1,4-Dimesityl-4-hydroxybutanone-1, XVII, was obtained as colorless crystals from dilute ethanol; m. p. 132–133° (corr.).

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.4; H, 8.6. Found: C, 81.6; H, 8.7.

Oxidation of XVII in concd. acetic acid with chromic acid and sulfuric acid took place readily at room temperature or at 70° and yields of di-(trimethylbenzoyl)-ethane ranging from 10–25% were isolated.

Summary

Di-(trimethylbenzoyl)-ethylene oxide has been prepared and transformed into di-(trimethylbenzoyl)-chloroethylene and dimesitylbutanetrione enol.

Reductions under a variety of conditions are reported. The oxide is converted by means of potassium iodide into di-(trimethylbenzoyl)-ethylene, by the iodine–phosphorus reagent into di-(trimethylbenzoyl)-ethane, by zinc–ammonium chloride into di-(trimethylbenzoyl)-hydroxyethane, by nickel and hydrogen into a mixture of di-(trimethylbenzoyl)-ethane and -hydroxyethane, and by platinum and hydrogen into dimesityl-4-hydroxy-2,3-epoxybutanone-1.

The reactions of di-(trimethylbenzoyl)-hydroxyethane are described, including reduction, dehydration, acylation, conversion to acetoxydimesitylfuran, oxidation and disproportionation.

Dimesityl-4-hydroxy-2,3-epoxybutanone-1 was reduced to dimesityl-4-hydroxybutanone-1 and dimesityl-3,4-dihydroxybutanone-1.

CHARLOTTESVILLE, VA. RECEIVED NOVEMBER 6, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Preparation of Acetylaldonic Acids

BY CHARLES D. HURD AND JOHN C. SOWDEN

The first preparation of a partially acetylated aldonic acid was reported by Upson and Bartz,[1] who found that acetylation of *d*-gluconolactone with zinc chloride and acetic anhydride resulted in rupture of the lactone ring with the formation of tetraacetylgluconic acid monohydrate. In 1936 Major and Cook[2] observed that further acetylation of this compound produced pentaacetylgluconic acid monohydrate, from which pentaacetylgluconic acid itself readily was obtained. These investigators converted the acid to the acid chloride and hydrogenated the latter to aldehydo glucose pentaacetate.

This new synthesis of aldehydo sugars, to be a general reaction, obviously requires a general method for the preparation of fully acetylated aldonic acids. Except for the glucose derivative, the only other such compounds mentioned in the literature are *d*-, *l*-, and *dl*-tetraacetylxylonic acids. These were also prepared by Major and Cook, not by acetylation of a δ-lactone but by oxidation of the corresponding aldehydoxylose tetraacetates. Although a few δ-lactones of aldonic acids are known, the γ-lactones are much more common. For purposes of this synthesis, however, the γ-lactones are unsatisfactory because Upson and Bartz found that γ-lactones undergo acetylation to yield an acetylated lactone, rather than the aldonic acid. They reported also that attempts to acetylate δ-mannonolactone yielded only 2,3,5,6-tetraacetyl-γ-mannonolactone. The method used by Major and Cook, therefore, cannot be regarded as a general one for the synthesis of acetylaldonic acids. Development of a general method for this purpose was the objective of the present work.

A satisfactory means of preparing the acids from the corresponding aldoses has been found through the following sequence of steps: aldose ⟶ aldose oxime ⟶ acetylaldononitrile ⟶ acetylaldonamide ⟶ acetylaldonic acid.

The first two reactions involved, being part of the familiar Wohl method of degradation, have been reported for all the simple aldose sugars. Precedent exists also for the next step inasmuch as the reaction of pentaacetylgluconpremitrile with hydrogen bromide in glacial acetic acid has been reported by Zemplén and Kiss[3] to produce pentaacetylgluconamide. This reaction was extended to the acetylated nitriles of *d*-galactose, *d*-xylose, and *l*-arabinose. In each instance, a satisfactory yield of the corresponding acetylaldonamide was obtained.

