

in vacuo or quenched in ice water. Residual or precipitated product was dried and recrystallized.

Method 8. Amides. METHOD A. COMPOUNDS 35, 37, 39 AND 41. A mixture of 0.1M of dicarbethoxyhomogentisyl chloride and 0.1M of the nitroaniline was refluxed one hour in *o*-dichlorobenzene. The product usually separated on cooling. Those that did not separate were precipitated by pouring the reaction mixture into hexane. The product was filtered off and recrystallized.

METHOD B. COMPOUNDS 31, 33 AND 43. A mixture of 0.02M of 2,5-diacetoxybenzoyl chloride, 0.02M of the nitroaniline, 0.02M of pyridine, and 60 ml. of ethylene dichloride was refluxed one hour. The cooled mixture was washed with water to remove pyridine hydrochloride. The organic layer was dried and evaporated to dryness in vacuo. Residual product was recrystallized.

Method 9. Debenzylation. COMPOUND 24. To a gently boiling solution of 15 grams of 4'-nitrophenylpropyl-2,5-dibenzyloxy phenyl ether in 150 ml. of acetic acid was slowly added 35 ml. of conc. HCl. The mixture was refluxed for 20 minutes after the addition, then poured into a liter of ice water. The brown gummy solid that separated was filtered off, and washed free of benzyl chloride with hexane on the Büchner funnel. The solid was crystallized from 30 ml. of toluene (charcoal) to give 5.5 grams of yellow crystals. m.p. 155-157°.

Method 10. Diaryl ethers. COMPOUND 27. A mixture of 25 grams of 2,5-dimethoxy potassium phenoxide, 0.13M (11), 25 grams of *p*-fluoronitrobenzene, 0.175M (17), 0.5 grams of 2,5-dimethoxyphenol (11), and 0.2 grams of copper powder was heated in a metal bath at 155-160° for one hour. The melt was poured into alkaline ice water. An oil separated which soon solidified, was filtered off, and recrystallized (filtering off the copper at this stage) from ethanol.

Method 11. Reductions. The nitro compound was dissolved or suspended in ethanol, the more insoluble ones in ethyl acetate, and hydrogenated in a Parr shaker over 10% Pd on BaSO₄ at room temperature. Theoretical uptake of

hydrogen took from 15 minutes to four hours. After removal of catalyst, the free bases were isolated by vacuum evaporation of solvent; hydrochlorides were precipitated by adding one equivalent of conc. HCl to the amine in ethyl acetate.

LITERATURE CITED

- (1) Alcalay, W., *Helv. Chim. Acta* **30**, 582 (1947).
- (2) Ballio, A., Almirante, L., *Ann. Chim. (Rome)* **41**, 421 (1951).
- (3) Blout, Elkan R., Corley, Richard S., Cohen, Saul G., Green, Milton, Rogers, Howard G., Simon, Myron S., Woodward, Robert B., (to International Polaroid Corporation), British Patent 804,974 (November 26, 1958); *C.A.* **53**, 13852c (1959).
- (4) Blout, Elkan R., Green, Milton, Rogers, Howard G., Simon, Myron S., Woodward, Robert B., (to Polaroid Corporation), U.S. Patent 3,019,107 (January 30, 1962); *C.A.* **56**, 9620h (1962).
- (5) British Patent 853,479, International Polaroid Corporation (November 9, 1960); *C.A.* **55**, 9125f (1961).
- (6) Brunetti, W., *J. prakt. Chem.* **128**, 44 (1930).
- (7) Burton, H., David, *J. Chem. Soc.* **1952**, 2195.
- (8) Carter, P.R., Hey, D.H., *Ibid.*, **1948**, 148.
- (9) Davis, W., Roberts, J.J., Ross, W.C.J., *Ibid.*, **1955**, 894.
- (10) Foreman, E.L., McElvain, S.M., *J. Am. Chem. Soc.* **62**, 1436 (1940).
- (11) Gilman, H., Van Ess, P.R., *Ibid.*, **61**, 1370 (1939).
- (12) Green, Milton, Husek, Helen P., (to Polaroid Corporation), U. S. Patent 3,019,254 (January 30, 1962); *C.A.* **57**, 9744a (1962).
- (13) Green, Milton, Solodar, Warren E., (to Polaroid Corporation), U. S. Patent 3,061,434 (October 30, 1962).
- (14) Kvalnes, D.E., *J. Am. Chem. Soc.* **56**, 2480 (1934).
- (15) Orton, K.J.P., Everatt, R.W., *J. Chem. Soc.* **1908**, 1021.
- (16) Price, C.C., Stacy, G.W., *J. Am. Chem. Soc.* **68**, 499 (1946).
- (17) Rarick, M.J., Brewster, R.Q., Dains, F.B., *Ibid.*, **55**, 1289 (1933).

