Summary

1. When aqueous alkalies act upon benzaldehyde, benzyl benzoate is a primary product.

2. Dihydroxy-dibenzyl ether is indicated as a prior intermediate, and a mechanism for its formation and its conversion into benzyl benzoate by a glycol-like rearrangement is given.

3. In the development of this problem, some properties of benzyl alcohol and of dibenzyl ether are studied.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORIES OF CANADA]

THE ACTION OF CHLORAL ON CELLULOSE

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Hefter[1] by heating a mixture of glucose and anhydrous chloral at 100° obtained two condensation products of chloral with glucose, namely chloralose (m. p., 187°) and parachloralose (m. p., 227°). Petit and Polonowski[2] and Hanriot and Richtet[3] catalyzed the reaction by the addition of a small quantity of hydrochloric acid and obtained the same condensation products. Meunier,[4] using a large quantity of concd. sulfuric acid, carried out the same condensation with chloral hydrate. In addition to the two chloraloses he isolated a dichloralglucose (m. p., 225°) and a chloralglucosan (m. p., 225°). F. H. Reichel[5] treated glucosan and levoglucosan with chloral hydrate and sulfuric acid and obtained two additional dichloralglucoses (m. p., 268°, 85°). From glucosan he obtained parachloralose but no chloralose, whereas from levoglucosan he obtained chloralose but no parachloralose.

The object of the present investigation was to obtain chloral derivatives of cellulose which might be degraded to chloral-substituted glucoses and to compare them with similar derivatives from starch.

No definite products were obtained by the action of chloral or its hydrate on cellulose even in the presence of catalysts such as hydrochloric acid or zinc chloride. By the use of concd. sulfuric acid and chloral hydrate, as described by Meunier, cellulose yielded considerable quantities of chloralglucoses but no chloral-substituted celluloses or cellulose dextrins.

Experimental Part

Fifty g. of surgical cotton was gradually stirred into a mixture of 100 g. of chloral hydrate and 100 cc. of concd. sulfuric acid contained in a beaker cooled in snow. The

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[1] Hefter, *Ber.*, **22**, 1050 (1889).

[2] Petit and Polonowski, *Bull. soc. chim.*, [3] **11**, 125 (1894).

[3] Hanriot and Richtet, *ibid.*, [3] 9, 947 (1893); [3] **11**, 37, 303 (1894).

[4] Meunier, *Compt. rend.*, **122**, 142 (1896); *Ber.*, (Ref.) **29**, 177 (1896).

[5] Reichel, *Thesis*, University of Geneva, **1921**. Pictet and Reichel, *Helvetica Chim. Acta*, **6**, 621 (1923).

dissolution of the cotton was rapid with little discoloration and small evolution of heat. The reaction was then allowed to proceed at room temperature and occasionally stirred.

At the end of 2 hours a skin had formed at the surface of the liquid and on 12 hours' standing a thick, solid layer had formed there. This was removed and ground under water in a mortar, giving a light gray flocculent, or at times granular, precipitate. The remaining liquid was poured into a large volume of cold water whereupon it gave a further quantity of the gray precipitate.

The precipitate was boiled in 600 cc. of water until it formed a soft gum, and only traces of chloral came off in the vapors. The water was decanted and a further 600 cc. containing from 5 to 10 cc. of concd. nitric acid was added and the mixture boiled for about 10 minutes, whereupon the water was decanted. The gum hardened as it cooled and was easily broken up under water in a mortar. Filtered and dried, it weighed about 69 g. When extracted with about 200 cc. of alcohol and filtered hot it left a residue which was further purified by solution in hot acetone from which it precipitated on cooling. This is named Fraction I.

From the alcohol as it cooled there precipitated a crystalline compound named Fraction II; when this is removed by filtration and the filtrate is concentrated to about $^1/_3$ of its original volume a further quantity of Fraction II is obtained.

