Mercuric Di-(*n*-butyl) Thiolthionophosphate from Di-(*n*-butyl) Chlorothionophosphate (IX) (GRN).—Di-(*n*-butyl) chlorothionophosphate (0.123 mole) was added dropwise to an alcoholic solution of sodium hydrosulfide (0.245 mole, from sodium ethoxide and hydrogen sulfide). After refluxing for two hours the alcohol solution was concentrated to a few milliliters. An excess of water was added and the water insoluble material removed by several extractions with ethyl ether. Addition of an aqueous solution of mercuric chloride resulted in the separation of a white oil and mercuric sulfide. The oil was extracted with ether, the solution dried and evaporated. The crystalline mass was taken up in methanol and filtered through a talc pad to remove last traces of mercuric sulfide. Long prismatic needles separated from the cooled solution, m. p. 61–62°.

Di-(*n*-butyl) Thiolthionophosphate (GRN).—Phosphorus pentasulfide (2 moles) was added in small portions to *n*-butanol (8 moles) at 70–80°. The temperature rose gradually until the reaction became violent. The flask was finally heated by an oil-bath at 100–110° for two hours. The reaction was accompanied by a copious evolution of hydrogen sulfide. Titration of the reaction product in a benzene-isopropanol mixture (1:1) indicated the solution was approximately 80% di-(*n*-butyl) thiolthionophosphate.

Mercuric Di-(*n*-butyl) Thiolthionophosphate from the Reaction Product of *n*-Butanol and Phosphorus Pentasulfide (IX) (GRN).—The reaction product (0.5 mole) of *n*-butanol and phosphorus pentasulfide was neutralized with a 10% solution of sodium hydroxide. The aqueous solution was washed twice with ethyl ether then treated with an aqueous solution of mercuric chloride (0.25 mole). The water-white oil which separated was taken up in ether, the solution dried, and evaporated in a large dish. The crystalline product melted at 56–57°. One recrystallization from methanol produced long white needles melting at 61–62°.

A mixed melting point with mercuric di-(*n*-butyl) thiolthionophosphate obtained from di-(*n*-butyl) chlorothionophosphate showed no depression.

Anal. Calcd. for $C_{16}H_{36}O_4P_2S_4Hg$: P, 9.06; S, 18.7; Hg, 29.20. Found: P, 9.06; S, 18.4; Hg, 28.5.

Apparatus

All melting points were taken on a Fisher melting point block.

The fractionating column employed was a three-foot column with a total reflux head. The column was externally heated and packed with glass helices.

Acknowledgment.—We are indebted to Dr. C. F. Prutton for continued interest during the course of this investigation.

Summary

1. Five acid chlorides of the thiophosphoric acid esters have been synthesized and identified in the chemical literature for the first time.

2. Certain new metallic salts and phenyhydrazide derivatives of dialkyl thiophosphoric acids have been synthesized.

3. The probability of the existence of resonance in the diethyl thionophosphate ion (or O,O-diethyl thiolphosphate ion) has been indicated.

4. The chief product obtained from the reaction of phosphorus pentasulfide with aliphatic alcohols has the O,O-dialkyl thiolthionophosphate structure. This is demonstrated by a comparison of the metallic salts of the phosphorus pentasulfide reaction product with corresponding salts obtained by unequivocal syntheses through the acid chloride intermediates.

CLEVELAND 17, OHIO RECEIVED MAY 31, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Tetraacetylglucosyl Chloride with Aromatic Hydrocarbons in the Presence of Aluminum Chloride

BY CHARLES D. HURD AND WILLIAM A. BONNER[1]