RECEIVED for review August 2, 1963. Accepted December 20, 1963. Portions of this work were presented by E.H. Land and Associates at the Symposium on Polacolor Film, Society of Photographic Scientists and Engineers, Atlantic City, N. J., May 1, 1963.

Syntheses of 1,2,3,4-Tetra-O-Acetyl-6-O-Benzhydryl- β -D-Glucose

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The benzhydrylation of 1,2,3,4-tetra-O-acetyl- β -D-glucose and the benzhydrylation of D-glucose followed by acetylation are described. Data presented indicate that both processes lead to the production of 1,2,3,4-tetra-O-acetyl-6-O-benzhydryl- β -D-glucose.

DURING A STUDY in this laboratory of the distribution of substituents in benzhydrylated cotton cellulose, the need arose for a D-glucose derivative having the benzhydryl group in the 6-position. A literature search showed that while Ohle and Tessmar (4) had attempted to prepare such a derivative by reacting benzhydryl alcohol with 5,6-anhydro-1,2-O-isopropylidene- α -D-glucose, they has not been successful. No other reference to such a compound was found.

The recent use of benzhydryl bromide in lutidine as a method for the benzhydrylation of cotton cellulose (6)

suggested that the benzhydrylation of a D-glucose derivative or even D-glucose itself might be feasible. Following this lead, a sample of 1,2,3,4-tetra-O-acetyl- β -D-glucose was prepared according to the method of Reynolds and Evans (5). This in turn was treated with benzhydryl bromide in 2,6-lutidine. Chemical analysis of the product indicated the presence of four acetyl groups and one benzhydryl group.

The infrared spectrum of the product (in a potassium bromide pressing) has an absorption band near 11.2 μ which is associated with a β -D-anomer, but no band at

11.8 μ , which is usually associated with an α -D-anomer (1). These data are in agreement with the statement (2) that with a basic catalyst, although α - and β -D-glucose can equilibrate, the acetates, once formed, maintain their anomeric integrity.

The product was therefore considered to be 1,2,3,4-tetra-*O*-acetyl-6-*O*-benzhydryl- β -D-glucose.

Next, D-glucose itself was treated with sufficient benzhydryl bromide in 2,6-lutidine to introduce only one benzhydryl group. The product was then fully acetylated. After isolation, chemical analysis of the product indicated the presence of one benzhydryl group and four acetyl groups in the glucose derivative.

Melting points, a mixed melting point, infrared spectra, and optical rotations showed the compound prepared directly from D-glucose to be identical with the 1,2,3,4-tetra-*O*-acetyl-6-*O*-benzhydryl- β -D-glucose prepared from the acetylated D-glucose derivative.

EXPERIMENTAL

Reagents. Benzhydryl bromide was synthesized by the bromination of diphenylmethane according to the method of Norris and coworkers (3). Mallinckrodt analytical grade D-glucose and Baker Analyzed reagent grade acetic anhydride were used as received. The 1,2,3,4-tetra-*O*-acetyl- β -D-glucose was prepared according to the method of Reynolds and Evans (5).

