cess diethanolamine and finally concentrated to small volume under reduced pressure. Dilution of the darkly-colored concentrated solution to excess with petroleum ether precipitated the crude product as a yellow orange oil, 41.5 g. The crude product in benzene was chromatographed through 400 g. of acid-washed alumina. A small amount of material was eluted with benzene and 200 cc. of benzene–acetone (1:1). Pure product was eluted with 500 cc. of acetone–methanol (1:1) and was obtained as a pale yellow oil, 31.8 g., $n^{25}D$ 1.5465.

Anal. Calcd. for $C_{18}H_{24}NPO_5$: C, 59.16; H, 6.62; N, 3.83. Found: C, 59.11; H, 6.73; N, 4.00.

Dibenzyl Di-(2-chloroethyl)-phosphoramidate (II).—A solution of 1.5 cc. (1.77 g.) of the dihydroxyphosphoramidate I, 2 cc. of thionyl chloride and one drop of pyridine in 15 cc. of chloroform was heated under reflux for 15 minutes. The mixture was distilled at reduced pressure to remove excess thionyl chloride and solvent. The residue, 1.83 g., dissolved in benzene was shaken with water. The benzene solution, dried and concentrated to small volume by distillation, was passed over acid-washed alumina from which the product was eluted with benzene as an oil, 0.4 g., $n^{28}D$ 1.5452.

Anal. Calcd. for $C_{18}H_{22}NPO_3Cl_2$: C, 53.74; H, 5.51; N, 3.48; Cl, 17.63. Found: C, 54.16; H, 5.66; N, 3.39; Cl, 18.20.

An additional 0.6 g. of pale yellow oil, probably unchanged starting material, was eluted from the column with acetone, $n^{28}D$ 1.5468.

Hydrolysis of Dibenzyl Di-(2-hydroxyethyl)-phosphoramidate (I) with Base.—A solution of 2 g. of dihydroxyphosphoramidate I in a mixture of 80 cc. of 95% ethanol and 80 cc. of 0.1 *N* sodium hydroxide was refluxed for 30 minutes. Acidification of the reaction mixture after concentration gave an oil that was extracted with ethyl acetate and which crystallized from ether after standing at 5°, 0.7 g., m.p. 77–79°. The m.p. of dibenzylphosphoric acid was variously reported from 78–80°.[9]

Anal. Calcd. for $C_{14}H_{15}PO_4$: neut. equiv., 278.2. Found: neut. equiv., 277.

The cyclohexylamine salt recrystallized from methanol–acetone, m.p. 174–175.5°.

Reaction of Dibenzyl Di-(2-hydroxyethyl)-phosphoramidate (I) with Lithium Chloride.—A solution of 12.5 g. of the dihydroxyphosphoramidate I in 110 cc. of cellosolve, saturated at the boiling point with freshly fused lithium chloride, was heated under reflux for 13.5 hours. Careful acidification of the reaction mixture cooled in ice gave an oil, 8.65 g., that was extracted with ethyl acetate. The cyclohexylamine salt crystallized from methanol–ethyl acetate as long white needles, m.p. 246–248°. The analytical results are in accord with cyclohexylammoniumbenzylphosphoric acid.

Anal. Calcd. for $C_{13}H_{22}NPO_4$: C, 54.33; H, 7.72; N, 4.87. Found: C, 53.29, 54.23; H, 7.66, 7.78; N, 4.68, 4.71.

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Preparation of Salts of Glucuronic Acid

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Methods have been developed for the preparation and isolation of three salts of glucuronic acid which are preferable to published procedures.[1,2] In addition, we have found that the potassium salt of glucuronic acid forms a dihydrate under ordinary conditions rather than one containing 1.5 molecules of water as previously reported.[2]

Preparation of Sodium and Potassium Salts of Glucuronic Acid.—Preparation of the sodium and potassium salts of glucuronic acid by titration of glucuronolactone with a stoichiometric amount of alkali is accompanied by extensive degradation. We have found that these salts are prepared best by rapid combination of aqueous alkali with glucuronolactone such that the reaction is complete in a few seconds. When the alkali is made up in aqueous alcohol these salts crystallize directly from the reaction medium. Sodium glucuronate crystallizes as a monohydrate and potassium glucuronate as a dihydrate.