In view of the widespread use of anhydrous aluminum chloride in organic chemistry, the very limited application of this catalyst to the carbohydrate series is rather surprising. The earliest study involving anhydrous aluminum chloride in the sugar series was in 1901 when Von Arlt[2] and Skraup and Kremann[3] showed that chloroform solutions of sugar acetates yielded the acetylated glycosyl chlorides if treated with aluminum chloride and phosphorus pentachloride. Hudson and Johnson[4] and Brauns[5] later extended the same reaction. A new observation was disclosed in 1926 by Kunz and Hudson[6] who found that aluminum chloride not only functioned as a chlorinating agent, but also served as catalyst for the inversion of certain of the asymmetric centers within the sugar molecule. In this reaction lactose octaacetate yielded heptaacetylneolactosyl chloride. By hydrolytic and oxidation methods[7] these investigators proved neolactose to be 4-(β-D-galactosyl)-D-altrose. The isomerization of lactose (4-(β-D-galactosyl)-D-glucose), therefore, affected positions 2 and 3 of the glucose part of the molecule. Hudson[8] noticed similar inversions of the second and third carbon atoms in the reducing sugar unit when cellobiose octaacetate was employed. More recently this reaction has been employed[9] as a means of preparing altrose.

The purpose of the present investigation was to ascertain whether hemiacetal halides in the sugar series could be induced to react with aromatic hydrocarbons in a manner analogous to the Friedel–Crafts reaction

$$RX + HAr \xrightarrow{AlCl_3} RAr + HX$$

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(1) Corn Products Refining Company Fellow, 1941–1944.

(2) Von Arlt, *Monatsh.*, **22**, 144 (1901).

(3) Skraup and Kremann, *ibid.*, **22**, 375 (1901).

(4) Hudson and Johnson, THIS JOURNAL, **38**, 1226 (1916).

(5) Brauns, *ibid.*, **44**, 401 (1922).

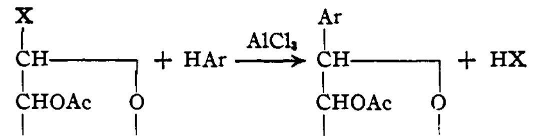
(6) Kunz and Hudson, *ibid.*, **48**, 1978, 2435 (1926).

(7) Kunz and Hudson, *ibid.*, **48**, 2435 (1926).

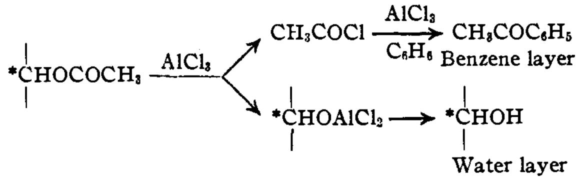
(8) Hudson, *ibid.*, **48**, 2002 (1926).

(9) Richtmyer and Hudson, *ibid.*, **57**, 1716 (1935); Hockett and Chandler, *ibid.*, **66**, 627 (1944).

Neglecting possible reaction at the ester function of the polyacetylglycosyl halide, the anticipated equation is as follows

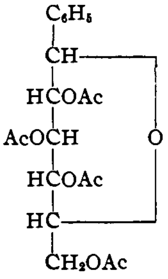


When either tetraacetyl-α-D-glucosyl chloride or β-D-glucose pentaacetate was allowed to react with benzene in the presence of trivial amounts of aluminum chloride, only starting material or indistinct products were obtained. A sweet, aromatic odor about the products, however, indicated that what reaction occurred did so at the ester functions in the acetylated sugar derivative, giving in part at least an aromatic ketone. Numerous investigators have found[10] that esters react with aromatic hydrocarbons in the presence of aluminum chloride to form alkyl or acyl derivatives of the hydrocarbons, depending both on the reactants and the conditions. In case the ester functions of tetraacetylglucosyl chloride should react with benzene to give acylation, one should expect retention of optical activity, and the formation of acetophenone. The glucose residue, having undergone deacetylation, should be found in the water layer on subsequent work-up as illustrated below.

