[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reduction of Acetobromoarabinose by Zinc and Acetic Acid[1]

BY GEORGE E. FELTON

The reaction of a suspension of zinc dust in acetic acid on an acetobromo sugar was carried out first by Emil Fischer.[2] The object of his experiment was to replace the bromine atom of the acetobromoglucose by hydrogen to obtain thereby an acetylated anhydrosorbitol derivative, tetraacetyl styracitol. As is now well known the product sought was not obtained by this method. However, a good yield of an unsaturated acetylated glucose derivative, named triacetyl glucal, was secured. The glucal and similar derivatives of other hexoses, pentoses and disaccharides have since proved of great value in the synthesis of new compounds, so that the discovery of this reaction is now considered a very fortunate occurrence in carbohydrate chemistry.

As a step in the preparation of *l*-arabinal, to be used for degradation to *l*-erythrose by means of ozone splitting[3] acetobromoarabinose was reduced numerous times by means of zinc and acetic acid. The yields obtained by Austin and Humoller[4] with zinc containing 5% of a copper–zinc couple were practically exactly duplicated by using a few drops of chloroplatinic acid for each preparation as had been suggested by Bergmann, Schotte and Rennert[5] in the preparation of rhamnal.

Gehrke and Aichner[6] reported that the products of the zinc and acetic acid reduction of acetobromoarabinose were a low boiling compound of watery consistency, diacetylarabinal and a higher boiling very viscous compound, triacetylarabinose. The triacetylarabinose was identified by acetylating to give a known tetraacetate. Besides the two reported compounds a third product has now been obtained. This product remained in the distilling flask after the diacetylarabinal and triacetylarabinose had been driven off as much as possible. The new compound was secured in crystalline form by taking up the residue in hot alcohol and allowing the solution to cool. If a large amount of sirup remained in the flask, the alcohol solution had to be seeded to effect a separation of the crystalline compound.

The properties of this new compound were as unexpected as those of the first glucal preparation. The derivative contained no halogen, unsaturated linkages, or free reducing groups detectable by boiling Fehling's solution. From benzene it was obtained in the form of needles melting at 167–169°, whereas from absolute alcohol it appeared as diamond-shaped plates melting at 184.5–185.5°. Each form was readily converted into the other and neither contained any solvent of crystallization. The compound was obtained from 95% alcohol occasionally in the lower melting form but most often in the higher.

After acid hydrolysis the compound reduced Fehling's solution, thereby suggesting a glycosidic linkage. The freezing point lowering in benzene showed a molecular weight of about 390. Four acetyl groups were found by alkaline hydrolysis. Carbon and hydrogen analyses agreed most closely with the values calculated for a tetraacetyl desoxypentose disaccharide.

The acetyl groups were removed by barium hydroxide hydrolysis and the acetyl free sugar obtained in crystalline form. It possessed an unsharp decomposition point of about 177–180°. The acetyl free product did not reduce Fehling's solution until after acid hydrolysis. The carbon and hydrogen analysis agreed with the values calculated for a desoxypentose disaccharide.

Attempts to prepare a benzylphenylhydrazone, after hydrolyzing by refluxing with dilute hydrochloric acid, failed to yield a crystalline derivative. This negative result may have been due to decomposition of the simple sugar formed by the hydrolysis.

Experimental

Reduction of Acetobromo-*l*-arabinose.—The reduction of acetobromoarabinose was carried out according to the procedure of Levene and Mori[7] for the preparation of diacetylxylal. The diacetylarabinal and triacetylarabinose formed from 90 g. of acetobromoarabinose were distilled

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[1] This investigation was supported in part by a grant from the Iowa State College Industrial Science Research fund for the study of carbohydrate degradation and utilization.

[2] Fischer and Zach, *Sitzb. kgl. preuss. Akad. Wiss.*, **16**, 311 (1913).

[3] Felton and Freudenberg, THIS JOURNAL, **57**, 1637 (1935).

[4] Austin and Humoller, *ibid.*, **56**, 1152 (1934).

[5] Bergmann, Schotte and Rennert, *Ann.*, **434**, 86 (1923).

[6] Gehrke and Aichner, *Ber.*, **60**, 918 (1927).