Preparation of Ammonium Glucuronate.—The ammonium salt of glucuronic acid cannot be prepared by direct reaction of glucuronolactone with ammonia because amino-amides are formed.[3] However, as reported in the literature,[2] ammonium glucuronate can be prepared by direct reaction of glucuronic acid with aqueous ammonia. The salt crystallizes as a monohydrate from aqueous acetone. We obtain glucuronic acid for this reaction by passing an aqueous solution of the sodium or potassium salt over a cation-exchange resin column.[4]

Experimental

Preparation of Sodium Glucuronate (Monohydrate).—18.5 g. (0.105 mole) of glucuronolactone was stirred rapidly into 60 ml. of 50% (by volume) methanol containing 4.1 g. (0.102 mole) of sodium hydroxide. Crystals formed almost immediately and were removed by filtration after overnight refrigeration. They were washed with 75% (by volume) methanol and then with absolute methanol. The yield was 19 g. (0.081 mole) of colorless crystals dried in air at room temperature.

Anal.[5] Calcd. for $C_6H_9O_7Na \cdot H_2O$: C, 30.8; H, 4.7; Na, 9.8; glucuronic acid, 83; water, 7.7. Found: C, 30.6; H, 5.0; Na, 9.6; glucuronic acid (naphthoresorcinol method), 82; water (Karl Fischer), 8.3.

This salt lost no weight when it was stored under vacuum over anhydrous calcium chloride for 24 hours.

Preparation of Potassium Glucuronate (Dihydrate).—18.5 g. (0.105 mole) of glucuronolactone was stirred rapidly at room temperature into 100 ml. of 30% (by volume) methanol containing 5.8 g. (0.103 mole) of potassium hydroxide. Crystals formed almost immediately and were removed by filtration after overnight refrigeration. They were washed first with 60% methanol and then with absolute methanol. The yield was 24.0 g. (0.09 mole) of colorless crystals dried in air at room temperature.

Anal. Calcd. for $C_6H_9O_7K \cdot 2H_2O$: C, 26.9; H, 4.8; K, 14.6; glucuronic acid, 72; water, 13.4. Found: C, 27.1; H, 4.8; K, 14.6; glucuronic acid, 74; water, 13.2.

This salt lost 7.3% of its weight after 72 hours under vacuum over anhydrous calcium chloride. It returned to its initial weight after overnight standing on the desk top. Thus it appears that the water of crystallization is not tightly bound.

Preparation of Ammonium Glucuronate (Monohydrate).—15.1 g. (0.078 mole) of crystalline glucuronic acid was stirred rapidly into 40 ml. of water containing 1.36 g. (0.080 mole) of ammonia. The glucuronic acid dissolved instantly, and 200 ml. of acetone was added gradually over a one-hour period with continuous agitation. A yield of 14.6 g. (0.065 mole) of crystals was separated by filtration, washed with acetone, and dried at room temperature.

Anal. Calcd. for $C_6H_9O_7NH_4 \cdot H_2O$: C, 31.4; H, 6.5; N, 6.1; glucuronic acid, 85; water, 7.9. Found: C, 31.7; H, 6.3; N, 6.0; glucuronic acid, 86; water, 7.8.

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(5) Microanalyses by G. Stragand, University of Pittsburgh.

This salt lost no weight when it was stored under vacuum over anhydrous calcium chloride for 24 hours.

