4. The absorption curves for the colorless solutions of phenolphthalein and isophenolphthalein in 33% aqueous potassium hydroxide have been determined. The absorption is due to the presence of the colorless tripotassium salt of the carbinol-carboxylic acid.

5. A table showing the frequency numbers of the peaks of the bands of the various solutions studied has been prepared.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE POLARIMETRY SECTION OF THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE][1]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XVI.[2] CONVERSION OF CELLOBIOSE TO ANOTHER DISACCHARIDE, CELTROBIOSE, BY THE ALUMINUM CHLORIDE REACTION. CHLORO-ACETYL CELTROBIOSE

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The new method of chlorinating sugar acetates by aluminum chloride which Kunz and the writer have described in the preceding article has been applied to cellobiose octa-acetate with the result that a considerable yield of the well-known crystalline α-chloro-acetyl cellobiose has been obtained, and in addition a yield of about 13% of an isomeric crystalline substance, the properties of which show that it is the chloro-acetyl derivative of a new disaccharide. It has been carefully purified by repeated crystallizations until its rotation became constant at $[\alpha]_D^{20} = +59.2$ in chloroform solution. The melting point was 137–138°. Its chlorine content was found to be 5.43% by heating it in acetic anhydride solution with silver acetate and 5.40% by Bacon's directions[3] for the Stepanoff method. The theoretical value for a chloro-hepta-acetyl dihexose, $C_{26}H_{35}O_{17}Cl$, is 5.41%. Its saponification by potassium hydroxide at 0° according to Kunz' method (see preceding article) shows its acid equivalent to correspond closely with that calculated. The alkaline saponification of the new chloro-acetate yields a dextrorotatory solution from the reading of which it is evident that the parent sugar is weakly dextrorotatory. After hydrolysis of the new chloro-acetate with 0.5 N hydrochloric acid for two and a half hours at 98°, by which treatment it is to be expected that the chlorine and acetyl groups are split off and the parent disaccharide largely hydrolyzed to its component hexoses, the solution is strongly levorotatory. These analytical, melting-point, rotation and hydrolysis data differentiate the sugar from all

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[1] Published by permission of the Director of the Bureau of Standards.

[2] See preceding Article XV.

[3] Bacon, THIS JOURNAL, **31**, 49 (1909).

known disaccharides and it is accordingly a new di-hexose and will be named *celtrobiose.* The crystalline derivative of it which results from the action of aluminum chloride upon the chloroform solution of cellobiose octa-acetate is accordingly named *chloro-acetyl celtrobiose.* Since the aluminum chloride reaction chlorinates the octa-acetates of both lactose and cellobiose and also partially changes them to chloro-acetyl derivatives of new sugars, it appears that the reaction is a general one for the chlorination of sugar acetates and possibly also for intramolecular rearrangement. In conformity with this view it has been found that α-chloro-acetyl glucose ($[\alpha]_D = +166$ in chloroform; m. p., 74°) is produced from β-glucose penta-acetate in considerable quantity by the reaction; whether some other chloro-acetate of a hexose is produced as a by-product in this case remains to be investigated. Studies of the application of the reaction to various sugar acetates and likewise an investigation of the possibility of preparing in analogous manner bromo- and iodo-acetyl sugar derivatives by the use of aluminum bromide or iodide are in progress at this Bureau.

