Summary.

A description has been given of various experiments carried out illustrative of the use of iodine as a dehydrating and condensing agent. In all the cases investigated, *viz.*:

(*a*) Conversion of alcohols into unsaturated hydrocarbons.

(*b*) Conversion of ketone-alcohols into unsaturated ketones.

(*c*) Conversion of aldols into unsaturated aldehydes.

(*d*) Conversion of glycols and glycerols into polyglycols and polyglycerols, respectively.

(*e*) Condensation of aldehydes with polyalcohols.

It has been found that a very small amount of iodine (in some cases as low as 1/10,000 part by weight) suffices to bring about the change. The reaction is apparently a general one, and a tentative theory has been advanced to explain the catalytic role played by the iodine in such processes.

In two recent patents[1] the claim is made that the presence of small traces of iodine induces in a remarkable manner the condensation of amines with alcohols (*e. g.*, formation of dimethylaniline from aniline and methyl alcohol) as well as the splitting off of HCl from amines and their hydrochlorides, so that it would not be at all surprising if this reagent should prove capable of an extremely wide application in synthetic organic work both in the laboratory and in the industry.

The greater part of the preceding investigation was carried out at the Experimental Station of the E. I. duPont de Nemours Powder Co., Wilmington, Del., and the author wishes to express his thanks to the officials of this company for the facilities placed in his way in enabling him to carry out the work.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORIES.]

THE ACETOLYSIS OF CARBOHYDRATES.

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The study of the acetolysis of the carbohydrate part of invertase[2] led to the following work on the acetolysis of other carbohydrates. It was hoped that by an extensive study of a large number of these disaccharides and polysaccharides, we might be able to formulate some general principle regarding the structure of these compounds from their behavior on acetolysis, and thus throw more light on the constitution of the carbohydrate part of invertase.

It has been noticed in the acetolysis of various disaccharides and poly-

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[1] Knoll and Co., D. R. P. 241,853, 250,326.

[2] THIS JOURNAL, 36, 398 (1914).

saccharides, that the breaking down of these sugars through the agency of acetyl chloride, acetyl bromide or acetyl sulfate (acetic anhydride + concentrated sulfuric acid), comes to an end at the monosaccharide stage in certain cases, while in others it stops at the disaccharide stage. The question whether this difference in behavior can be attributed to the nature of the oxygen linking connecting the monosaccharides, or to the character of the monosaccharides themselves, has led us to undertake the present investigation.

Syniewski,[1] from an exhaustive study of the behavior of starch on hydrolysis, suggested that there are three different types of linkings between the various glucose molecules. These three are the α-linking, which is readily hydrolyzed by malt, yielding maltose and a dextrin; the β-linking, which is difficultly broken by malt yielding glucose and a dextrin; and the γ-linking which connects the glucose in maltose itself. The above hypothesis readily explains why we obtain various products in hydrolyzing starch, the nature of the product depending upon which linking is attacked by our hydrolyzing agent.

When we treat polysaccharides, disaccharides and glucosides with acetolytic agents, we notice a similar behavior. That this difference in behavior depends on the nature of the linking and not on the character of the monosaccharides constituting the sugars, may be seen most readily in the case of those polysaccharides where the monosaccharides are all the same, like cellulose and starch.

Hardt and Strehmayer,[2] and more recently Klein,[3] studied the acetolysis of cellulose with acetic anhydride and sulfuric acid. They obtained products ranging from cellulose acetates down to cellobiose acetates, but in no case could they obtain glucose acetates, although Klein looked for them, showing that there must be a different linking between the glucose molecules composing cellobiose, and those linking it to the rest of the molecule.

Skraup[4] and Klein both noted that the amount of sulfuric acid and temperature influenced the speed of reaction, and not the final products. In no case could cellobiose acetate be broken down further.

Pregl[5] investigated the acetolysis of soluble starch with acetic anhydride and sulfuric acid, and isolated several dextrin acetates. His work does not, however, indicate what happens to these on further acetolysis.

The action of the three acetolytic agents on the various disaccharides which have been studied is indicated briefly in Table I.

[1] *Ann.*, **324**, 212 (1901).

[2] *Monatsh.*, **28**, 63 (1907).

[3] *Z. angew. Chem.*, **25**, 1409 (1912).

[4] *Ber.*, **32**, 2413 (1899).

[5] *Monatsh.*, **22**, 1049 (1901).

TABLE I.