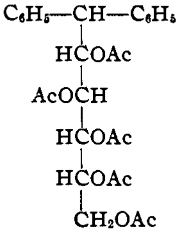


It should be noted that for acylations involving esters, two moles of catalyst are required theoretically for complete reaction. The first mole cleaves the ester and the second mole catalyzes the subsequent acylation. Thus if the ester functions of tetraacetylglucosyl chloride underwent cleavage involving acylation, eight equivalents of aluminum chloride would be required, plus an additional catalytic amount to promote the desired reaction at the halogen position. Actually, the theoretical requirement for eight equivalents of catalyst did not have to be fulfilled in practice. When tetraacetyl-α-D-glucosyl chloride was dissolved in a large excess of benzene and slightly over five equivalents of catalyst added, a vigorous reaction ensued on warming. Hydrogen chloride was liberated and the catalyst phase changed gradually from a powder to a thick gum, becoming finally homogeneous with the solvent. After the reaction mixture was decomposed with water the reddish, fluorescent benzene layer yielded the acetophenone plus a small quantity of higher boiling tar which distilled over a continuous range. The water layer, containing the carbohydrate portion, was processed to yield a sirupy residue which was readily acetylated to give a new, crystalline acetate. Structure I, supported by analytical data, is that anticipated for the product if the phenyl group replaced the chlorine atom. As expected, the substance displayed no reducing action toward hot Fehling solution, indicating the absence of a reducing group. β-D-Glucose pentaacetate, it should be noted, is strongly reducing under similar conditions. Confirmation of the presence of the phenyl group was afforded by the oxidation of the compound to benzoic acid by potassium permanganate. It is thus apparent that tetraacetylglucosyl chloride is capable of glucosylating benzene in a manner quite analogous to that in which alkyl halides alkylate benzene. Two names for I are tetraacetyl-D-glucopyranosylbenzene and 2,3,4,6-tetraacetyl-1-phenyl-1,6-anhydro-D-glucitol. Evidence to be presented in this and future papers will show that the assumptions inherent in these names are valid, namely, the D-glucose configuration and the 6-atom ring.

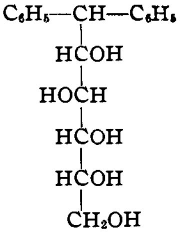
In an attempt to increase the yield of I an experiment was performed using the theoretical eight equivalents of aluminum chloride. Instead of isolating I, m. p. 156.5°, a second acetate was isolated, m. p. 95°. This lower melting compound could be deacetylated to give a crystalline substance melting at 157.5°, different from I in spite of the close melting points. It strongly depressed the melting point of I in a mixture of the two. This same non-acetylated substance could be isolated from the unacetylated residue from the experiment by direct extraction without the acetic anhydride treatment. As a matter of fact, one can isolate the same compound from the mother liquors of the first experiment where only five equivalents of aluminum chloride were used, but the quantity was only one-fifth the weight of I. The identity of the deacetylated product and its non-acetylated progenitor indicates the absence of structural changes on acylation and deacylation. Oxidation of both the low melting acetate and its deacetylation product led to benzophenone, and neither product showed reducing action toward hot Fehling solution. On the basis of this evidence and the analytical data the structures assigned to these two products are 1,1-diphenyl-1-desoxy-D-glucitol pentaacetate (II) and 1,1-diphenyl-1-desoxy-D-glucitol monohydrate



I



II



III

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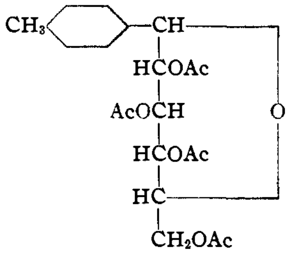
[10] C. A. Thomas, "Anhydrous Aluminum Chloride," Reinhold Publishing Corp., New York, N. Y., 1941, p. 673ff.

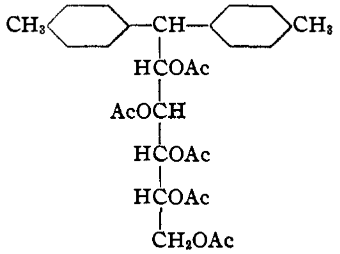
(III), respectively. Again, retention of the glucose stereochemical structure is implied in these names. Products like II and III could arise only through rupture of the amylene oxide ring in compound I, followed by further glycosylation of the solvent. Such a hypothesis conforms to the observations of Smith and Natelson[11] on the behavior of alkylene oxides and benzene in the presence of aluminum chloride, wherein ethylene oxide led to 2-phenylethanol and dibenzyl. A product corresponding to dibenzyl, however, was not observed in the present amylene oxide ring fission.

