[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

A New Method for the Preparation of Aldehydo Sugar Acetates

BY ELMER W. COOK AND RANDOLPH T. MAJOR

Aldehydo sugar acetates have been prepared by acetylation of the aldehydo mercaptals[1] followed by removal of the thio-acetal groups and also by acetylation of the aldehydo semicarbazones or oximes[2] with the subsequent removal of the semicarbazone or oxime groups.

A new method based upon Rosenmund's[3] method for the reduction of acyl chlorides to aldehydes by means of hydrogen in the presence of palladiumized barium sulfate has been found. The acetyl derivatives of the sugar acid chloride may be reduced almost quantitatively to aldehydo sugar acetates.

Experimental

Aldehydo-*d*-glucose Pentaacetate.—Pentaacetyl-*d*-gluconyl chloride[4] (5 g.) in 25 cc. of anhydrous xylene (dried over sodium) was heated under reflux in the presence of 2 g. of 5% palladiumized barium sulfate. Hydrogen was passed in at such a rate that the catalyst was kept in a lively suspension. The reduction was complete within one and one-half hours as shown by the absence of ammonium chloride fumes when a rod moistened with ammonium hydroxide was held in the escaping gases. Complete reduction may also be determined by passing the exit gases through water and testing for chloride ion. After reduction the hot xylene solution was filtered. Upon cooling aldehydo-glucose pentaacetate[5] crystallized. It was recrystallized from xylene; yield was nearly quantitative; m. p. 117–118°; $[\alpha]^{20}_D$ −3° (dry chloroform, *c*, 2); $[\alpha]^{20}_D$ +10° (in methanol, 5 min., *c*, 2) changing slowly in the dextro direction.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.21; H, 5.68. Found: C, 49.52, 49.34; H, 5.85, 5.60.

Summary

Aldehydo-*d*-glucose pentaacetate has been prepared by the reduction of pentaacetyl-*d*-gluconyl chloride.

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[1] Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

[2] Wolfrom, Georges and Soltzberg, *ibid.*, **56**, 1794 (1934).

[3] Rosenmund, *Ber.*, **51**, 585 (1917).

[4] Major and Cook, THIS JOURNAL, **58**, 2474 (1936).

[5] Wolfrom, *ibid.*, **51**, 2191 (1929).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Temperature–Concentration Equilibria in the Systems Chloroform–Chlorine and Chloroform–Bromine. The Chloroform Chlorinates[1]

BY J. ALLEN WHEAT, II, AND A. W. BROWNE

In view of the well-known fact that chlorine occupies a higher position than bromine in the activity series of electronegative elements and radicals[2] arranged in the descending order of electronegativity, it has seemed reasonable to suppose that dissolved chlorine should be removed from chloroform more readily than dissolved bromine on treatment with metallic sodium. Quite the opposite is true.

As the result of an extended series of experiments in which chloroform solutions containing free bromine and chlorine in molar ratios (Br_2:Cl_2) ranging from about 0.25 to 2.50 were subjected at room temperature to the action of metallic sodium in excess, it was found that a considerable amount of free chlorine remained in solution in every case after complete removal of the bromine had been effected.

This entirely unanticipated result might conceivably be attributable either (1) to chemical action of the chlorine upon the chloroform and lack of similar action on the part of the bromine, or (2) to formation of one or more coördination compounds between molecular chlorine and chloroform and either (a) non-formation of similar bromine compounds, or (b) formation of relatively less stable bromine compounds. The first explanation is clearly invalidated by the presence of "free" (though possibly coördinated) chlorine in the residual solutions, as already noted, and by

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by Joseph Allen Wheat, II, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Birckenbach and Kellermann, *Ber.*, **58**, 786, 2377 (1925).