

obtained from syntheses on the one millimole scale by this procedure melted at 110–129°, and melted at 125–130° after purification. On a five millimole scale the products melted at 123–131°, and melted at 131–133° after purification. These products were considered sufficiently pure for syntheses and were not purified further.

A typical isotopic synthesis, using 2.53 millimoles (0.500 g. containing 5 mc. of C¹⁴) of barium carbonate gave a yield of 144.8 mg. of urea (95.2%) melting at 125–130°. Recrystallized from acetone, the yield was 123 mg. melting

at 132–133°. This product contained 1.98 millicuries/millimole.

Summary

Urea has been synthesized using barium carbonate containing C¹⁴ to give a 95.2% yield of product containing 1.98 millicuries of radioactivity per millimole. The method employed involved a new synthesis of cyanamide.

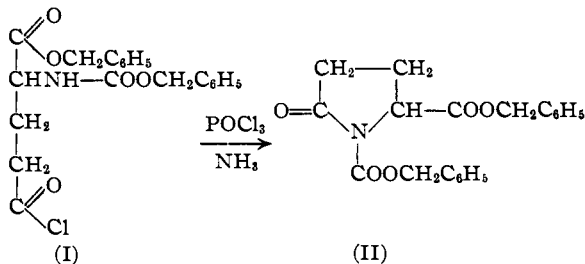
LOS ALAMOS, NEW MEXICO RECEIVED NOVEMBER 1, 1948

NOTES

The Preparation of Benzyl N-Carbobenzoxy-pyrrolidone-2-carboxylate-5

BY MAX BERENBOM¹ AND JULIUS WHITE

In the synthesis of glutamine by the method of Bergmann, Zervas and Salzmann,² one of the steps is the formation of α -benzyl N-carbobenzyloxyglutamoyl chloride (I) by treating the corresponding carboxylic acid with phosphorus pentachloride. The phosphorus oxychloride formed in this reaction is washed out with petroleum ether. (I) is then treated with an ice cold solution of ammonia in ether to form the amide which is subsequently hydrogenated to yield glutamine. We wish to point out that if the phosphorus oxychloride is not removed in the preparation of (I), subsequent treatment with ammonia yields benzyl N-carbobenzyloxy-pyrrolidone-2-carboxylate-5 (II), instead of the desired amide.



This compound (II), m. p. 110° (uncorrected), $[\alpha]^{25D} - 39.5$ (in ethanol), which has not been described previously can be obtained in 70% yield. It is insoluble in water, ether, petroleum ether, and benzene, soluble in ethanol and methanol.

Anal. Calcd. for C₂₀H₁₉NO₅: C, 68.0; H, 5.7; N, 4.0. Found: C, 68.1; H, 5.7; N, 3.9.

(II) was identified by hydrogenation in methanol in the presence of palladium to yield 90% of 2-pyrrolidone-5-carboxylic acid, m. p. 162–164°

(1) Senior Research Fellow, National Cancer Institute.

(2) M. Bergmann, L. Zervas and L. Salzmann, *Ber.*, **66**, 1288 (1933).

(uncorrected), $[\alpha]^{25D} - 11.4$ (in water).³ A mixed melting point of the hydrogenated product with synthetic 2-pyrrolidone-5-carboxylic acid showed no depression.

Anal. Calcd. for C₆H₇NO₃: C, 46.5; H, 5.7; N, 10.9. Found: C, 46.8; H, 5.7; N, 10.9.

(3) M. Bergmann and L. Zervas, *Z. physiol. Chem.*, **221**, 51 (1933).

