Found by the Dumas method: N, 21.86. Curiously, the Kjeldahl method (two different operators) gave 14.30, 14.38, 14.27, 14.19; values which are quite close to the calculated 14.25 per cent. nitrogen in dipiperidino carbonyl. This latter compound cannot be formed if the accepted mechanism[1b] for the reaction is correct. Dipiperidinocarbonyl was therefore prepared from piperidine and phosgene and the melting point determined to be 45–46°. Reported by Kuhn,[5] 42–43°. From this it is apparent that the Kjeldahl method fails in this instance and that the mechanism of Davis and Underwood[1b] for the reaction is completely substantiated.

Summary

The formation of substituted ureas by heating a primary or secondary amine with urea has been applied to basically-substituted aliphatic amines. Five new compounds of this nature are described.

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(5) Kuhn, *Ber.*, **33**, 2900 (1900).

[CONTRIBUTION FROM DEPARTMENTS OF PHARMACOLOGY AND BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE]

β-D-Galactose-1-(barium phosphate)[1]

BY F. J. REITHEL

A new sugar phosphate ester has been synthesized which has properties indicating it to be the β isomer of D-galactose-1-(barium phosphate). The only synthesis of the β isomer of a hexose-1-phosphate which has appeared in the literature is that of Wolfrom, *et al.*[2]

Lipmann and Tuttle have published a method[3] for the synthesis of acetyl phosphate with "monosilver phosphate" as the phosphorylating agent and have suggested the use of this reagent for the synthesis of the Cori ester. It was found that α-bromo-D-glucose tetraacetate reacted with "monosilver phosphate" to form β-D-glucose-1-(barium phosphate), isolated as the barium salt.

β-D-Galactose-1-(barium phosphate) was synthesized both by the method of Wolfrom, *et al.*,[2] and by the use of "monosilver phosphate." The products obtained were very similar with respect to rotation and phosphorus content. Rotational changes during hydrolysis of the compound were in the right direction for the β isomer. It is concluded that the new compound is β-D-galactose-1-(barium phosphate) and that the method employing "monosilver phosphate" is generally applicable to the synthesis of the β isomer of hexose-1-phosphates.

Experimental

β-D-Galactose-1-(barium phosphate).—Monosilver phosphate, prepared from 1.05 g. of dry trisilver phosphate and 0.33 ml. 90% phosphoric acid, was suspended in 3 ml. of dry ether. To this suspension, kept at 5°, was slowly added 3.0 g. of pure dry α-bromo-D-galactose tetraacetate in absolute chloroform and the mixture allowed to react for ten minutes with good stirring. After centrifuging, the supernatant fluid was shaken with 10 ml. water at 0° and the mixture adjusted to *p*H 8 with normal sodium hydroxide. The chloroform layer was discarded and to the aqueous layer was added 2 g. of barium acetate in 10 ml. of water. The precipitate was centrifuged down and discarded. The aqueous solution was evaporated to dryness *in vacuo* at 30° and the residue taken up in 25 ml. of 98% alcohol. No attempt was made to crystallize this intermediate which is presumably the barium salt of D-galactose-1-phosphoric acid tetraacetate. It was deacetylated by pouring the above solution into alcohol containing sodium ethylate whereupon crude β-D-galactose-1-(barium phosphate) precipitated. The crude salt was purified by dissolving in water, adjusting to *p*H 8.5, and precipitating with 1.5 volumes 95% alcohol. After three such treatments there was obtained 270 mg. of a white amorphous solid which was completely soluble in water and which reduced alkaline copper solutions after mild acid hydrolysis. The specific rotation in water was $[\alpha]^{30}\mathrm{D}$ +31.2° (*c*, 1.2).

Anal. Calcd. for $C_6H_{11}O_5PO_4Ba\cdot3H_2O$: C, 16.05; H, 3.56; P, 6.90; Ba, 30.6. Found: C, 16.14, 16.16; H, 3.0, 3.2[4]; P, 6.88; Ba,[5] 30.6.

β-D-Galactose-1-(barium phosphate) was also synthesized by the method of Wolfrom, *et al.*[2] The phosphorylating agent, silver dibenzyl phosphate, was prepared from pure dibenzylphosphoric acid by adding an alcoholic solution of silver nitrate to an alcoholic solution of the acid. The pure silver salt thus obtained melted at 222° with decomposition.

Two grams of pure dry α-bromo-D-galactose tetraacetate, 2.8 g. pure silver diphenyl phosphate and 11 ml. of pure dry benzene were introduced into a flask equipped with a sealed stirrer and a condenser fitted with a calcium chloride tube. The mixture was heated slowly to 50° for thirty minutes, then at 65° for ninety minutes, vigorous stirring being maintained. After removal of the benzene, the sirup obtained was taken up in 4 ml. of absolute ether and allowed to stand overnight in the ice box. This procedure allowed any excess silver diphenyl phosphate to separate. To the filtered solution low boiling petroleum ether was added to incipient turbidity at 0°. After some days a mass of crystals appeared which were very difficult to separate from a small amount of adhering sirup. The impure crystalline mass, weighing 2.1 g., was taken up in 25 ml. of absolute ethanol and hydrogenated at room temperature and atmospheric pressure in the presence of 0.32 g. of palladous oxide catalyst.[6] The hexose phosphoric acid was made into the lead salt according to Wolfrom, *et al.*[2] After decomposing the lead salt with hydrogen sulfide, the filtered, aerated solution was made alkaline with barium hydroxide. The crude barium salt was obtained by adding 1.5 volumes 95% ethanol and was purified by alcohol precipitation as described above. Two hundred and fifty mg. of a white amorphous product was obtained which had a rotation in water of $[\alpha]^{30}\mathrm{D}$ +34°.