Since compound I (or its unacetylated analog) is the substance from which III is produced it is evident that ring opening was accompanied by further reaction with benzene. Since tetraacetylglucosyl chloride contains an amylene oxide ring, it is reasonable to infer that this ring remained intact during formation of I and that any opening of the ring which might have given rise to a different ring size caused formation of III instead.

It should be emphasized that the pyranose ring in I is no longer that of a cyclic acetal or hemiacetal, but rather that of a cyclic ether. An interesting theoretical correlation has been pointed out in this connection by Dr. S. M. Cantor. Syntheses of the Friedel–Crafts type normally involve a process of reduction. Acyl halides change to ketones (or aldehydes), and alkyl halides change to hydrocarbons, the former process involving reduction from an acid type of carbon to an aldehyde type and the latter from an alcohol type to a hydrocarbon type. Much less common among Friedel–Crafts processes is the reduction from an aldehyde type of carbon to an alcohol type, but the present transformation of tetraacetylglucosyl chloride into a glucosylbenzene is such a process. The further reaction of the glucosylbenzene to yield III represents, of course, a change from the alcohol type of carbon to the hydrocarbon type.

Extension of the glucosylation reaction to toluene was outwardly similar to the benzene experiments. From the dark, fluorescent toluene layer was obtained methyl *p*-tolyl ketone as well as comparatively larger quantities of tar. Acetylation of the carbohydrate material in the water layer led to a glassy acetate. This substance as well as its crude, unacetylated progenitor was oxidized with alkaline permanganate. The acids thus formed were converted to their methyl esters. Two distinct methyl esters were separated which were shown to be methyl 4,4′-benzophenonedicarboxylate and methyl terephthalate. It was thus established that the reaction with toluene proceeded analogously to that with benzene to yield two products, *p*-(tetraacetyl-D-glucopyranosyl)-toluene (IV) and 1,1-di-*p*-tolyl-1-desoxy-D-glucitol pentaacetate (V). On oxidation IV should yield terephthalic acid, and V should yield 4,4′-benzophenonedicarboxylic acid. Compounds IV and V were not separated as such, but after deacetylation of the crude, glassy acetate there was isolated 1,1-di-*p*-tolyl-1-desoxy-D-glucitol monohydrate in pure crystalline form.


IV


V

In the attempted glucosylation of naphthalene no identifiable carbohydrate product could be isolated, although methyl naphthyl ketone was obtained as anticipated.

Experimental

Attempted Glucosylation with a Small Amount of Aluminum Chloride.—A mixture of tetraacetyl-α-D-glucosyl chloride (20 g.), benzene (100 ml.), and aluminum chloride (1.33 g.) was stirred for eight hours. From the mixture only impure starting chloride, m. p. 70–72°, was obtained. The same was true if the reaction was performed under reflux.