[7] Levene and Mori, *J. Biol. Chem.*, **83**, 809 (1929).

off in a vacuum as completely as possible without heating the bath to over 150°. The residue remaining in the distilling flask was dissolved in 10 cc. of warm 95% alcohol. This solution was allowed to stand at room temperature until crystallization of the new compound reached completion. Cooling to 0° would precipitate sirupy reducing compounds which had not been removed by the distillation. The crystallization at room temperature was very satisfactory although low yields of the non-reducing compound necessitated the use of seed crystals. The solid product was then filtered and purified by recrystallization from a small amount of absolute alcohol. One recrystallization served to free the product from reducing materials and further recrystallizations caused no more change in its physical constants. The crystals were diamond-shaped plates and melted at 184.5–185.5°; $[\alpha]^{23}_{\mathrm{D}}$ +69.2° (0.1705 g. in 9.98 cc. of chloroform in a 1.1-dm. tube rotated 1.30° to the right). Recrystallized from benzene the compound formed needles which melted at 167–169°; $[\alpha]^{23}_{\mathrm{D}}$ +69.5° (0.1774 g. in 9.98 cc. of chloroform in a 1.1-dm. tube rotated 1.36° to the right). Neither crystalline form lost any weight on drying over phosphorus pentoxide at 78° in a vacuum.

The new compound was secured in yields of from 0.1 to 1 g. for each 90 g. of acetobromoarabinose reduced. The yields of diacetylarabinal and triacetylarabinose were 34 g. and 8 g., respectively.

The compound was easily soluble in chloroform, warm alcohol, ethyl acetate and acetic acid, slowly soluble in benzene, insoluble in cold alcohol and ether and very insoluble in water.

The non-reducing material gave a molecular weight of 390 (0.5706 g. in 80.5 g. benzene gave a freezing point lowering of 0.094°). A tetraacetyl desoxypentose disaccharide would have a molecular weight of 418.

Anal. Calcd. for $C_{18}H_{26}O_{11}$ (418): C, 51.65; H, 6.26; CH_3CO, 41.1. Found: C, 51.44; H, 6.25; CH_3CO, 40.7.

Desoxypentose Disaccharide.—Three-tenths gram of tetraacetyl desoxypentose disaccharide was deacetylated by dissolving in 25 cc. of water containing 1 g. of barium hydroxide. The solution was freed of excess barium hydroxide by carbon dioxide. The barium carbonate was removed by filtration and the water evaporated off under reduced pressure. The residue, which still contained inorganic salts, was extracted several times with warm absolute alcohol and the alcohol was removed by a vacuum distillation. The residue remaining in the distilling flask was extracted with a small amount of water to free the preparation from any compound which had not been deacetylated. The water solution was evaporated slowly in a vacuum desiccator over phosphorus pentoxide. After the water had been removed the compound solidified. The yield was 0.16 g. or 90%. After recrystallization from isopropyl alcohol and ether the desoxypentose disaccharide melted at 177–180°. The melting point was not sharp and there was a great deal of decomposition.

Anal. Calcd. for $C_{10}H_{18}O_7$ (250): C, 48.00; H, 7.25. Found: C, 47.80; H. 6.81.

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Summary

The reduction of acetobromoarabinose was found to yield a non-reducing compound which had not been previously reported. The analysis of the new compound showed it to be a tetraacetyl desoxypentose disaccharide. The free disaccharide was also prepared in crystalline form.

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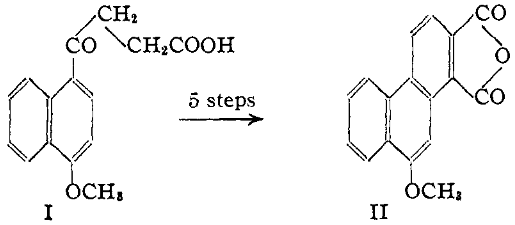
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. IV. Hydroxylated Compounds

BY L. F. FIESER AND E. B. HERSHBERG

This work was undertaken with the idea that the introduction of hydroxyl or methoxyl groups into the phenanthrene dicarboxylic anhydrides(1) and the hexa- or octahydrophenanthrene dicarboxylic anhydrides(2) previously described might afford substances of oestrogenic activity, the presence of hydroxyl and carbonyl groups in different parts of the molecule establishing at least a superficial resemblance to oestrone. One such compound was prepared from the condensation product of succinic anhydride and α-methoxynaphthalene, I, by reduction, esterification, condensation with ethyl oxalate, cyclization and dehydrogenation, giving 9-methoxyphenanthrene-1,2-dicarboxylic anhydride, II.



I II

An anhydride of a second type was obtained

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(1) Fieser and Hershberg, THIS JOURNAL, 57, 1851 (1935).

(2) Fieser and Hershberg, *ibid.*, 57, 2192 (1935).