cooled overnight. The formation of ammonia was almost quantitative. The colorless crystals were filtered and weighed 1.60 g. The mother liquor was further evaporated to dryness to give 4.77 g. same crystals. Yield of cyanoformamidine 6.37 g. (92%), m.p. after recrystallization from hot ethanol, 137–138°.

Anal. Calcd. for $C_2N_3H_3$: C, 34.78; H, 4.38; N, 60.85. Found: C, 35.04; H, 4.47; N, 60.68. Mol. wt. (from freezing point depression: solvent H_2O): 69. Calcd.: 69.

Hydrolysis of cyanoformamidine. To a solution of 0.69 g. (0.01 mole) cyanoformamidine in 30 cc. water was added 2.00 g. (0.02 mole) concentrated sulfuric acid. The mixture was refluxed for 5 hr. in a Kjeldahl flask. After hydrolysis, the solution was diluted with 50 cc. of water and distilled; 100 cc. of distillate was collected. This was titrated with 6.76 cc. of 1*N* NaOH to neutrality. This corresponded to 0.0068 mole of formic acid. The neutralized distillate was then decolored by charcoal and evaporated to dryness to give sodium formate. Recrystallization from hot water, m.p. 255°.

The residue in a Kjeldahl flask was diluted with water and to it, a small amount of amberite IR4B was added to remove free acid. The resulting solution, after treating with charcoal, was evaporated to dryness to leave the solid. This was extracted with methanol and the extract was evaporated to dryness to give urea (0.3 g.), m.p. 132°; m.p. of the nitrate, 152°. The final residue (0.55 g.) was proved to be ammonium sulfate.

Formoguanamine (III) *from* II *and guanidine.* An ethanolic solution of free guanidine was prepared by treating 4.78 g. (0.05 mole) of guanidine hydrochloride with an equivalent amount of sodium ethylate in 50 cc. ethanol. After separating the precipitated sodium chloride, 2.07 g. (0.03) cyanoformamidine was added to the solution which was then heated at 70° for 3.5 hr. with agitation. Formoguanimine crystals separated out gradually and there was a noticeable evolution of ammonia. The yield was 2.39 g. (72%), m.p. after recrystallization from hot water, 317–318°. A mixed melting point with an authentic sample of formoguanamine showed no depression; m.p. of picrate, 245–246°.

Formoguanamine (III) *from I, cyanamide and guanidine.* An ethanolic solution of formamidine and guanidine was prepared by treating 4.00 g. (0.05 mole) guanidine hydrochloride with an equivalent amount of sodium ethylate in 90 cc. ethanol with cooling in an ice bath. After separating the precipitated sodium chloride, 2.10 g. (0.05 mole) cyanamide was added to the solution followed by heating to 60–75° with agitation for 2.5 hr. The evolution of ammonia was quantitative. Colorless crystals separated out gradually; after standing overnight the yield of III was 4.72 g. (85%), m.p. 316–317°.

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A New Derivative from *aldehydo*-D-Glucose Pentaacetate: Dimethyl 2,3,4,5,6-D-*gluco*-Pentaacetoxy-1-hydroxy-*n*-hexylphosphonate

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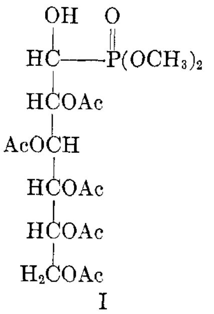
A number of dialkyl α-hydroxyphosphonates derived from chloral and dialkyl hydrogen phosphite have been described in previous papers.[1] In our extension of this study of dialkyl hydroxyphosphonates as possible insecticidal agents, dimethyl 2,3,4,5,6-D-*gluco*-pentaacetoxy-1-hydroxy-*n*-hexylphosphonate (I) was synthesized from D-glucose in four steps. Although I proved to be of little value as an insecticide, it may be of interest to the carbohydrate chemist for the preparation of new derivatives.

aldehydo-D-Glucose pentaacetate,[2] prepared from D-glucose through penta-*O*-acetyl-D-glucose diethyl dithioacetal,[3] was condensed with dimethyl hydrogen phosphite in the presence of triethylamine as catalyst. This reaction, incidentally, leads to a compound with a new asymmetric carbon atom whose configuration remains to be established.



I

EXPERIMENTAL

*Dimethyl 2,3,4,5,6-*D*-gluco-pentaacetoxy-1-hydroxy-n-hexylphosphonate. aldehydo*-D-Glucose pentaacetate[2] (0.005 mole) and freshly distilled dimethyl hydrogen phosphite (0.02 mole) were mixed. To this mixture was added 8 drops of a solution of triethylamine or trimethylamine containing 1 part by weight of amine to 2 parts absolute ethanol. Since the heat of reaction was insufficient to effect solution, the mixture was heated on the steam bath, with shaking, until solution was complete (about 30 sec.). After standing at 5° for several days, crystallization occurred. The mixture was filtered and the crystals (0.001 mole) were washed with ether. Pure material was obtained on one recrystallization from acetone or ethanol; yield 20%, m.p. 172–173° unchanged on additional recrystallizations, $[\alpha]^{24}_{D}$ +25° (*c* 2, $CHCl_3$).

Anal. Calcd. for $C_{18}H_{29}O_{14}P$: C, 43.28; H, 5.84; P, 6.19. Found: C, 43.11; H, 5.71; P, 6.45.

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[3] We are indebted to Messrs. J. E. Hodge and C. E. Rist of the USDA Northern Utilization Research Division, Peoria, Ill., for seed crystals of this dithioacetal.