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(1) This work was aided by a research grant from the Rockefeller Foundation. Original manuscript received October 16, 1944.

(2) Wolfrom, Smith, Pletcher and Brown, THIS JOURNAL, **64**, 23 (1942).

(3) Lipmann and Tuttle, *J. Biol. Chem.*, **153**, 571 (1944).

(4) The carbon and hydrogen analyses were kindly done by Dr. S. A. Thayer, St. Louis University School of Medicine.

(5) King, *Biochem. J.*, **26**, 586 (1932).

(6) Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924)

The phosphorus content of the freshly prepared compound was 6.2%. After several weeks drying over phosphorus pentoxide the phosphorus content was found to be 6.7%.

β-D-Glucose-1-(barium phosphate).—This compound was synthesized from α-bromo-D-glucose tetraacetate using monosilver phosphate as a phosphorylating agent. A white amorphous solid was obtained which had a specific rotation in water of $[\alpha]^{30}\text{D}$ +20.6° and contained 6.7% phosphorus.

Changes in Optical Rotation during Hydrolysis of β-D-Galactose-1-phosphoric Acid.—Twenty-five mg. of β-D-galactose-1-(barium phosphate) was dissolved in 1 ml. of water, the *p*H adjusted to 7, and the barium precipitated with the calculated amount of potassium sulfate. After centrifuging, the solution was made up to a volume of 2.00 ml. One ml. of this solution was mixed with 1.00 ml. normal hydrochloric acid and the change in rotation at 30° was observed. After nine minutes the observed rotation was +0.11° (D-line, 1 dm.). In the course of twenty-four hours the rotation rose to +0.185° (D-line, 1 dm.). Since the phosphorus content of this solution was found to be 38.5 γ per 0.1 ml., the galactose content could be calculated as 0.22%. Thus the final reading in terms of galactose was $[\alpha]^{30}\text{D}$ +84°. The specific rotation for galactose is $[\alpha]^{20}\text{D}$ +80.2°.

A similar experiment was done with α-D-galactose-1-(barium phosphate) made by the method of Colowick.[7] The rotational change was in a downward direction and reached a specific rotation $[\alpha]^{30}\text{D}$ +85°

Rate of Hydrolysis of β-D-Galactose-1-phosphoric Acid.—β-D-Galactose-1-(barium phosphate) was dissolved in water and the barium removed with the calculated amount of potassium sulfate. One-tenth ml. of the resulting solution contained 60.5 γ of total phosphorus. To 0.1-ml. samples in glass-stoppered tubes were added 0.1-ml. portion of 0.5 *N* hydrochloric acid. The tubes were immersed in a water-bath at 37° ± 0.1. Tubes were removed at intervals and the contents analyzed for inorganic phosphorus. The results are given in Table I.

TABLE I

Time, min.	γ Inorganic P	Hydrolysis, %
15	9.5	15.7
30	19.7	32.6
45	26.7	44.0
60	31.6	52.3
120	51.3	85.0

The rate of hydrolysis is nearly identical with that found for the α isomer by Kosterlitz.[8]

Acknowledgment.—It is a pleasure to thank Dr. C. F. Cori for his help and interest in this work.

Summary

A method employing monosilver phosphate has been described for synthesizing the β isomer of hexose-1-phosphates.

Using this method, β-D-galactose-1-(barium phosphate) was synthesized and characterized. For comparison, this compound was also synthesized by the method of Wolfrom, *et al.*, which is known to yield the β isomer of D-glucopyranose-1-phosphate. The products obtained by the two methods were identical.

The rate of hydrolysis in 0.25 *N* hydrochloric acid at 37° has been measured for β-D-galactose-1-phosphoric acid.

β-D-Glucose-1-(barium phosphate) has been synthesized by the new method described and its rotation determined.

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[7] Colowick, *J. Biol. Chem.*, **124**, 557 (1938).

[8] Kosterlitz, *Biochem. J.*, **33**, 1087 (1939).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

On the Mechanism of the Reaction between Methyl Chloride and Silicon–Copper

BY DALLAS T. HURD AND EUGENE G. ROCHOW

It has been found[1] that elementary silicon reacts at elevated temperatures with hydrocarbon halides to form organo-halosilanes, and that the reaction is greatly facilitated by the use of copper as a catalyst. Inasmuch as this synthesis is important in the rapidly expanding field of silicone materials, the authors have undertaken an investigation into the mechanism of the reaction or reactions involved in the production of methyl chlorosilanes from methyl chloride and silicon–copper.

Experimental

The first experiment consisted in passing pure methyl chloride at 350° over a polished section of silicon crystals embedded in copper. This section was prepared by crushing crystals of pure silicon between two cleaned copper blocks, then polishing down the interface until the silicon–copper boundaries became apparent. At 350° the attack of methyl chloride was quite rapid. Comparison photomicrographs taken before exposure and after two hours of exposure to methyl chloride at 350° are shown in Figs. 1 and 2.

A close examination and measurement of the photomicrographs showed two significant facts: (1) silicon was removed much faster where it was in contact with or in close proximity to copper, and (2) copper was also removed from the block, somewhat more rapidly in the neighborhood of silicon. The removal of both copper and silicon thus left a V-shaped depression at the boundary, suggesting a mutual catalytic action or interaction.

The reaction of copper with methyl chloride was investigated further by using thin films of copper evaporated onto clean microscope slides. One such copper mirror was broken in two pieces, one piece being heated in a current of methyl chloride at 250° while the other was kept as an analytical control. The mirror which was heated in methyl chloride slowly became transparent, and traces of copper were transferred to the cooler parts of the tube. Close examination of this exposed piece revealed that a

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[1] E. G. Rochow, THIS JOURNAL, **67**, 963 (1945).