The mother liquors were concentrated on a bath until two layers were formed. The upper layer was quite clear, the lower layer was dark brown. This latter solidified as it cooled. The upper layer was decanted and the solid dissolved in carbon tetrachloride from which a crystalline compound separated on cooling, named Fraction III. The carbon tetrachloride solution was evaporated to a thick sirup which hardened as it cooled and was named Fraction IV.

Fraction I.—This was obtained as triangular or 6-sided plates from hot acetone or alcohol; m. p., 268°. It is slightly soluble in hot acetone, pyridine, acetic acid, alcohol, or concd. nitric acid, and is insoluble in ether, chloroform, carbon tetrachloride, petroleum ether, water, or hot or cold alkalies. Its solution in pyridine is levorotatory. It does not reduce Fehling solution.

Analyses. Subs., 0.1465: AgCl, 0.2833. Subs., 0.1627: CO_2, 0.1621; H_2O, 0.0334. Calc. for $C_{10}H_{10}O_6Cl_6$ (Reichel's dichloral glucose): C, 27.40; H, 2.30; Cl, 48.59. Found: C, 27.17; H, 2.30; Cl, 47.84.

The mono-acetate was prepared from acetic anhydride and sulfuric acid. It crystallizes from ether in needles; m. p., 198°; $[\alpha]_D$ $-12°$ (c. 5.0)[6] in $CHCl_3$.

Analysis. Subs., 0.1518: AgCl, 0.2178. Calc., mono-acetate: Cl, 44.25. Found: 44.30.

Upon *methylation* with dimethyl sulfate and sodium hydroxide, hairy needles were obtained from alcohol; m. p., about 200°; $[\alpha]_D$ -17 (c. 5.0) in 1:1 acetone-pyridine.

Analysis. Subs., 0.1612: AgCl, 0.3055. Calc. for $C_{11}H_{12}O_6Cl_6$: Cl, 46.98. Found: 46.89.

Fraction II.—Recrystallized from alcohol, this was obtained as needles; m. p., 225; $[\alpha]_D$ -15 (c. 1.2) in chloroform. It is not very soluble in carbon tetrachloride, and is insoluble in cold petroleum ether, water or alkalies. It does not reduce Fehling solution.

Analyses. Subs., 0.1377: AgCl, 0.2728. Subs., 0.1840: CO_2, 0.1830; H_2O, 0.0379. Found: C, 27.12; H, 2.30; Cl, 49.01.

Acetylation gives a product that forms thick, rectangular crystals from alcohol or ether; m. p., 126°; $[\alpha]_D$ -21.4 (c. 4.67) in chloroform.

Analysis. Subs., 0.1567: AgCl, 0.2799. Calc. for $C_{12}H_{12}O_7Cl_6$: Cl, 44.25. Found: 44.19.

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[6] A concentration of 5 g. in 100 cc. of solution.

After *methylation* the substance became too soluble in organic solvents to purify by crystallization; m. p., about 110°; $[\alpha]_D$ −23 (c. 5) in chloroform.

Analysis. Subs., 0.1540: AgCl, 0.2820. Found: Cl, 45.46.

Fraction III.—This crystallizes from hot water in long needles that are soluble in most organic solvents; m. p., 135–136°; $[\alpha]_D$ +32 (c. 7.754) in benzene; $[\alpha]_D$ +10.5 (c. 7.617) in chloroform. The substance is soluble in cold, concd. nitric acid, but insoluble in alkalies.

It does not reduce Fehling solution even after it has been boiled with acids.

Analyses. Subs., 0.1433: AgCl, 0.2745. Subs., 0.1616: CO_2, 0.1471. H_2O, 0.0331. Found: C, 24.82; H, 2.29; Cl, 47.39.

Fraction IV.—This was a very impure fraction. The chief impurity seems to be Fraction II which may be precipitated from solution in alcohol by cautiously adding petroleum ether; m. p., about 74–75°; $[\alpha]_D$ +14 (c. 8.12) in chloroform. It is insoluble in water and alkalies.