Tetraacetylglucosylbenzene.—Tetraacetyl-α-D-glucopyranosyl chloride (20.0 g., 0.0545 mole), benzene (300 ml., 3.39 moles; dried over calcium chloride), and anhydrous aluminum chloride (38.0 g., 0.286 mole) were mixed and refluxed on the steam-bath in a three-necked flask equipped with mercury-sealed stirrer and reflux condenser, beyond which was a drying tube and hydrogen chloride trap. After four hours an additional five grams of catalyst was introduced. During the period of refluxing the solution darkened to a deep red, and the catalyst phase went from a powder to a gum, then to a thick sirup, and finally dissolved in the benzene. After seven hours, heating and stirring were discontinued and the reaction was permitted to stand overnight. It was then poured into cold water (500 ml.) to decompose the catalyst complex. The benzene layer was separated and washed with water, twice with 10% sodium hydroxide solution, and twice with water, the washings being added to the aqueous layer. The benzene solution was next dried over sodium sulfate. Removal of the solvent under diminished pressure on the steam-bath resulted in a thin oil (15.8 g.) having no optical activity. The oil, on fractionation, gave 11 g. boiling up to 195° (chiefly acetophenone, its 2,4-dinitrophenylhydrazone melting at 249°), 3 g. boiling at 240–250° (110 mm.), and 0.5 g. of residue. The aqueous layer was neutralized to litmus and filtered free of the precipitated aluminum hydroxide (Celite), the residue being washed several times with hot water. The clear filtrate was taken to dryness *in vacuo* at 100°, and the 50 g. of yellow residue (chiefly sodium chloride) was pulverized and extracted several

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[11] Smith and Natelson, This Journal, 53, 3476 (1931).

times with 200-ml. portions of boiling pyridine. Removal of the pyridine *in vacuo* at 100° left 5.6 g. of a brownish sirup. This was acetylated by stirring on the steam-bath for two hours with acetic anhydride (40 ml.) and anhydrous sodium sulfate (2 g.). The mixture was then cooled, poured into water, and permitted to hydrolyze overnight, then extracted into ether. A small amount of undissolved solid was filtered off, dissolved in acetone, and transferred to the ether. The extract was then washed with water, 4% sodium hydroxide, water, and finally dried over sodium sulfate. The dried solution was decolorized by filtration through a bed of Norite, and the solvent distilled off. There remained 6.0 g. (27%) of crude tetraacetyl-D-glucopyranosylbenzene. After three recrystallizations from 2-propanol, fine, white needles were obtained which melted at 156.5° and had $[\alpha]^{25}_{\rm D}$ −16.4° (concn. 0.855 g./100 ml. $CHCl_3$).

Anal. Calcd. for $C_{12}H_{12}O_5(OCCH_3)_4$: C, 58.8; H, 5.88; acetyl, 42.2. Found: C, 58.97; H, 5.97; acetyl,[12] 42.3.

The conditions of the above were duplicated exactly. From the benzene layer was obtained 21 g. of acetophenone and from the water layer 11.0 g. of crude, black sirup (after pyridine extraction). Before acetylation a small portion (1.8 g.) of this sirup was crystallized from water, after clarification by filtration through Norite, to yield crude 1,1-diphenyl-1-desoxy-D-glucitol hydrate, m. p. 154–155°, mixed m. p. with a pure sample, 156–157° (see below). The remaining 9.2 g. of crude sirup was acetylated as usual to give 8.1 g. of crude acetate. After one recrystallization the tetraacetyl-D-glucosylbenzene melted at 152.5–154.5° and weighed 3.0 g. From the mother liquors, on concentration in an air stream, coarse crystals of 1,1-diphenyl-1-desoxy-D-glucitol pentaacetate (0.5 g.) were obtained, m. p. 93–94°.

Oxidation of Tetraacetylglucosylbenzene.—The crystalline acetate (0.5 g.) was added to a solution of potassium permanganate (2.0 g.) and 10% sodium hydroxide (0.5 ml.) in water (40 ml.). The mixture was refluxed for three hours, acidified with sulfuric acid, and refluxed another one-half hour. On cooling, the permanganate color was discharged by addition of sufficient saturated sodium bisulfite solution, and the resulting clear liquid was extracted with ether. After washing with water and drying, the solvent was removed, and the residue recrystallized from water to give platelets, m. p. 121.5–122°; mixed m. p. with benzoic acid, 122–122.5°.

