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°, $[\alpha]^{23}\mathrm{D}$ −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.

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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

RECEIVED JULY 23, 1952

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 (0*k*0) 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).

(D_{2d}^3). Space group $P\bar{4}2_1$ does not permit a tetrahedral arrangement of atoms around the phosphorus atom. Since the structure appeared to be isotypic with tetramethylammonium dichloroiodide[4] and since the Patterson projection could be explained on the basis of this structure, the structure based on $P\bar{4}2_1m$ was chosen.

Crystal Structure.—Using (*hk*0) data, a Patterson projection was made on (00*l*) and the approximate *x*- and *y*-parameters determined. From these parameters the signs of the $F(hk0)_{\text{obsd}}$ were calculated and used in a Fourier projection on (00*l*). The *x*- and *y*-parameters were refined as much as possible by a repetition of this Fourier projection. The *z*-parameters were obtained from a Patterson projection on (110). In order to obtain better agreement between the calculated and observed *F* values, an empirical temperature correction factor of the form $e^{-1.51 \sin^2\theta}$ was applied to the calculated *F* values. It was felt by the authors that the usual scheme of computing R_1 does not make sufficient allowance for reflections, which, while not zero, are not sufficiently strong to record on film with ordinary exposures. Accordingly, a slightly modified method of calculating the R_1 values, consisting of assigning each absent or unobserved reflection an *F* value which was calculated as follows, was used. The minimum intensity observable was corrected by the angle factors corresponding to each of the unobserved reflections. Taking one-half of the square roots of the quantities thus obtained yielded *F* values which were arbitrarily assigned to the absent reflections for the purpose of calculating R_1. The R_1 calculated in this manner is defined as R_1^*. Using the parameters chosen an R_1^* value of 0.27 was obtained.

The compound proved to be isostructural with tetramethylammonium dichloroiodide,[4] with the following atoms at the following positions of space group D_{2d}^3-$P\bar{4}\,2_1m$: 2 P at (*b*) $(0\ 0\ ^1/_2)$, $(^1/_2\ ^1/_2\ ^1/_2)$; 2 I at (*c*) $(0\ ^1/_2\ z)$, $(^1/_2\ 0\ \bar{z})$ with $z = 0.161$; 4 Cl at (e) $x, ^1/_2 + x, z$; $\bar{x}, ^1/_2 - x, z$; $^1/_2 + x, \bar{x}, \bar{z}$; $^1/_2 - x, x, \bar{z}$ with $x = 0.18_0$, $z = 0.16_1$; 8 Cl at (f) xyz; $^1/_2 - x, ^1/_2 + y, \bar{z}$; $\bar{x}\bar{y}z$; $^1/_2 + x, ^1/_2 - y, \bar{z}$; $\bar{y}x\bar{z}$; $^1/_2 + y, ^1/_2 + x, z$; $y\bar{x}\bar{z}$; $^1/_2 - y, ^1/_2 - x, z$ with $x = 0.15_5$, $y = 0.07_9$, $z = 0.29_8$.

This structure consists of regularly tetrahedral PCl_4^+ ions, and linear $ClICl^-$ ions with the interatomic distances in ångström units are

P–8-fold Cl	1.98
I–4-fold Cl	2.36
8-fold Cl–8-fold Cl (within PCl_4^+ tetrahedra)	3.23
8-fold Cl–8-fold Cl (from one PCl_4^+ to the next)	3.50
4-fold Cl–8-fold Cl	3.56

Extensive calculations of intensities based on selected chlorine positions near those given above showed that the positions of chlorine atoms could be changed considerably without affecting the R_1^* value. For example

x for 4 (e)	0.16	0.17	0.18	0.19	0.20
R_1^*	.285	.271	.270	.272	.277

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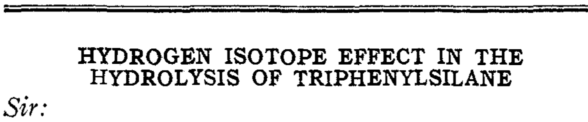
[4] R. C. L. Mooney, *Z. Krist.*, [A] **100**, 519 (1939).

COMMUNICATIONS TO THE EDITOR

HYDROGEN ISOTOPE EFFECT IN THE HYDROLYSIS OF TRIPHENYLSILANE

Sir:

Recently, Gilman, Dunn and Hammond reported[1] that triphenylsilane-*d* was hydrolyzed in moist piperidine "almost six times faster than its protium analog." They attributed this unusual isotope effect to the displacement of a hydride ion in such a manner that a hydrogen–hydrogen bond of considerable strength is present in the transition state of the reaction. This picture of the reaction path might be formulated as



$$OH^- + Ph_3SiH + HNC_5H_{10} \longrightarrow$$
$$Ph_3\overset{OH}{\overset{|}{Si}}\text{---}H\text{---}H\text{---}NC_5H_{10} \longrightarrow Ph_3SiOH + H_2 + C_5H_{10}N^-$$

Because of the unusual effect reported for this reaction, we have examined several similar reactions which involve the formation of hydrogen, presumably by abstraction of a hydride ion. To enhance any isotope effects, tritium, rather than deuterium, was used in competitive measurements of k_T/k_H, the ratio of the isotopic reaction rates.

The alkaline alcoholic hydrolysis[2] of tripropylsilane-*t* was found to be about 0.7 as fast as that of its protium analog. The alcoholysis of lithium aluminum hydride-*t*[3] and of lithium borohydride-*t*[4] did not give consistent values of k_T/k_H, possibly because of changes in the reacting species; the observed values fell between 1.2 and 0.8.

In view of these results we have reinvestigated the hydrolysis of triphenylsilane in moist piperidine. Tritium-labeled triphenylsilane was prepared[5] by the reduction of triphenylchlorosilane with lithium aluminum hydride-*t*.[3] The triphenyl-silane-*t* was dissolved in a 1.0 *M* solution of water in piperidine, in a previously evacuated system, and permitted to react at 25°. At intervals, the reaction was stopped by cooling to −80°, and the evolved hydrogen was collected. The volume of each fraction was measured manometrically and its tritium content was determined in an ion chamber with a vibrating reed electrometer. The total volume and tritium content of the fractions agreed with those expected from analysis[5] of the triphenylsilane-*t* by hydrolysis with moist piperidine and potassium hydroxide. The experimental results are given in Table I. The ratio of the rate constants is calculated for each gas fraction from the expression

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[1] H. Gilman, G. E. Dunn and G. S. Hammond, THIS JOURNAL, **73**, 4499 (1951).

[2] F. P. Price, *ibid.*, **69**, 2600 (1947).

[3] K. E. Wilzbach and L. Kaplan, *ibid.*, **72**, 5795 (1950).

[4] W. G. Brown, L. Kaplan and K. E. Wilzbach, *ibid.*, **74**, 1343 (1952).

[5] H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).