Although the original substance does not reduce Fehling solution, reduction of this reagent takes place after the substance has been boiled with dil. acids. Nitric acid produces a compound that is precipitated by sodium hydroxide. Heated in a vacuum it loses 2.8% of its weight and then reduces Fehling solution. Its chlorine content is within 1% of that of a dichloralglucose.

Hydrocellulose, starch and glucose treated with sulfuric acid and chloral hydrate yield four fractions similar to those mentioned above. Glucose gives a lower yield of Fraction IV than do the other carbohydrates by this reaction. The liquors remaining from the precipitation of the dichloral sugars in water, when heated on the water-bath, precipitate a quantity of parachloralose. A large quantity of parachloralose is deposited from the water and dil. nitric acid after the precipitate obtained from starch and glucose has been boiled; this does not happen in the case of cellulose and hydrocellulose.

Conclusions

The action of chloral hydrate on starch and cellulose gives rise to identical dichloralglucoses.

Monochloralglucoses could not give rise to dichloralglucoses by condensation with a second molecule of chloral. The former have four free hydroxyls, which points to aldol condensation; while the latter possess but one free hydroxyl, which indicates acetal condensation throughout.

Since it has been claimed by previous workers in this field that parachloralose is produced by the α-anhydro-glucosidic linkage of *d*-glucosan and never by the β-anhydro-glucosidic linkage of *l*-glucosan, the formation of parachloralose from cellulose might indicate the pre-existence of one or more α linkages in the cellulose molecule.

Summary

1. Cotton cellulose was acted on by chloral hydrate using a large excess of sulfuric acid as a condensing agent. No chloral-substituted cellulose or cellulose dextrines were isolated, but from the reaction mixture four compounds were obtained, two of which corresponded in every way to two known dichloral glucoses (both levorotatory), m. p. 268° and 225°, respectively. The other two compounds gave analyses approximately

that of dichloral glucose (both dextrorotatory), m. p., 135° and 74°, respectively.

The same four compounds were formed in a similar manner from starch and glucose.

2. Acetylation and methylation of the two levorotatory compounds showed the presence of only one free hydroxyl group. No crystalline compounds were obtained by these reactions on the dextrorotatory compounds.

3. Parachloralose was formed when the crude water-insoluble products of starch and glucose, but not those of cellulose, were boiled. The soluble reaction products from all three, however, produced parachloralose when heated, after dilution, on the water-bath.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

MOLECULAR REARRANGEMENTS OF THE CAMPHOR SERIES. XIV. STRUCTURE OF ISOCAMPHOLACTONE[1]

BY PHILIP KELSEY PORTER WITH WILLIAM A. NOYES

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Isocampholactone was first prepared by Noyes[2a] by the action of nitrous acid on aminolauronic acid. It was later prepared by Bredt[2b] in a pure condition by decomposing the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide. Noyes and Homberger[3] oxidized isocampholactone with nitric acid and isolated two products, one the nitro-isocampholactone and the other a lactone acid which was the lactone of an hydroxy dicarboxylic acid and has the formula, $\mathrm{O} = \underbrace{\mathrm{C}-\mathrm{O}-\mathrm{C}_7}\mathrm{H}_{11}\mathrm{COOH}$. The amide of this lactone acid was prepared. Nitro-isocampholactone was decomposed by dil. alkaline reagents forming an acid which has the formula $C_5H_8NO_2COOH$. Three carbon atoms and four hydrogen atoms were lost by the reaction but the other product of the reaction was not isolated. The amide of this acid was also prepared.

The structure of isocampholactone had not been determined when the investigation here described was begun. We have shown that it has Formula I.

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[1] An abstract of a thesis presented by Philip K. Porter in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois, June, 1923.

[2a] Noyes, *Am. Chem. J.*, **17,** 432 (1895).

[2b] Bredt., *Ber.*, **35,** 1291 (1902).

[3] Noyes and Homberger, THIS JOURNAL, **32,** 1665 (1910).