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[1] Upson and Bartz, THIS JOURNAL, **53**, 4226 (1931).

[2] Major and Cook, *ibid.*, **58**, 2410, 2474 (1936).

[3] Zemplén and Kiss, *Ber.*, **60**, 165 (1927).

Although the conversion of amides to the corresponding acids by the action of aqueous nitrous acid, or nitrous anhydride in non-aqueous media, is a familiar reaction, no previous record of its application in the sugar series was found. Pentaacetylgluconamide was observed to be quite stable to the action of nitrous acid, both in glacial acid and in solutions containing water in the presence of mineral acids. Treatment of the amide in glacial acetic acid solution with nitrous anhydride, however, produced the desired fully-acetylated acid. The reaction was applied successfully to the acetylaldonamides obtained from *d*-glucose, *d*-galactose, and *l*-arabinose.

Experimental Part

The Acetylaldonamides

Pentaacetyl-*d*-gluconamide.—This substance, m. p. 187–187.5°, was prepared in 84% yield from pentaacetylgluconitrile by the method of Zemplén and Kiss.[3]

Pentaacetyl-*d*-galactonamide.—Pentaacetyl-*d*-galactononitrile, m. p. 136–137°, was prepared by the method of Wohl and List.[4] A solution of 19 g. of it in 20 cc. of glacial acetic acid was treated with 30 cc. of acetic acid saturated with hydrogen bromide. The mixture was shaken for one hour. After standing four and one-half hours at room temperature, the resulting clear solution was poured into 1 liter of water containing 80 g. of sodium bicarbonate. The product began to separate at once, and was collected after standing overnight at 0°. Recrystallization from absolute alcohol yielded 13 g. of pure pentaacetyl-*d*-galactonamide; m. p. 166–167°; $[\alpha]^{24}\text{D}$ +27° (concn., 2 g. per 100 cc. in chloroform).

Anal. (Kjeldahl). Calcd. for $C_{16}H_{23}O_{11}N$: N, 3.46. Found: N, 3.39.

Tetraacetyl-*d*-xylonamide.—Tetraacetyl-*d*-xylononitrile, m. p. 79–81°, was prepared by the method of Maquenne.[5] Ten grams of the nitrile in 10 cc. of glacial acetic acid was shaken with 15 cc. of acetic acid which was saturated with hydrogen bromide. The nitrile dissolved almost immediately. The clear solution was allowed to stand for nineteen hours at room temperature after which it was poured into 600 cc. of ice water. The aqueous solution was made alkaline to litmus by the addition of sodium bicarbonate and extracted with chloroform. Distillation of the chloroform from the dried extract left a sirupy residue which crystallized readily from absolute alcohol (40 cc.). Recrystallization from absolute alcohol produced 6.4 g. of pure tetraacetyl-*d*-xylonamide; m. p. 110.5–111.5°; $[\alpha]^{24}\text{D}$ +8° (*c*, 2; $CHCl_3$).

Anal. (Kjeldahl). Calcd. for $C_{13}H_{19}O_9N$: N, 4.20. Found: N, 3.98.

Tetraacetyl-*l*-arabonamide.—Tetraacetyl-*l*-arabononitrile, m. p. 118–120°, was prepared by the method of Wohl.[6] Twenty grams of the nitrile, dissolved in 20 cc. of glacial acetic acid, was shaken during forty minutes with 30 cc. of acetic acid saturated with hydrogen bromide. The resulting clear solution was allowed to stand for nine hours at room temperature and then was poured into a mixture of 80 g. of sodium bicarbonate and 1 liter of water. The aqueous alkaline solution was extracted with chloroform, the extract dried, and the chloroform distilled. Crystallization of the residual sirup from 70% alcohol resulted in a product, which melted between 75–85°. Apparently it was a hydrate of the desired amide. This material was dissolved in dry benzene and the solution boiled until no further evolution of water vapor was apparent. On cooling, 12.4 g. of anhydrous tetraacetyl-*l*-arabonamide separated; m. p. 119–120°; $[\alpha]^{24}\text{D}$ −23° (*c*, 2; $CHCl_3$).

