**, 619 (1930); *Angew. Chem.*, **46**, 252 (1933).