NATIONAL INSTITUTE OF HEALTH

BETHESDA, MARYLAND

RECEIVED MARCH 11, 1949

The Exchange between a Formamido Group and Formamide, Studied with C¹³

BY LIEBE F. CAVALIERI AND GEORGE BOSWORTH BROWN

Adenine (I) may be prepared by heating 4,6-diamino-5-formamidopyrimidine (II) in formamide.² In order to prepare adenine labeled with C¹³ in the 8-position, 4,5,6-triaminopyrimidine (III) as the sulfate was converted to II by formylation with C¹³ labeled formic acid. When the sulfate of II was heated in formamide, extensive exchange with the formamide occurred and only 25% of the carbon isotope contained in II was found in the adenine (I) which resulted. Formamide decomposes to ammonia and carbon monoxide when heated³ and it is probable that the mechanism for the exchange involves ammonolysis of the formyl group.⁴

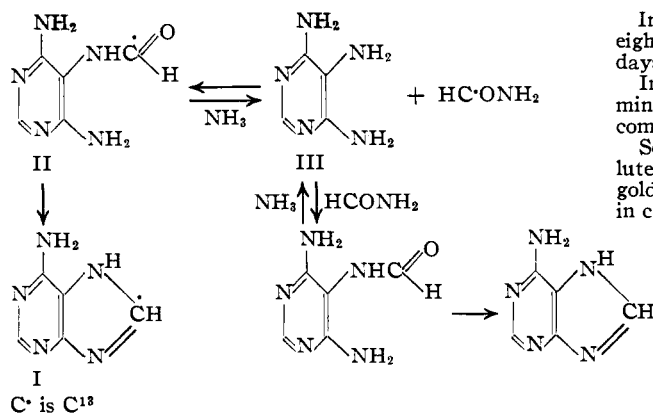
Evidence in support of this mechanism is found in the fact that the triamine (III) when heated with formamide is converted to adenine in 62% yield. Further, it appears that once the adenine is formed it remains intact, since a sample of adenine subjected to the reaction conditions was recovered in quantitative yield (95%).

(1) The authors wish to acknowledge the assistance of the Office of Naval Research and the National Cancer Institute of the United States Public Health Service.

(2) Cavalieri, Tinker and Bendich, *THIS JOURNAL*, **71**, 533 (1949).

(3) Freer and Sherman, *Am. Chem. J.*, **20**, 223 (1898).

(4) In general when pyrimidine sulfates are cyclized to purines in formamide one mole of ammonium sulfate is recovered; Bendich, Tinker and Brown, *THIS JOURNAL*, **70**, 3109 (1948).



Experimental

4,6-Diamino-5-formamidopyrimidine Sulfate² (II).—4,5,6-Triaminopyrimidine sulfate (III) (500 mg., 0.0022 mole) was warmed with 2 cc. of 25% aqueous formic acid, prepared by the hydrolysis of hydrogen cyanide.⁵ (22.2 atom per cent. excess C¹³) until all the solid had gone into solution. Upon cooling, 360 mg. (78%) of 4,6-diamino-5-formamidopyrimidine sulfate ((C₅H₇ON₅)₂·H₂SO₄·H₂O) separated. Isotope analysis showed 4.37 atom per cent. excess C¹³ (calcd. 4.44). The product was characterized by a comparison of its ultraviolet absorption spectrum with that of an authentic sample: $\epsilon_{\max} = 4600$, $\lambda = 259$ m μ ; another sample $\epsilon_{\max} = 4690$, $\lambda = 259$ m μ .

Adenine Sulfate² (I).—(a) Compound II (345 mg.) was heated with 3 cc. of freshly distilled formamide for two and one-half hours at 165° in a sealed tube. On cooling the adenine which separated was recrystallized from 2 N sulfuric acid and contained 1.06 atom per cent. excess C¹³, or about one-quarter of the expected value; yield, 280 mg., 70%.

Anal. Calcd. for C₅H₅N₅·H₂SO₄·1/2H₂O: N, 28.9, S, 13.2. Found: N, 28.7; S, 13.7.⁶

(b) Under the same conditions, 4,5,6-triaminopyrimidine sulfate resulted in a 62% yield of adenine sulfate.

(5) Krieble and McNally, *THIS JOURNAL*, **51**, 3368 (1929).

(6) Adenine is obtained as (C₅H₅N₅)₂·H₂SO₄·H₂O if crystallization is rapid.