Anal. (Kjeldahl). Calcd. for $C_{13}H_{19}O_9N$: N, 4.20. Found: N, 4.24.

The Acetylaldonic Acids

Pentaacetyl-*d*-gluconic Acid.—A solution of 10 g. of pentaacetyl-*d*-gluconamide and 40 cc. of glacial acetic acid was cooled to 10° and treated with nitrous anhydride until a green color persisted in the solution. The nitrous anhydride[7] was generated by the action of arsenious oxide and concentrated nitric acid. A lively evolution of nitrogen occurred almost immediately after introduction of the nitrous anhydride. The reaction mixture was allowed to stand for three and one-half hours, during which time it warmed spontaneously to 18°. Then it was poured into a mixture of 200 cc. of water and 70 g. of sodium bicarbonate. The resulting alkaline solution was made just acid to congo red by the addition of 150 cc. of hydrochloric acid (1:1) and was warmed to 40° on the steam-bath. After cooling, the solution was extracted with chloroform, the extract dried over sodium sulfate, and the chloroform removed at reduced pressure. Crystallization of the residual sirup from 35 cc. of water, produced 6.4 g. of pentaacetylgluconic acid monohydrate, m. p. 69–71°. A mixed m. p. with the acid hydrate prepared from δ-gluconolactone by Major and Cook's method, m. p. 72–73°, was undepressed. The latter was prepared by Mr. M. E. McDougle of this Laboratory.

The acid hydrate, when heated at 55° in an Abderhalden drier, changed to a brittle glass of anhydrous pentaacetylgluconic acid. After crystallization from a mixture of toluene and petroleum ether, the anhydrous acid, m. p. 110–111°, showed no melting point depression when mixed with authentic pentaacetylgluconic acid prepared by the method of Major and Cook.

Pentaacetyl-*d*-galactonic Acid.—Ten grams of pentaacetyl-*d*-galactonamide in 33 cc. of glacial acetic acid was treated, at 5 to 8°, with nitrous anhydride until a green color persisted in the solution. After standing for four and one-half hours at room temperature, the solution was poured into a mixture of 165 cc. of water and 60 g. of sodium bicarbonate. The resulting alkaline solution was made just acid to congo red by the addition of 177 cc. of hydrochloric acid (1:1) and warmed to 40° on the steam-bath. After cooling, the acid solution was extracted with chloroform, the extract dried, and the chloroform distilled at reduced pressure. The sirupy residue began to crystallize at once. Recrystallization from dry toluene produced

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(4) Wohl and List, *Ber.*, **30**, 3103 (1897).

(5) Maquenne, *Compt. rend.*, **130**, 1402 (1900).

(6) Wohl, *Ber.*, **26**, 744 (1893); **32**, 3667 (1899).

(7) *Organic Syntheses*, **4**, 27 (1925).

7.7 g. of pure pentaacetyl-*d*-galactonic acid; m. p. 131–132°, $[\alpha]^{25}\text{D}$ +12° (*c*, 3; $CHCl_3$).

Anal. Calcd. for $C_{16}H_{22}O_{12}$: C, 47.27; H, 5.46; sapon. equiv., 67.7. Found: C, 46.86; H, 5.59; sapon. equiv., 68.6.

Tetraacetyl-*l*-arabonic Acid.—The reaction of tetraacetyl-*l*-arabonamide with nitrous anhydride was carried out in a manner identical with that already described for pentaacetyl-*d*-galactonamide. The anhydrous, crystalline acid was obtained directly, in 73% yield, by removal of the solvent from the chloroform extract. Recrystallization from dry toluene produced pure tetraacetyl-*l*-arabonic acid; m. p. 135–135.5°; $[\alpha]^{25}\text{D}$ −32° (*c*, 1.5; $CHCl_3$). The saponification equivalent was found to be 67.9 (calcd., 66.8).