	Acetic anhydride + sulfuric acid.	Acetyl chloride.	Acetyl bromide.
Cellulose	Cellobiose octacetate (Hardt and Strehmayer)[1]	Acetchlorocellobiose (Bates)[7]	Acetbromocellobiose (Bates)[7]
Starch	Dextrin acetates (Pregl)[2]		
Maltose	Maltose octacetate (Born and Nelson)[8]	Acetchloromaltose (Born and Nelson)[8]	Acetbromomaltose (Fischer)[3]
Lactose	Lactoseoctacetate (Bodart)[4]	Acetchlorolactose (Born and Nelson)[8]	Acetbromolactose (Ditmar)[5]
Sucrose	α-Glucose pentacetate (Skraup)[6]	Acetchloroglucose (Born and Nelson)[8]	Acetbromoglucose (Born and Nelson)[8]
α-Methyl glucoside	α-Pentacetyl glucose (Born and Nelson)[8]		

As can be noticed from the table, the knowledge up to the time we started our work was not in such condition that any comparison could be made as to the acetolytic action of these reagents on the various carbohydrates. By filling in the gaps in the table this has been made possible. The experimental work follows.

Experimental.

I. Action of Acetyl Bromide on Sucrose.—Five grams of sucrose, dried at 50° in a vacuum over phosphorus pentoxide, were treated with 25 g. of acetyl bromide, and heated gently on a water bath until all had gone into solution. The pale yellow syrup was dissolved in ether, washed with sodium sulfite and sodium carbonate, dried over calcium chloride, and then evaporated *in vacuo* at room temperature to a thick syrup. This syrup was dissolved in hot ligroin, b. p. 70–80°. On cooling, needle-shaped rosets, easily soluble in xylene, separated, m. p. 88–9° (uncor.). Reduces Fehling's solution. Identified as acetbromoglucose.

On analysis: Found, Br = 19.55%. Calc., Br = 19.46%.

II. Action of Actetyl Chloride on Sucrose.—Five grams of dried sucrose were treated with 15 g. of acetyl chloride and allowed to stand at room temperature for three days, when most had gone into solution. The light yellow solution was treated in the same way as the product from the action of acetyl bromide, but all attempts to obtain crystals from it have failed.

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[1] *Monatsh.*, **28**, 63 (1907).

[2] *Ibid.*, **22**, 1049 (1901).

[3] *Ber.*, **34**, 2895 (1902); **35**, 840 (1903).

[4] *Chem. Ztg.*, **25**, 1039 (1901); *Monatsh.*, **23**, 1 (1902).

[5] *Ber.*, **35**, 1953 (1902); *Monatsh.*, **23**, 865 (1902).

[6] *Ber.*, **32**, 2413 (1900).

[7] Private communication. J. S. Bates, working in this laboratory, has prepared the above compounds by the action of acetyl chloride and bromide on cellulose. The details will be published shortly.

[8] These gaps in the table have been filled in by our work.

The syrup gave strong tests for halogen and reduced Fehling's solution, showing that it was probably acetochloroglucose, which is very difficultly crystallizable.

III. Action of Acetyl Bromide on Maltose.—Five grams maltose dried at 100° in vacuum over phosphorus pentoxide were treated with 20 g. of acetyl bromide. Reaction started immediately and all went into solution in a short while. The solution was dissolved in ether, washed with ice-cold solution of sodium sulfite and carbonate, the ethereal solution dried over calcium chloride, and evaporated *in vacuo* at room temperature. A white, amorphous powder was obtained, soluble in benzene, acetone, alcohol, slightly in ligroin and petroleum ether. All attempts to crystallize it failed. Our substance agreed in every respect with that obtained by Fischer,[1] who used the same method. The substanee is acetbromomaltose.

Analysis: Found, Br = 11.24%. Calc., Br = 11.44%.

IV. Action of Acetyl Chloride on Maltose.—Five grams of maltose dried at 100° *in vacuo* over phosphorus pentoxide were treated with 25 g. acetyl chloride. Over night most had gone into solution. The solution was dissolved in ether, washed with sodium sulphite and sodium carbonate, dried over calcium chloride, evaporated *in vacuo* to a glistening, white powder. All attempts to crystallize this substance failed. Attempts were made to purify it by dissolving it in benzene, and precipitation with ligroin. The crude substance melted at about 65°, not sharply, is soluble in ether, benzene, toluene, xylene, alcohol, reduces Fehling's solution. Analysis showed Cl content about that of acetchloromaltose.

Analysis: Found, Cl = 4.35%. Calc., Cl = 5.42%.

V. Action of Acetic Anhydride and Sulfuric Acid on Maltose.—Five grams of maltose dried at 100° *in vacuo* over phosphorus pentoxide were treated with a mixture of 25 cc. acetic anhydride and 0.25 cc. of sulfuric acid previously cooled. All went into solution without charring. The solution was poured into water. A gum precipitated, which was washed well with water, till free of acetic anhydride, dissolved in alcohol, and reprecipitated with water. A white, amorphous powder, which we were unable to crystallize, separated out. The substance is octacetylmaltose.

Acetyl values: 49.6, 49.0; calc., 50.7%.

