2. This mixture when subjected to the condensing action of phosphoric anhydride has not yielded sucrose octa-acetate, the only crystalline product obtained being the octa-acetate of *iso*-sucrose.
3. Tri-acetylanhydrofructose has been converted into tetra-acetyl-γ-fructose, thereby proving that one oxygen ring in the former is in the same position which it occupies in the remainder of the inulin molecule.
4. Tetra-acetyl-γ-fructose obtained as described in 3 above has been condensed with tetra-acetylglucose. In this case also, *iso*-sucrose octa-acetate was the only crystalline derivative isolated.
5. In none of the condensations now described has any evidence been forthcoming that sucrose derivatives are formed.

ST. ANDREWS, SCOTLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

PREPARATION OF AMINO-ACETAL

BY JOHANNES S. BUCK AND SAMUEL N. WRENN

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Amino-acetal, $NH_2CH_2CH(OC_2H_5)_2$, on account of its reactivity and versatility, is a synthetic reagent of considerable importance. A search of the literature revealed only three reasonably promising methods, the reduction of nitro-acetal[1] by sodium and alcohol, the reduction of glycine ester by sodium amalgam to amino-acetaldehyde and the conversion of this into amino-acetal,[2] and the action of ammonia on the halogen acetals, which has been investigated by several different workers.[3]

No record was found of attempts to prepare amino-acetal in quantity. For this purpose the action of ammonia on the halogen substituted acetals was investigated. The authors have made use of a steel autoclave of 1100-cc. capacity, fitted with a special ammonia gage and having a working pressure of 1000 pounds. Provision was made for connecting the apparatus to an ammonia tank. With this apparatus a number of runs were made, using chloro-, bromo- and iodo-acetal, and varying the amount of ammonia, the time of heating and the temperature. Chloro- and bromo-acetal proved to be unsatisfactory on account of the low yield and the amount of tarry matter produced; iodo-acetal gave good results.

Experimental

Iodo-acetal was prepared by iodinating acetal in the presence of iodic acid, substantially as described by Hesse[4] and employed by Losanitsch.[5]

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[1] Losanitsch, *Ber.*, **42**, 4044 (1909).

[2] Fischer, *ibid.*, **41**, 1019 (1908); Neuberg, *ibid.*, **41**, 956 (1908).

[3] Natterer, *Monatsh*, **5**, 507 (1884); Wohl, *Ber.*, **21**, 616 (1888); **39**, 1951 (1906); Wolff, *ibid.*, **21**, 1481 (1888); Marckwald, *ibid.*, **25**, 2354 (1892); Hartung and Adkins, THIS JOURNAL, **49**, 2517 (1927).

[4] Hesse, *Ber.*, **30**, 1442 (1897).

[5] Losanitsch, *ibid.*, **42**, 4044 (1909).

Amino-acetal and Iodo-acetal.—In the autoclave were placed 108 g. of iodo-acetal and 600 cc. of alcoholic ammonia, saturated at 0°, and further ammonia was introduced by connecting the autoclave with an ammonia tank for six hours. A pressure of 150 pounds was registered. The cylinder was disconnected and the autoclave heated directly for eleven hours at 110–125°. During the heating period the pressure rose to 375–400 pounds and then fell slowly. After allowing the apparatus to cool and releasing any remaining pressure, the reaction mixture was removed, filtered and the alcohol and ammonia distilled off. The residue was taken up in a little water and extracted several times with ether to remove any unchanged iodo-acetal and higher bases. The ether extract thus obtained was dried over solid potassium hydroxide for twelve hours. The aqueous solution was saturated with potassium carbonate and the oil which separated removed. As a precaution the aqueous solution was extracted with ether. The extract was added to the oil and the whole dried over potassium hydroxide for twelve hours, the ether removed and the residue distilled under reduced pressure to remove tar. The distillate was then fractionated at atmospheric pressure, the amino-acetal being collected between 162 and 165°, and the higher-boiling residue worked up as below.

The ether extraction of the reaction mixture, after removal of the ether, was fractionated under reduced pressure, two fractions being obtained (a) up to 125° (10 mm.), (b) 125–140° (10 mm.). The higher fraction, combined with the high-boiling residues from the amino-acetal, gave on refractionation 7 g. of diacetalamine, b. p. 130–138° (10 mm.). The low-boiling fraction was redistilled and the portion boiling at 162–165° (760 mm.) combined with the amino-acetal previously obtained and redistilled several times. In this way 21 g. of amino-acetal, b. p. 162–163°, was obtained.

No unchanged iodo-acetal was found and comparatively little tar was present. The preparation could doubtless be substantially improved by pouring Babbitt metal between the shell and liner of the autoclave and heating the latter in a bath or by steam. Stirring would probably help matters. The temperature of heating should not exceed 125°, as much tar forms above this temperature. The duration of heating should be such that all of the halogen acetal is changed; otherwise general decomposition takes place on distilling the product. As large an excess of ammonia as practicable should be employed, to avoid the formation of secondary and tertiary products.

Amino-acetal from Chloro-acetal.—Thirty-five grams of chloro-acetal and 700 cc. of alcoholic ammonia, saturated at 0°, were placed in the autoclave and treated in a manner similar to the previous preparation. The combined yield of amino-acetal, boiling at 160–165°, from four preparations was 12 g. (11.1%).

Amino-acetal from Bromo-acetal.—In this preparation 188 g. of bromo-acetal and 400 cc. of saturated alcoholic ammonia were used, and the heating was continued for fourteen hours at 110–115°. From this experiment 24.5 g. of amino-acetal, b. p. 162–166°, and 27 g. of diacetalamine, b. p. 130–140° (8 mm.), were obtained.

Summary

The preparation of amino-acetal is conveniently carried out in a steel autoclave, using iodo-acetal. Iodo-acetal is far superior to chloro- and bromo-acetal and may be readily prepared.

Durham, North Carolina