alcoholic to aqueous supporting electrolyte. The result confirms other chemical evidence that the ferricinium ion in neutral aqueous solution partially decomposes quite rapidly to form some ferrocene.

The Ruthenocene–Ruthenicinium Ion System.—Ruthenocene has similarly been found to give a well defined anodic wave at the dropping mercury electrode; the supporting alcoholic electrolyte used was the same as the one used for ferrocene. The half-wave potential was +0.26 v. *versus* the S.C.E. The value of the polarographic constant, $i_d/Cm^{2/3}t^{1/6}$ was found to be 1.62 µa./mM/l. mg.$^{2/3}$ sec.$^{-1/2}$.

A controlled potential oxidation at a mercury anode of 23.0 mg. of ruthenocene in 50 ml. of the same supporting electrolyte has been made at a potential of 0.40 v. *versus* the S.C.E. The initial current of 6.7 ma. decreased to 0.1 ma. in 60 minutes electrolysis. During the course of the electrolysis an insoluble yellow crystalline solid, ruthenicinium perchlorate, precipitated from the solution. The quantity of electricity measured as before was 8.76 coulombs, agreeing well with the calculated value, 9.57 coulombs, for a one-electron oxidation. The solid was removed leaving a pale yellow solution of ruthenicinium perchlorate in the supporting electrolyte; a polarogram of this solution gave a well defined wave at a potential of +0.22 v. *versus* the S.C.E. The separated perchlorate was dissolved in water and the solution made 0.1 M in sodium perchlorate; after removal of oxygen with nitrogen, a cathodic wave with a half-wave potential of +0.11 v. *versus* the S.C.E. was obtained; ruthenicinium perchlorate slowly separated from this solution in which it is very sparingly soluble.

The Cobalticinium Ion.—Solutions of cobalticinium perchlorate were prepared from cobalticinium picrate solutions by use of an anion exchange resin column. In an oxygen free, 0.1 M sodium perchlorate aqueous supporting electrolyte at *p*H 6.2, the cobalticinium ion gave a well-defined cathodic wave at the dropping mercury electrode. The half-wave potential was −1.16 v. *versus* the S.C.E. The value of the polarographic constant, $i_d/Cm^{2/3}t^{1/6}$, was found to be 1.77 µa./mM/l. mg.$^{2/3}$ sec.$^{-1/2}$.

Unsuccessful attempts were made to prepare cobaltocene, $(C_5H_5)_2Co$, by controlled potential electrolysis of a neutral one millimolar cobalticinium perchlorate solution. A mercury cathode and divided cell were used, and the potential was −1.5 v. *versus* the S.C.E. The initial current was 7.0 ma. which decreased very slowly being 5 ma. after 60 minutes electrolysis. On continued electrolysis, the polarographic wave for the cobalticinium ion disappeared, indicating that complete destruction of the complex occurs, rather than the simple oxidation of cobaltocene by water.

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DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

Acetylated Thioacetals of D-Glucosamine

BY M. L. WOLFROM AND KIMIKO ANNO[1]

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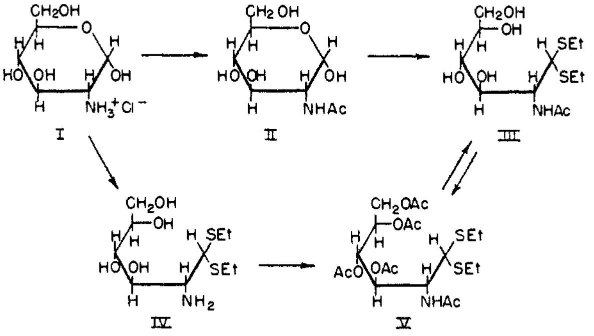
Wolfrom, Lemieux and Olin[2] reported that the mercaptalation and acetylation of N-acetyl-2-amino-2-deoxy-D-glucose (II, N-acetyl-D-glucosamine)[3,4] produced a crystalline product, m.p. 126–127°, $[\alpha]^{22}_{\rm D}$ −32° (chloroform), which was described as a pentaacetyl derivative. Further investigation shows that this substance was actually a tetraacetyl derivative obtained in low yield and not again encountered in subsequent preparations. The correct pentaacetyl derivative V is herein described: m.p. 75–77°, $[\alpha]^{28}_{\rm D}$ +1° (*c* 4, chloroform). Kent[5] has reported, without experimental detail, the same substance with the constants: m.p. 160–161°, $[\alpha]^{23}_{\rm D}$ +2° (*c* 1, chloroform). It is then apparent that either the melting point of Kent is in error or we have at hand a low melting dimorph. N-Acetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal (III, N-acetyl-D-glucosamine diethyl mercaptal) has been described by Wolfrom, Lemieux and Olin[2]; m.p. 130–131°, $[\alpha]^{23}_{\rm D}$ − 35° (*c* 4, water). This compound has now been prepared from N-acetyl-2-amino-2-deoxy-D-glucose (II) by an improved method and the above constants verified. For this compound Kent[5] has reported the constants: m.p. 121–122°, $[\alpha]^{23}_{\rm D}$ −24° (*c* 0.4, water). It is apparent that his preparation was impure. Kent[5] further records that he treated 2-amino-2-deoxy-D-glucose (D-glucosamine) hydrochloride (I) at room temperature with ethanethiol and hydrochloric acid (the recorded[5] density of 1.4 is undoubtedly in error). Treatment of 2-amino-2-deoxy-D-glucose hydrochloride (I) with ethanethiol in the concentrated hydrochloric acid of commerce (*ca.* 12 N) gave a very slow reaction from which we obtained after hydrogen chloride removal, 2-amino-2-deoxy-D-glucose diethyl thioacetal (IV); m.p. 109–110°, $[\alpha]^{23}_{\rm D}$ −24° (*c* 1, water). Kent[5] records for the hydrochloride: m.p. 75–76°; $[\alpha]^{22}_{\rm D}$ −18° (*c* 0.16, water). Acetylation of our preparation of 2-amino-2-deoxy-D-glucose diethyl thioacetal (IV) led to the above-mentioned pentaacetyl derivative V while de-O-acetylation of this yielded N-acetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal (III)