1,1-Diphenyl-1-desoxy-D-glucitol Pentaacetate.—Tetraacetyl-α-D-glucosyl chloride (118 g., 0.311 mole), dry benzene (1800 ml., 20.3 moles), and aluminum chloride (347 g., 2.61 moles) were placed in a 5-liter, three-necked flask arranged as previously described. After refluxing for two hours, another charge of catalyst (20 g.) was added, and the refluxing continued for four more hours. The mixture stood at room temperature overnight, and was then treated as before. A 115.1-g. (74.6%) yield of acetophenone resulted from the benzene layer. Acetylation of the residue from the pyridine extraction of the water layer residue was accomplished as before with acetic anhydride (240 ml.) and sodium acetate (13 g.). The crude, sirupy 1,1-diphenyl-1-desoxy-D-glucitol pentaacetate isolated weighed 31.6 g. (17%). This was crystallized from 2-propanol to give 23.5 g. of a solid melting from 90–95°.

A repetition of the experiment using tetraacetylglucosyl chloride (106 g.), benzene (2000 ml.), and aluminum chloride (607 g.), in which refluxing was continued for forty-one hours before work-up, led to 135 g. (97%) of acetophenone, but only 3.3 g. (2%) of the crystalline pentaacetate, m. p. 94.5–95°. After two recrystallizations from 2-propanol a sample of the acetate from the latter experiment had these constants: m. p. 95–95.5°, $[\alpha]^{25}_{\rm D}$ +28.0° (concn. 1.756, $CHCl_3$).

Anal. Calcd. for $C_{18}H_{17}O_5(OCCH_3)_5$: C, 63.6; H, 6.06; acetyl, 40.6. Found: C, 63.48; H, 5.90; acetyl,[12] 40.8.

Oxidation of 1,1-Diphenyl-1-desoxy-D-glucitol Pentaacetate.—The pentaacetate (2.5 g.), potassium permanganate (10 g.), 10% sodium hydroxide (2.5 ml.), and water (200 ml.) were refluxed for 2.6 hours, then treated as previously described. Removal of the ether left 1.30 g. of aromatic-smelling oil. The fact that oxidation had not gone to completion was shown by the weight (theoretical is about one-half the weight isolated) and the slight rotation of the oil. That it was chiefly benzophenone was established by converting it to its 2,4-dinitrophenylhydrazone in good yield, m. p. 241.5–242°.

1,1-Diphenyl-1-desoxy-D-glucitol.—The crude pentaacetate (31.7 g.) was dissolved in methanol (400 ml.) at 25°, and about 0.2 g. of sodium was added. After standing forty-five minutes the flask had filled with fine, white crystals. These were collected after two hours, washed in methanol, and refiltered; yield, 18.4 g.; m. p., 156.5–157.5°. A small second crop (1.7 g.) was obtained by concentration of the mother liquors; m. p. 154–156°. The combined crops were recrystallized from the minimum quantity (2000 ml.) of boiling water, coming out as exquisite, long needles in 92% yield; $[\alpha]^{25}_{\rm D}$ +47.4° (*c*, 1.680 in dioxane). The melting point of the 1,1-diphenyl-1-desoxy-D-glucitol monohydrate was 157.5–158°, with preliminary sintering due to dehydration at 140–150°.

Anal. Calcd. for $C_{18}H_{22}O_5 \cdot H_2O$: C, 64.4; H, 7.14; H_2O, 5.36. Found: C, 64.11; H, 7.04; H_2O (by drying in an Abderhalden pistol), 6.86.

Oxidation of 1,1-Diphenyl-1-desoxy-D-glucitol Hydrate.—The hydrate (0.30 g.) was oxidized as previously described, using proportional quantities of reagents. The yield of benzophenone was 0.12 g. (74%). Conversion of the ketone to its 2,4-dinitrophenylhydrazone yielded a product having m. p. 241–242°, and a mixed m. p. with an authentic sample 242.5–243°.