Preparation of Chloro-acetyl Celtrobiose ($C_{26}H_{35}O_{17}Cl$).—Ten g. of recrystallized cellobiose octa-acetate ($[\alpha]_D = +36$ in chloroform; m. p., 221°) was dissolved in 100 cc. of absolute chloroform, 40 g. of powdered active aluminum chloride was added and the mixture was gently refluxed for five hours, using a calcium chloride tube to keep out moisture. It was then poured upon cracked ice, the mixture was well shaken and the chloroform layer was washed twice with ice water, dried with calcium chloride and evaporated under reduced pressure to small volume. The addition of ether caused an immediate voluminous precipitation of needle-like crystals which were filtered off and recrystallized by dissolving in a little chloroform and adding ether. The weight was 3.5 g.; $[\alpha]_D^{20} = +58.2$ in chloroform. The crystals are a mixture of substances which are difficult to separate, but by fractional crystallization from alcohol one component ($[\alpha]_D^{20} = +70$ in chloroform; m. p., 184°) was obtained fairly pure and the data indicate that it is the well-known α-chloro-acetyl cellobiose ($[\alpha]_D = +73$; m. p., 187°).[4] The original mother liquor was concentrated under reduced pressure to small volume, taken up with ether and filtered from a new crop of needle crystals. The filtrate soon deposited on the beaker walls a new type of crystal, hexagonal plates, with which needles could also be seen. By fractional crystallization from ether the two substances were separated and 1.3 g. of hexagonal plates, free from needles, was obtained. They were dried at 35° in air, then in a desiccator over lime and it was found that heating them at 100° caused no further loss in weight. The substance is a chloro-hepta-acetate of a new disaccharide (di-hexose), celtrobiose. After several recrystallizations from chloroform or ether by the addition of petroleum ether the rotation of the chloro-acetate became constant at the

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[4] Schliemann, *Ann.*, **378**, 374 (1911).

value $[\alpha]_D^{20} = +59.2$ in pure chloroform (1.0878 g. of substance, 25 cc. of chloroform solution; 5.154° rotation to the right in a 200mm. tube). The substance melted at 137–138° without decomposition but slowly decomposed with gas evolution in the range 155–165°. A chlorine estimation was made by heating 1.056 g. of substance with 0.4 g. of pure silver acetate in acetic anhydride solution for one hour on the steam-bath and weighing the silver chloride (0.2269 g.); 5.43% of chlorine was found as compared with 5.41% calculated for $C_{26}H_{35}O_{17}Cl$. A measurement by Bacon's directions for the Stepanoff method showed 5.40% of chlorine (0.1938 g. of substance gave 0.0414 g. of silver chloride), which proves that the substance contains only one chlorine atom in its molecule. The ease of removal of this atom by silver acetate corresponds with the behavior of chloro-acetyl derivatives of the sugars. The acid equivalent was found by saponifying in an ice-salt bath 0.2011 g. of substance dissolved in 50 cc. of acetone with 50 cc. of 0.1 *N* potassium hydroxide aqueous solution for two hours; the alkali that was neutralized was 24.4 cc. as compared with the calculated value 24.5 cc. Chloro-acetyl celtrobiose is very soluble in chloroform or acetone, somewhat soluble in warm ether, nearly insoluble in cold ether, insoluble in petroleum ether or water. It reduces Fehling's solution on boiling. It is a stable halogeno-acetyl sugar derivative and may be kept in moist air without decomposition.

Summary

The action of active aluminum chloride on a chloroform solution of cellobiose octa-acetate produces the well-known α-chloro-acetyl cellobiose and in addition an isomeric substance that proves to be the chloro-hepta-acetate of a new di-hexose to which the name celtrobiose is given.

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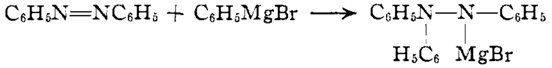
NOTE

The Mechanism of Reduction of Azobenzene by Organomagnesium Halides.—Several theories have been proposed for the mechanism of reduction of azobenzene by organomagnesium halides. Busch and Hobein[1] suggested tentatively that phenylmagnesium bromide added to azobenzene as follows.



$$C_6H_5N{=}NC_6H_5 + C_6H_5MgBr \longrightarrow \underset{H_5C_6}{C_6H_5N}-\underset{MgBr}{N}-C_6H_5 \qquad (I)$$

This was proposed as a possible explanation for the formation of triphenylhydrazine from β-phenylhydroxylamine and phenylmagnesium bromide. Franzen and Deibel[2] interpreted the formation of hydrazobenzene as follows.

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[1] Busch and Hobein, *Ber.*, **40**, 2099 (1907).

[2] Franzen and Deibel, *Ber.*, **38**, 2716 (1905).