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[1] Special Postdoctoral Research Fellow of the National Institutes of Health, United States Public Health Service.

[2] M. L. Wolfrom, R. U. Lemieux and S. M. Olin, *Abstracts Papers Am. Chem. Soc.*, **112**, 12Q (1947); THIS JOURNAL, **71**, 2870 (1949).

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[4] T. White, *J. Chem. Soc.*, 428 (1940).

[5] P. W. Kent, *Research* (London), **3**, 427 (1950).

showing the constants reported by us. Oxidation of pentaacetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal (V) to the disulfone derivative has been described by MacDonald and Fischer.[6] These workers employed the thioacetal as an intermediate but did not isolate it in crystalline form.

Experimental

Tetraacetyl-2-amino-2-deoxy-D-glucose Diethyl Thioacetal.—This material was previously described[2] incorrectly as the pentaacetyl derivative. After the authentic pentaacetyl derivative was crystallized in this Laboratory, the tetraacetyl derivative was not again encountered. A file sample, however, was available for examination; m.p. 126–127° (from methanol–water), $[\alpha]^{22}\mathrm{D}$ −32° (*c* 4, chloroform).

Anal. Calcd. for $C_{18}H_{31}O_8NS_2$: C, 47.66; H, 6.89; N, 3.09; S, 14.14. Found: C, 47.87; H, 6.63; N, 3.01; S, 14.08.

Preparation of N-Acetyl-2-amino-2-deoxy-D-glucose Diethyl Thioacetal (III).—N-Acetyl-2-amino-2-deoxy-D-glucose[4] (30.0 g.) was dissolved in 120 ml. of concentrated hydrochloric acid (*ca.* 12 *N*) and stirred mechanically with 120 ml. of ethanethiol for 24 hr. at 0°. The reaction mixture was then neutralized with an excess (*ca.* 700 g.) of basic lead carbonate. After the addition of 500 ml. of water, the solids were removed by filtration and washed with 1000 ml. of water. The filtrate and washings were dewatered under reduced pressure and the residue was extracted at room temperature with 150 ml. of abs. ethanol. The solvent was removed under reduced pressure from the filtered extract and the residue was crystallized from methanol–ether; yield 36 g. (81%), m.p. 124–127°, $[\alpha]^{30}\mathrm{D}$ −30° (*c* 4, water). Pure material was obtained on further crystallization from methanol–chloroform–ether as described previously[2]; m.p. 129.5–130.5°, $[\alpha]^{28}\mathrm{D}$ −35° (*c* 4, water).

Pentaacetyl-2-amino-2-deoxy-D-glucose Diethyl Thioacetal (V).—N-Acetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal (3.0 g.) was acetylated with acetic anhydride (10 ml.) and pyridine (10 ml.) for 24 hr. at room temperature. This solution was then poured into 250 ml. of ice and water and the resultant mixture was extracted with chloroform. The chloroform extract was treated with a saturated aqueous solution of cadmium chloride and the filtered chloroform layers were washed successively with water, saturated aqueous sodium bicarbonate and again with water. The sirup obtained on solvent removal from the dried chloroform solution crystallized on standing for several days in a desiccator over phosphorus pentoxide. Pure material (elongated prisms) was obtained on recrystallization from ligroin (b.p. 65–110°); yield 3.6 g. (79%), m.p. 75–77°, $[\alpha]^{28}\mathrm{D}$ +1° (*c* 4, chloroform).

Anal. Calcd. for $C_{20}H_{33}O_9NS_2$: C, 48.47; H, 6.71; N, 2.83; S, 12.94. Found: C, 48.69; H, 6.53; N, 2.89; S, 13.07.