Preparation of 1,2,3,4-Tetra-*O*-acetyl-6-*O*-benzhydryl- β -D-glucose. A. FROM 1,2,3,4-TETRA-*O*-ACETYL- β -D-GLUCOSE. A 0.3 gram (0.001 mole) sample of 1,2,3,4-tetra-*O*-acetyl- β -D-glucose (5) was mixed with 0.26 gram (0.001 mole) of benzhydryl bromide and 0.75 ml. of 2,6-lutidine. The mixture was heated overnight on a steam bath and then poured into a solution made from 14 ml. of iced water and 1 ml. of acetic acid. The cold suspension obtained was stirred for two hours. The dilute acid was removed by filtration and replaced with 15 ml. of iced water. After two hours of stirring the solid was isolated on a sintered glass filter and washed with iced water; yield 0.32 grams (64%). The dried precipitate was crystallized from ethyl alcohol to yield crystals, m.p. 157–161°, $[\alpha]_D^{22} + 55.5^\circ$ (*c* 2.09, pyridine). The product has strong infrared absorption at 5.68, 7.27, 7.99, 8.16, 9.31, and 9.66 μ . In addition there is a band near 11.2 μ [a band usually associated with a β -D-anomer (1)].

Anal. Calcd. for $C_{27}H_{30}O_{10}$: C, 63.03; H, 5.88. Found: C, 63.13; H, 5.99.

B. FROM D-GLUCOSE. To a stirred suspension of 24 grams (0.133 mole) of Mallinckrodt analytical reagent D-glucose in 100 ml. of redistilled Eastman 2,6-lutidine was added 34.6 grams (0.140 mole) of benzhydryl bromide. The mixture was heated in a boiling water bath with stirring for eight hours, after which time 72 ml. of acetic anhydride was added. Heating was continued for an additional 18 hours. The reaction mixture was then poured with stirring into a solution made from two liters of iced water and 100 ml. of glacial acetic acid. The sticky mass which resulted was broken into fine lumps by vigorously stirring the cold suspension for two hours. The wet solid was isolated on a filter and dissolved in 300 ml. of ether. A water layer which formed at this stage was discarded. The ether was removed by evaporation and the residue was dissolved in 600 ml. of hot 95% ethyl alcohol. The solution was treated with charcoal to remove color and then passed through a filter. Crystals appeared in the filtrate almost immediately. The solution containing the crystals was allowed to stand in the refrigerator for two days during which time more crystals formed; yield 13.7 grams. Recrystallization from alcohol gave the final product, m.p. 161–162°, $[\alpha]_D^{22} + 54.5^\circ$ (*c* 3.78, pyridine), m.m.p. with the benzhydrylated derivative prepared from 1,2,3,4-tetra-*O*-acetyl- β -D-glucose, 158–161.5°, infrared spectrum superimposable on the spectrum obtained from the benzhydrylated derivative prepared from 1,2,3,4-tetra-*O*-acetyl- β -D-glucose.

ACKNOWLEDGMENT

Thanks are extended to L.E. Brown and coworkers for the microanalyses and to S. Miles for the infrared spectra.

LITERATURE CITED

- (1) Higgins, H.G., Stewart, C.M., Harrington, K.J., *J. Polym. Sci.* 51, 59 (1961).
- (2) Hudson, C.S., *Ind. Eng. Chem.* 8, 380 (1916).
- (3) Norris, J.F., Thomas, R., Brown, B.M., *Ber.* 43, 2940 (1910).
- (4) Ohle, H., Tessmar, K., *Ber.* 71, 1843 (1938).
- (5) Reynolds, D.D., Evans, W.L., *Org. Syntheses, Coll. Vol. III*, 432 (1955); Helferich, B., Klein, W., *Ann.* 450, 219 (1926); 455, 173 (1927).
- (6) Stanonis, D.J., King, W.D., *Textile Res. J.* 30, 802 (1960).

RECEIVED for review September 11, 1963. Accepted December 24, 1963. Use of a company name by the U.S.D.A. does not imply approval or recommendation to the exclusion of other products which may also be suitable.