Anal. (by Mr. S. Cristol). Calcd. for $C_{13}H_{18}O_{10}$: C, 46.69; H, 5.43. Found: C, 46.82; H, 5.47.

Non-reaction of Nitrous Acid and Pentaacetylgluconamide.—Five grams of the amide in 50 cc. of warm glacial acetic acid was treated dropwise with a solution of 5 g. of sodium nitrite in 20 cc. of water over a period of one hour. The mixture was stirred mechanically and was maintained at 45° during this period. Then it was stirred for two hours more and poured into 200 cc. of ice water. The amide separated at once. More was obtained by neutralizing the solution with sodium bicarbonate. In all, 4.6 g. was recovered (m. p. 187–188°).

Similarly, most of the amide was recovered in the following experiments which were of three to seven hours duration. The amide (5 g.) was dissolved in warm methyl β-hydroxyethyl ether (65 cc.) and to it was added a solution of 13 g. of sodium nitrite in 50 cc. of water. When 25 cc. of 1:1 hydrochloric acid (or an equivalent amount of dilute sulfuric acid) was gradually added to the solution at 40–70°, there was no formation of the desired pentaacetylgluconic acid.

Summary

A general method for the conversion of aldoses into fully-acetylated aldonic acids has been developed. The aldoses are converted in three steps to acetylaldonamides. Treatment of the latter in glacial acetic acid solution with nitrous anhydride gives the corresponding acetylaldonic acids in good yields.

The following new amides and acids related to sugars were prepared: pentaacetyl-*d*-galactonamide, tetraacetyl-*d*-xylonamide, tetraacetyl-*l*-arabonamide, pentaacetyl-*d*-galactonic acid, and tetraacetyl-*l*-arabonic acid.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 22, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

An X-ray Study of Stretched Rubber

BY HENRY A. MORSS, JR.

Despite the many attacks which have been made upon it, the phenomenon of the stretching of rubber remains only little understood. Because of the tremendous complications involved, the best approach to the problem seems to lie in finding better quantitative data from which to work. Of especial interest during recent years have been the configuration of the molecule and the changes in its shape during stretching and retraction. This paper aims to report some investigations on this subject.

Experimental

There is some hope of learning in full detail the configuration of the molecule in stretched rubber, because stretched rubber gives an X-ray diffraction pattern which shows the material to be mostly crystalline and there is a possibility of solving the crystal structure. This possibility has been explored.

For the present work a cylindrical camera (diameter 94 mm.) was chosen, with the line of stretch of the rubber lying on the cylindrical axis. In order to get as many high order reflections as possible, the sample was cooled in some exposures to about −120°. All samples were of racked rubber. ("Racking" is stretching to an extensive degree by repeating several times a cyclic process of quick stretching, holding under tension until the sample cools and the stretch "freezes in," and relaxing the stretch in water at about 90°.[1] The X-ray pattern is easily shown to be the same as that of ordinary stretched rubber except that perhaps the "amorphous ring" is reduced in intensity.)[2]

The best diffraction pattern of a cooled sample was exposed seven hours (at 15 ma.) to copper radiation filtered by nickel foil. A room-temperature exposure of fifty hours was made in which the radiation was monochromatized by reflection from a rock-salt crystal. This film was made especially in the hope of revealing any weak, low-order reflections which might be masked by the general blackening due to the continuous spectrum present in the nickel-filtered radiation.

Inasmuch as more weak, higher order spots were found when the sample was cooled, all numerical data quoted in this paper refer to the low temperature. Table I gives the positions and estimated intensities of all known spots of the fiber diagram (including two "diatropic" points). Positions are indicated by cylindrical coördinates in the Bernal[3] reciprocal lattice: ζ, the coördinate parallel to

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[1] Feuchter, *Kautschuk*, **2**, 260 (1926).

[2] Hauser and Rosbaud, *ibid.*, **3**, 17 (1927).

[3] Bernal, *Proc. Roy. Soc.* (London), **A113**, 117 (1926).