This substance was also obtained in high yield on acetylation, effected in the above manner, of the 2-amino-2-deoxy-D-glucose diethyl thioacetal described below.

De-O-acetylation of pentaacetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal (0.50 g.) in abs. methanol (30 ml.) was effected by passing in a stream of anhydrous ammonia for 20 min. at 0° followed by standing of the solution at room temperature for 2 hr. The residue obtained on solvent removal under reduced pressure was crystallized from methanol–chloroform–ether; yield 0.33 g. (100%), m.p. 127–128° unchanged on admixture with the above described N-acetyl-2-amino-2-deoxy-D-glucose diethyl thioacetal.

2-Amino-2-deoxy-D-glucose Diethyl Thioacetal (IV).—2-Amino-2-deoxy-D-glucose hydrochloride (5.00 g.) was shaken mechanically with 20 ml. of concentrated hydrochloric acid (*ca.* 12 *N*) and 20 ml. of ethanethiol in a sealed tube at room temperature for 2 days. The tube was allowed to stand at room temperature with occasional shaking until all of the starting material had dissolved; 2.5 months were required. The tube was opened and the solution was neutralized with an excess of lead carbonate, filtered and the filtrate was treated with an excess of silver carbonate. The filtered solution was treated with an excess of hydrogen sulfide, filtered and dewatered under reduced pressure to a sirup which was crystallized from ethanol–ether; yield 2.65 g. (40%), m.p. 102–107°, $[\alpha]^{27}\mathrm{D}$ −21° (*c* 1.8, water). Pure crystals (needles) were obtained on further crystallization effected in the same manner; m.p. 109–110°, $[\alpha]^{23}\mathrm{D}$ −24° (*c* 1, water). The aqueous solution of this substance was basic in reaction and gave a positive ninhydrin test.

Anal. Calcd. for $C_{10}H_{23}O_4NS_2$: C, 42.08; H, 8.12; N, 4.91; S, 22.47. Found: C, 42.22; H, 8.20; N, 4.97; S, 22.37; Cl^-, absent.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

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[6] D. L. MacDonald and H. O. L. Fischer, THIS JOURNAL, **74**, 2087 (1952).

The Crystal Structure of Tetrachlorophosphonium Dichloroiodide[1,2]

BY WILLIAM F. ZELEZNY AND NORMAN C. BAENZIGER

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Although tetrachlorophosphonium dichloroiodide[3] (PCl_6I) has been known for almost a century, its crystal structure has not been reported. Accordingly, this structure was made the topic of an investigation.

Experimental

The compound was prepared by the reaction of phosphorus pentachloride and iodine monochloride in solution in carbon disulfide, yielding a finely divided, light yellow precipitate. Contact with the moisture of the air was prevented by keeping the precipitate covered with carbon tetrachloride, this protection being necessary since this compound reacts vigorously with water.

Tetrachlorophosphonium dichloroiodide readily yields crystals by sublimation in a small evacuated container. The handling of these crystals was made difficult by the compound's reactivity with moisture which precluded handling them in the atmosphere, and by its high vapor pressure which prevented manipulation of the crystals within a dry-box. To overcome these difficulties the compound, with its protective covering of carbon tetrachloride, was introduced into a 10-mm. glass tube, one end of which had been drawn to a capillary. The carbon tetrachloride was then removed by evacuation of the 10-mm. tube, care being taken that evacuation was not continued long enough to permit the vaporization of the solid PCl_6I. The 10-mm. tube was sealed off and the section containing the PCl_6I heated to 140°, resulting in rapid sublimation of the compound with deposition of crystals in the capillary section of the tube. The capillary tube was then sealed off and held in a constant temperature oven at 80° until grain growth had taken place and only one crystal remained. Many such trials were necessary in order to obtain crystals of suitable size and orientation.

X-Ray Diffraction Data.—Intensity data and approximate unit cell dimensions were obtained from zero-layer Weissenberg diagrams of single crystals recorded on multiple films with unfiltered Mo radiation. Intensities were estimated by the visual comparison method. Molybdenum radiation was chosen for obtaining the intensity data in preference to Cu Kα radiation since the latter was strongly absorbed by these crystal. However, the final unit cell dimensions were obtained from powder diagrams taken with CuKα radiation.

The unit cell is tetragonal, with the dimensions a = 9.26 Å., c = 5.68 Å., and contains two molecules. From these data the density is calculated to be 2.53 g./cc. Systematic extinction was observed only for the ($0k0$) reflections when k was odd, indicating space groups $P\bar{4}2_1$ (D_4^2) and $P\bar{4}2_1m$

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[1] From a thesis submitted by Wm. F. Zelezny in partial fulfillment of the requirements for a Ph.D. degree at the State University of Iowa, August, 1951.

[2] For material supplementary to this article order Document 3681 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[3] E. Baudrimont, *Compt. rend.*, **55**, 362 (1862).