1,1-Diphenyl-1-desoxy-D-glucitol Pentaacetate from the Hydrate.—The hydrate (10.0 g.) was dissolved in pyridine (200 ml.), and acetic anhydride (100 ml.) added. After standing at 25° for twenty-four hours, more anhydride (50 ml.) was added. After another twenty-four hour period the mixture was poured into water, left there for ninety minutes, extracted with ether, and the ether solution washed with water, dilute hydrochloric acid, water (twice), saturated sodium bicarbonate solution (until gas evolution ceased), again with water, and finally dried over sodium sulfate. Removal of the solvent left 17.0 g. of crude sirup which was readily recrystallized from 2-propanol to yield 14.4 g. (89%) of 1,1-diphenyl-1-desoxy-D-glucitol pentaacetate, m. p. 94–94.5°.

Investigation of High-boiling Tars from Benzene Experiments.—Tars (60 g.) from several glycosylations of benzene were fractionated at 0.5 mm. into four fractions as follows: (A) residual acetophenone (15 ml.; b. p. 71°), (B) thin oil (5 ml.; b. p. 91–130°), (C) thin oil (15 ml.; b. p. 132–190°), (D) tarry residue (30 ml.). Fraction C was redistilled at 0.5 mm. using a 25-ml. distilling flask with an 8-inch Vigreux side neck. The following cuts were taken: (C1) thin oil (2 ml.; b. p. 100–128°), (C2) thin oil partially crystallizing (3 ml.; b. p. 127–137°), (C3) thin oil partially crystallizing (5 ml.; b. p. 137–147°), (C4) residual tar (5 ml.). All of these fractions were placed at 0° for several days, but only fraction C2 gave sufficient crystalline material for characterization. This material was collected, washed well with alcohol, and air dried. It was shown by m. p. (212.5–214.5°) and mixed m. p. (213.5–214°) to be anthracene.

Reaction of Toluene with Tetraacetyl-α-D-glucopyranosyl Chloride.—Tetraacetylglucosyl chloride (20.0 g., 0.0545 mole), toluene (362 ml., 3.4 moles, dried over sodium), and aluminum chloride (45 g.) were placed in the previously described apparatus and the mixture heated to 75–80° with stirring for five hours. The physical changes accompanying the reaction paralleled those observed in the reaction with benzene. After cooling and standing overnight the reaction mixture was manipulated exactly as described before. From the toluene layer, after removal of the solvent and fractional distillation, was obtained 20 ml.

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[12] Analyzed by the method of Kunz and Hudson, THIS JOURNAL, 48, 1982 (1926).

of methyl *p*-tolyl ketone and 20 ml. of pungent, black tar. The ketone was characterized by its semicarbazone, m. p. and mixed m. p., 207–208°. The water layer was treated as usual, yielding 4.0 g. of residue from the pyridine extraction. This was acetylated using acetic anhydride (25 ml.) and sodium acetate (2 g.) to give 3.24 g. of an amber sirup which set to a hard glass; $[\alpha]^{25}\text{D}$ +15.6° (concn. 5.015, $CHCl_3$).

In a duplicate experiment of somewhat shorter heating time (60–83° for two hours), 11.5 g. of methyl *p*-tolyl ketone and 25.4 g. of tar were obtained from the toluene layer. In this run the final acetylation product was 2.21 g. of a clear, amber glass having a somewhat higher specific rotation, +30.2° (concn. 2.690, $CHCl_3$). A second duplication of the experiment with double quantities of reagents and again slightly altered temperature conditions (65–83° for three hours) yielded 32.1 g. of methyl *p*-tolyl ketone and 35.4 g. of tar. The final acetate from the water layer was 2.13 g. of a glass having a specific rotation of +15.7° (concn. 1.210, $CHCl_3$).