VI. Action of Acetyl Chloride on Lactose.—Five grams of lactose dried in vacuum at 110° over phosphorus pentoxide were treated with 20 cc. acetyl chloride. After all had gone into solution, the syrup was dissolved in chloroform diluted with ether, washed with ice-cold sodium sulfite and sodium bicarbonate, the ethereal solution dried over calcium chloride, and evaporated *in vacuo* at room temperature. A glistening, white pow-

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[1] *Ber.*, 42, 2523 (1910).

der, which could not be crystallized, was obtained. It is soluble in benzene, xylene, alcohol, slightly soluble in petroleum ether and ligroin.

VII. Action of Acetic Anhydride and Sulfuric Acid on α-Methyl Glucoside.—Two grams of α-methyl glucoside dried to constant weight at 100° were treated with a mixture of 10 cc. of acetic anhydride and 0.5 cc. sulfuric acid. All went into solution in a short while. The solution was poured into water and the precipitate recrystallized from alcohol. White needles, m. p. 111–112°. It reduces Fehling's solution and was identified as α-pentacetyl glucose by the melting point, and mixing some with a known sample of α-pentacetyl glucose. The melting point of the mixture was the same.

VIII. Action of Acetyl Bromide on α-Methyl Glucoside.—Five grams of dried α-methyl glucoside were treated with 20 g. of acetyl bromide. The reaction started at ordinary temperature with brisk evolution of hydrobromic acid. When all had gone into solution, it was dissolved in ether, washed with sodium sulfite and sodium bicarbonate, the ethereal solution dried over calcium chloride, evaporated *in vacuo*. A light brown syrup, soluble in benzene, alcohol, insoluble in ligroin, and which could not be crystallized was obtained.

IX. Action of Acetyl Bromide on Inulin.—Inulin was purified by dissolving a good grade of inulin in hot water, filtering from insoluble matter, and precipitating with three times its volume of alcohol. This was repeated three times when the inulin no longer reduced Fehling's solution. The inulin was first dried over sulfuric acid in a vacuum desiccator and then for five hours at 100° over phosphorus pentoxide *in vacuo*.

Five grams of inulin thus purified were placed in a flask, packed with ice, and 25 cc. of acetyl bromide, also cooled, added. The mixture was allowed to stand in ice about twelve hours, when all had gone into solution. Great care must be used in keeping down the temperature to avoid charring. The yellow syrup obtained above was dissolved in ether, washed with ice-cold sodium sulfite and sodium carbonate solution; the ethereal solution was dried over calcium chloride, filtered, and the ether was evaporated *in vacuo* at low temperature. A yellow syrup remained which resisted all attempts to crystallize it. The syrup reduced Fehling's solution. Several bromine determinations were made on this syrup, but as the product is very impure they did not check.

An average analysis is:

0.8685 g. subs. gave 0.2610 g. AgBr = 12.7% Br. Calc. for acetbromofructose = 19.46% Br; for acetbromodisaccharide = 11.44% Br.

Five grams of crude acetate prepared above were shaken with an excess of barium hydroxide solution until nearly all had gone into solution. The solution was filtered, the filtrate saturated with carbon dioxide, the barium carbonate filtered off, and the filtrate evaporated *in vacuo* to syrup. The syrup is soluble in alcohol, reduces Fehling's solution, and gives an osazone which was identified as fructosazone (glucosazone). The substance resisted all attempts to crystallize it.

Summary.

1. Sucrose treated with acetyl bromide gives acetbromoglucose.
2. Sucrose treated with acetyl chloride gives acetchloroglucose.
3. Maltose treated with acetyl bromide gives acetbromomaltose.
4. Maltose treated with acetyl chloride gives acetchloromaltose.
5. Maltose treated with acetic anhydride and sulfuric acid gives octacetyl maltose.
6. Lactose treated with acetyl chloride probably gives acetchlorolactose.
7. α-Methyl glucoside treated with acetic anhydride and sulfuric acid gives α-pentacetyl glucose.
8. α-Methyl glucoside treated with acetyl bromide gives an unidentified syrup.
9. Inulin treated with acetyl bromide gives an unidentified syrup.
10. From the work so far we feel justified in concluding that there is a marked difference in stability toward acetolysis by different oxygen linkings in disaccharides and polysaccharides.
11. Acetyl chloride, bromide, and sulfate show similar acetolytic action.

Acetolysis.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY.]

SOME CONSTITUENTS OF THE ROOT OF BRAUNERIA ANGUSTIFOLIA.

BY FREDERICK W. HEYL AND MERRILL C. HART.

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In a report of the Council on Pharmacy and Chemistry[1] of the American Medical Association, the root of *Brauneria angustifolia*, commonly

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[1] *J. Am. Med. Assoc.*, **53**, 1836 (1909).