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A Qualitative Test for Silicon in Organosilicon Compounds and for Germanium in Organogermanium Compounds

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Silicomolybdic acid was first described by Parmentier[1] in 1882. Sixteen years later a method for the detection of silicic acid in water by the use of the yellow silicomolybdate solution for a colorimetric determination was reported.[2]

Feigl and Krumholz[3] first described the use of benzidine in conjunction with silicomolybdic acid as a sensitive spot test for silicon; the benzidine becomes oxidized to "benzidine blue" and simultaneously the silicomolybdic acid is reduced to "molybdenum blue." It has been reported that 0.001 mg. of silica in a concentration of 1:50,000 can be detected by this method. The benzidine–molybdic acid test has been used to detect silica in minerals,[4] silicon in steel[5] and silicic acid in limestone and related materials.[6]

Germanates react similarly with molybdic acid to form the insoluble germanomolybdic acid which like its silicon analog will oxidize benzidine to "benzidine blue" with the concurrent formation of "molybdenum blue."[7] The quantitative methods for germanium in organogermanium compounds have been reviewed recently.[8]

A qualitative test for silicon in organosilicon compounds has been reported,[9] the compound being oxidized to silica with concentrated sulfuric acid plus either glacial acetic acid or 70% nitric acid. Another qualitative test[10] for silicon in organic compounds involves treatment with sodium fluoride and sulfuric acid; the resulting silicon tetrafluoride vapors are allowed to contact an asphalt-covered rod which has been previously dipped in water. A white deposit of silica indicates the presence of silicon.

The benzidine–molybdic acid test recently has been applied to organosilicon compounds.[11] The organosilicon compound was decomposed to the soluble silicate by fusion on a platinum loop with sodium carbonate and sodium peroxide; subsequent reaction with ammonium molybdate and benzidine resulted in the blue coloration when neutralized with ammonia.

The benzidine–molybdic acid test has been employed in this Laboratory; several modifications and refinements have been made and the method has been extended to include organogermanium compounds. Although a platinum loop is more convenient and available than a small platinum spoon, the spoon has several advantages over the loop. Liquids may be tested with greater facility, a smaller amount of the organosilicon (or organogermanium) compound is required and no transferal of the fused mixture is necessary when employing the platinum spoon. Sodium acetate was found more practical than ammonia for neutralizing the acidic solution. Commercially available sodium peroxide contains iron as an impurity which causes a brown color on neutralization with ammonia and thus masks the blue color which is characteristic of a positive test for silicon or germanium. Only with some sulfur-containing organosilicon compounds was any difficulty encountered in obtaining a positive test; with certain of these compounds a large excess of sodium peroxide was necessary in order to ensure complete oxidation of the sulfur atom. If the sulfur is not completely oxidized, the resulting sulfide will reduce the ammonium molybdate solution to "molybdenum blue" and therefore give a positive test in the absence of silicon. A variety of organosilicon and organogermanium compounds has been tested, a positive result being obtained in every case.

Experimental

Approximately 0.02 g. of the organosilicon (or organogermanium) compound, 0.01 g. of sodium peroxide[12] and 0.06 g. of sodium potassium carbonate (1:2 fusion mixture) are mixed thoroughly. If the sample to be tested is a liquid, it is best to mix the materials on a small piece of platinum foil, possibly a platinum crucible lid; 2 or 3 drops of the liquid should be used, and if the liquid is relatively volatile, the mixture should not be made up until the bead is ready to be prepared. A platinum loop (approximately 4 mm. in diameter), which has previously been rid of any silicate by fusion with sodium potassium carbonate, is heated and brought into contact with the mixture. After a bead has been formed, it is heated in a bunsen or meeker burner flame for approximately 1 minute. The mixture should not be heated too rapidly at first or some spattering may occur. After placing about 1 ml. of water in a platinum crucible, the bead is immersed in the water, and the solution is warmed to boiling in order to dissolve the fused mixture; glassware cannot be used since the boiling mixture may dissolve sufficient silica to give a positive test. On a piece of filter paper are placed 2 or 3 drops of ammonium molybdate solution. The 2 drops of the solution to be tested are added to the ammonium molybdate on the filter paper. If the test is run rapidly, the solution will still be warm; however, if the solution has cooled, the filter paper should be warmed gently following the addition of the molybdate and test solutions. Subsequently, 1 drop of benzidine solution and 2–5 drops of

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(12) If the organosilicon or organogermanium compound being tested contains sulfur, the amount of sodium peroxide should be two or three times the sample weight.