SLOAN-KETTERING INSTITUTE
FOR CANCER RESEARCH
NEW YORK 21, N. Y.

RECEIVED FEBRUARY 14, 1949

The Solution of Gold by Selenic Acid

BY WILLIAM E. CALDWELL AND LOWELL P. EDDY

The solvent action of concentrated selenic acid at temperatures of 250° and over is known.¹ It has seemed to us worth while to ascertain the rapidity of this reaction at lower temperatures and in less concentrated solutions.

In the first experiments 50-mg. portions of flattened fine gold wire, 0.49 mm. in diameter, were sealed in three thick-walled Pyrex glass tubes with 0.5 ml. of 67, 87 and 98% selenic acid, respectively, and heated in the vapor of boiling chlorobenzene (130°). In the second experiments similar tubes were charged with 20 mg. of the gold in the same amount of the same acids and were heated in the vapor of boiling bromobenzene (154°).

In the most dilute acid at 130° no action was evident for thirteen days, and at 154° none for twenty-six days.

(1) Lenher, *THIS JOURNAL*, **24**, 354 (1902).

In the 87% acid at 130° some action was evident after eight hours and solution was complete after twenty-six days; at 154° solution was complete after thirteen days.

In the 98% acid at 130° dissolution began after ten minutes and was complete in three days; at 154° it was complete in thirteen hours.

Solutions of the gold in the concentrated acid when diluted with water yielded small golden-yellow crystals of gold selenate. These crystals were found to be insoluble in common organic solvents but in every case the crystals showed blackening, indicating oxidation of the organic material and reduction of the selenate.

Since both gold and selenium are used to color glass a pink or red, it was of interest to try use of powdered gold selenate for this purpose. A small quantity of glass was prepared by fusing two grams of sodium carbonate, one gram of calcium carbonate, four grams of silica, with a milligram of gold selenate. A lovely pink-violet glass resulted.

OREGON STATE COLLEGE
CORVALLIS, OREGON

RECEIVED FEBRUARY 5, 1949

Molecular Properties of Water-soluble Polysaccharides from Western Larch

BY GERD LYSTAD BORGIN¹

Previous studies of the molecular properties of the water-soluble polysaccharides from larch (exact species, age and part of tree, sapwood and heartwood, not given) by Mosimann and Svedberg³ using the sedimentation velocity ultracentrifuge technique indicate that the material consists of two components with molecular weights of 100,000 and 16,000.

Present studies were made on the extract from both the sapwood and the heartwood of a 30-year old butt log of Western larch. The water-soluble extract of the heartwood obtained at 30° was 8.4% of the wood and that of the sapwood was 0.9%. The pentosan content of the extracts was 13.7 and 11.9%, respectively.

The pentosan content of the single heartwood component, 13.7%, is within the range of the pentosan contents given by Peterson and collaborators⁴ for three different types of larch, 13.1 to 14.3%. The pentosan content of the combined α - and β -constituents of the sapwood, 11.9%, is almost identical to the value given by Wise and Peterson,⁵ 11.95%. Neither of these groups of investigators indicated what part of the wood was used. It is hence possible that Peterson and collaborators may have used heartwood and Wise and Peterson sapwood.

Sedimentation velocity runs showed the heart-

(1) Foreign collaborator, Oslo, Norway. The author wishes to thank Drs. Alfred J. Stamm and Geo. J. Ritter of the Forest Products Laboratory² for making available the facilities of their laboratory and for suggestions in the chemical phase of the work and Prof. J. W. Williams of the Chemistry Department of the University of Wisconsin for making available the University's ultracentrifuge, which was used in this research.

(2) Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

(3) Mosimann and Svedberg, *Kolloid Z.*, **100**, 1 (1942).

(4) Peterson, Barry, Unkauf and Wise, *THIS JOURNAL*, **62**, 2361 (1940).

(5) Wise and Peterson, *Ind. Eng. Chem.*, **22**, 362 (1930).