Oxidation of the Crude Glucosylation Mixture from Toluene.—One gram of the reaction product from the preceding experiment was removed prior to acetylation for purposes of oxidation with potassium permanganate (4 g.), 10% sodium hydroxide solution (0.8 ml.), and water (80 ml.). After refluxing for three hours and discharging the permanganate color with bisulfite, the mixture was filtered. The filtrate was acidified, and the white, colloidal product coagulated by digestion for several hours at 100°. It was then collected and washed on a small Witt funnel; yield, 0.08 g. This was melted in a test-tube with thrice its volume of phosphorus pentachloride, kept molten for several minutes, cooled, and cautiously decomposed with methanol. The methyl esters were isolated by adding water and filtering. The product was recrystallized from acetone into two fractions: m. p. 180–200° (0.01 g.), and m. p. 136–138° (0.01 g.). The first fraction was recrystallized from acetone to give pure methyl 4,4′-benzophenone-dicarboxylate, m. p. 229–229.5°, mixed m. p. with an authentic sample, 228–229°. The second fraction, when mixed with a pure sample of methyl terephthalate of m. p. 139.5–140°, melted at 139–139.5°.

1,1-Di-*p*-tolyl-1-desoxy-D-glucitol.—Two grams of the glassy acetate, $[\alpha]^{25}\text{D}$ +30.2°, was dissolved in methanol (200 ml.) and a chip of sodium added. After ninety minutes the solvents were removed under reduced pressure leaving 1.43 g. of an amber sirup. This was dissolved in hot water (50 ml.). On slow cooling fine, white needles of 1,1-di-*p*-tolyl-1-desoxy-D-glucitol hydrate separated, m. p. 149–153.5°. After two recrystallizations from water, including filtration through Norite, the m. p. was raised to 158.5–160.5°.

Anal. Calcd. for $C_{20}H_{28}O_6$: C, 65.9; H, 7.74. Found: C, 65.36; H, 7.58.

Attempted Glucosylation of Naphthalene.—Tetraacetyl-α-D-glucopyranosyl chloride (10 g.), naphthalene (218 g.), and aluminum chloride (20 g.) were melted together at 90° and heated for four hours at 80–86°. On processing the mixture there was obtained 33.6 g. of black, benzene-soluble reaction product from which was obtained 4.3 g. of 1-acetylnaphthalene (oxime, m. p. 137.5–139°; *cf.* m. p. 137–138° and 139.5–140.5°[13]), some 2,2′-binaphthyl of m. p. 185.5–186.5° (picrate, m. p. 181–181.5°; *cf.* 184–185°[14]) from the 9.4-g. fraction collected at 245–290° (0.2 mm.), but no other crystalline products.

The water layer yielded 1.47 g. of an amber sirup but no definite crystalline products were obtainable from it.

Acknowledgment.—The carbon and hydrogen microanalyses reported in this paper (but not the other determinations) were performed by Dr. T. S. Ma.

Summary

Tetraacetyl-α-D-glucosyl chloride has been shown to react with benzene in the presence of aluminum chloride to give a variety of products, the nature of which depends upon the quantity of catalyst. When five equivalents of catalyst are used, acetophenone, tar, tetraacetyl-D-glucopyranosylbenzene, and some 1,1-diphenyl-1-desoxy-D-glucitol pentaacetate are formed. When eight equivalents of catalyst are employed, tetraacetyl-D-glucopyranosylbenzene is not among the isolated products.

Tetraacetyl-D-glucopyranosylbenzene is formed by an alkylation reaction analogous to the Friedel-Crafts hydrocarbon synthesis. 1,1-Diphenyl-1-desoxy-D-glucitol pentaacetate arises as a cleavage product of the pyranose ring in the glucopyranosylbenzene under the influence of the catalyst. Acetophenone is formed by a preliminary reaction of the acetyl functions of tetraacetylglucosyl chloride with benzene.

Analogous reactions have been observed for toluene and naphthalene leading, for the most part, to analogous products. The reactions here, however, are less clean-cut, and the yields are inferior to the benzene reaction. The products from naphthalene did not crystallize.

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[13] St. Pfau and Offner, *Helv. Chim. Acta*, **9**, 669 (1926); Fieser, Holmes and Newman, THIS JOURNAL, **58**, 1055 (1936).

[14] Friedel and Crafts, *Compt. rend.*, **100**, 692 (1885); Chattaway, *J. Chem. Soc.*, **67**, 657 (1895); Ferko, *Ber.*, **20**, 662 (1887).