experience in this laboratory indicates that the yield in such a preparation is 70 ± 10%.[13]

Kinetic measurements were by nitrogen evolution using the apparatus described previously.[14] For the 50.00 ± 0.05° (measured by a National Bureau of Standards calibrated thermometer) runs, approximately 3×10^{-2} *M* solutions of phenylazotriphenylmethane in chlorobenzene or in the chlorobenzene solution of triphenylmethyl prepared as above were used.

Volume measurements were made over 4- to 8-hr. periods, final volumes being read after 24 hr., or after heating the reaction vessels to 70–80° for 30 min., then cooling to 50°. The data gave good straight line plots in $\ln V_\infty/(V_\infty - V)$ *vs.* time. The same line was obtained both in the presence and absence of added triphenylmethyl. The observed first order rate constant was 0.88×10^{-2} min.$^{-1}$ Alder and Leffler[9] report 1.00×10^{-2} min.$^{-1}$ at 322.9° K. Their measurements were spectrophotometric. When oxygen was bubbled through the solution containing added triphenylmethyl after all the azo compound had been decomposed, ditriphenylmethyl peroxide (m.p. 184–185° uncorr.; lit, 185–186°) precipitated. The amount of peroxide was considerable but the weight was not recorded. For runs at 27.00 ± 0.05° approximately 2×10^{-1} *M* solutions of phenylazotriphenylmethane were used. These runs were followed for about 8 hr. (approximately one fourth of one half-life), then the temperature of the reaction vessel was raised to 70–80° for 30 min. The vessel and contents were cooled to 27° and final volumes were read. A plot of $\ln V_\infty/(V_\infty - V)$ *vs.* time gave reasonably straight lines corresponding to $k = 3.6 \times 10^{-4}$ min.$^{-1}$ (Alder and Leffler[9] report $2.14–2.38 \times 10^{-4}$ min.$^{-1}$) in both the presence and absence of added triphenylmethyl. However, at times greater than 400 min. deviations from linearity occurred, but these were identical in the absence and presence of added triphenylmethyl.

Acknowledgments. We are indebted to the National Science Foundation for a predoctoral fellowship held by John F. Garst and additional collateral support through a research grant. Many thanks are due to Dr. S. K. Liu for his assistance in the use of the apparatus for kinetic measurements.

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(13) G. S. Hammond and F. J. Modic, unpublished studies.

(14) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, 72, 3233 (1955).

Cyanamide Derivatives (LIV).[1] Cyanoformamidine and Its Reactions

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Received May 29, 1957

In previous work[2] it was found that cyanamide reacts in ethanol solution with the reduction product of guanidine in the presence of free guanidine to produce formoguanamine (III).

(1) Part LIII, *J. Org. Chem.*, 22, 1715 (1957).

(2) K. Odo, K. Shirai, and K. Sugino, *Bull. Chem. Soc. Japan*, 28, 614 (1955).

A study of the mechanism of this reaction, which is now reported, has shown that this reduction product of guanidine is formamidine (I) and that it reacts with cyanamide to give cyanoformamidine (II). This latter compound, which is formed in nearly quantitative yield from cyanamide and I, was characterized by its analysis and hydrolysis by dilute sulfuric acid to urea, formic acid, and ammonium sulfate.

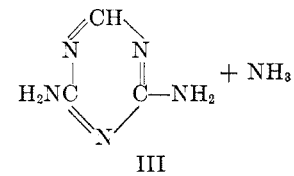
$$NH_2C(NH)NH_2 \xrightarrow{[H]} \underset{\text{I}}{NH_2CH{=}NH} + NH_3$$

$$NCNH_2 + I \longrightarrow \underset{\text{II}}{NCNHCH{=}NH} + NH_3$$

$$II + 3H_2O \longrightarrow H_2NCONH_2 + HCOOH + NH_3$$

Cyanoformamidine (II) is a neutral substance, m.p. 137–138°. It is shown to be the intermediate in the formation of formoguanamine (III)[2] by the fact that it reacts readily with guanidine in ethanol solution at 70° to give III in 72% yield. The reaction mechanism thus established invalidates the one suggested earlier.[2]

$$NCNHCH{=}NH + NH_2C(NH)NH_2 \longrightarrow$$



$+ NH_3$

III

EXPERIMENTAL[3]

Isolation of formamidine (I). To a solution of 19.1 g. (0.2 mole) thoroughly dried guanidine hydrochloride in 100 cc. absolute ethanol was added 4.6 g. (0.2 mole) of clean sodium cuttings piece by piece with agitation, keeping the temperature at 15–25°. After separating the precipitated sodium chloride, 45.8 g. (0.2 mole) picric acid dissolved in 200 cc. of hot methanol was added and the precipitate was filtered off while hot. This amounted to 53 g. and consisted mainly of guanidine picrate. Then, by cooling the filtrate, 4.4 g. crude formamidine picrate, m.p. 227°, was obtained; 0.7 g. of the same picrate (purity, a little less) was recovered by subsequent evaporation of the mother liquor. A hot water extract of the crude guanidine picrate gave 2.3 g. formamidine picrate, m.p. 237°. The combined picrate was recrystallized from hot water. Yield 6.7 g. (24%), m.p. 246–247°. Formamidine hydrochloride derived from the picrate melts at 78°.

Cyanoformamidine (II). An ethanolic solution of free formamidine was prepared by treating 7.95 g. (0.1 mole) formamidine hydrochloride with an equivalent amount of sodium ethylate in 50 cc. ethanol. After separating sodium chloride, 4.20 g. (0.1 mole) cyanamide was added to the solution. During this procedure, cooling in an ice bath was necessary to avoid the decomposition of formamidine. Crystals began to separate from the ice-cooled mixture. It was then heated for 2 hr. at 50–75° to evolve ammonia and

(3) All melting points are uncorrected.

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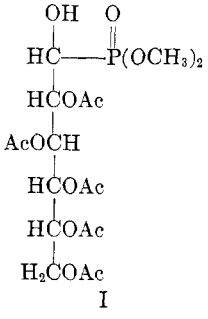
A New Derivative from *aldehydo*-D-Glucose Pentaacetate: Dimethyl 2,3,4,5,6-D-*gluco*-Pentaacetoxy-1-hydroxy-*n*-hexylphosphonate

B. H. ALEXANDER AND W. F. BARTHEL

Received May 31, 1957

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, $[\alpha]_D^{24}$ +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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(1) W. F. Barthel, P. A. Giang, and S. A. Hall, *J. Am. Chem. Soc.*, **76**, 4186 (1954); W. F. Barthel, B. H. Alexander, P. A. Giang, and S. A. Hall, *J. Am. Chem. Soc.*, **77**, 2424 (1955).

(2) M. L. Wolfrom, *J. Am. Chem. Soc.*, **51**, 2188 (1929); M. L. Wolfrom, M. Konigsberg, and D. I. Weisblat, *J. Am. Chem. Soc.*, **61**, 574 (1939).

(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.