

diseases other than cancer are not known. The work will be continued along these lines, and attempts will be made to find differences by means other than optical rotation.

Acknowledgments.—The able technical assist-

ance of Miss Elouise Oliver is acknowledged. We appreciate also the coöperation of Drs. C. D. Howe and B. J. Trunnell of the Anderson Hospital in providing the blood samples.

HOUSTON, TEXAS

NOTES

8-Azaganine Analogs^{1,2}

BY CARL TABB BAHNER, DOROTHY ELLIS BILANCIO AND
EMMA MARGARET BROWN

RECEIVED SEPTEMBER 21, 1953

The effects of 8-azaganine³ as an inhibitor of the growth of microorganisms and certain tumors led to a request that we prepare similar compounds for studies which might throw light on the relation of structure to biological activity. As one of the simplest possible changes we undertook to replace the oxygen atom by a sulfur atom. Klingsberg and Papa⁴ have reported the use of a pyridine solution of P₂S₅ for replacing the oxygen atom in 3,5-diiodo-2-pyridone and other compounds which are soluble in pyridine. 8-Azaganine is practically insoluble in pyridine, but dissolves in a hot solution of P₂S₅ in pyridine. 5-Amino-7-mercapto-1-v-triazolo(d)pyrimidine and 5,7-dimercapto-1-v-triazolo(d)pyrimidine have been prepared from 8-azaganine by taking advantage of this fact.

5-Amino-7-mercapto-1-v-triazolo(d)pyrimidine.—Thirteen grams of 8-azaganine was added rapidly to a solution of 27 g. of P₂S₅ in 300 g. of pyridine. As refluxing was continued the clear, brown solution began to deposit crystals. After 6 hours the hot mixture was poured into 640 ml. of boiling water. Upon cooling and filtering 10 g. of buff colored solid was obtained. The crude solid which consisted partly of a phosphorus-containing compound was treated with boiling water. The crystals which deposited on cooling the water were dissolved in hot 0.05 N KSH. The precipitate which appeared upon acidification of the KSH solution with acetic acid and cooling was dried with care to avoid atmospheric oxidation and the methanol soluble fraction was recrystallized to give 2 g. of a final product which decomposed at 270°. In paper chromatography using a solvent consisting of 60 ml. of water, 3.6 ml. of acetic acid and 300 ml. of *n*-butanol, the *R_f* was 0.57; ultraviolet absorption: at pH 10 log *E*_{293, mμ} 4.132, log *E*₃₂₅ 3.950; at pH 6.51 log *E*₂₃₁ 4.097, log *E*₃₄₁ 3.925. *Anal.* Calcd. for C₄H₄N₆S: C, 28.51; H, 2.39; N, 49.97. Found: C, 28.39; H, 2.45; N, 49.81.

5,7-Dimercapto-1-v-triazolo(d)pyrimidine.—The crude solid obtained by a single treatment of 13.0 g. of 8-azaganine with P₂S₅ in pyridine was dissolved in hot 1:1 hydrochloric acid and thrown out of solution by neutralization with ammonia. Six and seven-tenths grams of the recrystallized material was added to a solution of 11.0 g. of P₂S₅ in pyridine. After refluxing the mixture for 6 hours it was poured into boiling water and the crystals which formed were recrystallized by dissolving in hot 1:1 HCl and neu-

tralizing with ammonia; yield 1 g. The *R_f* for this compound, using butanol-acetic acid-water solvent, was 0.76; ultraviolet absorption: at pH 6.51 log *E*₂₈₃ 4.153, log *E*₃₄₃ 4.002; at pH 10.0 log *E*₂₈₃ 4.076, log *E*₃₄₃ 3.801. *Anal.* Calcd. for C₄H₄N₆S₂: C, 25.95; H, 1.63; S, 34.60. Found: C, 26.20; H, 1.88; S, 34.58.

Data on the biological effects of these compounds are to be reported elsewhere.

We are indebted to Dr. R. O. Roblin and Dr. J. M. Rueggsegger of Lederle Laboratories for the 8-azaganine used in these experiments, to Oldbury Electro-Chemical Company for phosphorus pentasulfide, to Dr. Alfred Gellhorn of Columbia University Institute of Cancer Research for calling our attention to the need for substituted triazolo-pyrimidines in his study of the mechanism of action of 8-azaganine, to Dr. Howard Skipper and Dr. Lee Bennett and their associates of Southern Research Institute for determining the ultraviolet absorption spectra of these compounds and screening them against certain tumors, and to Dr. Harry W. Galbraith of Galbraith Analytical Laboratories for the carbon, hydrogen, nitrogen and sulfur analyses.

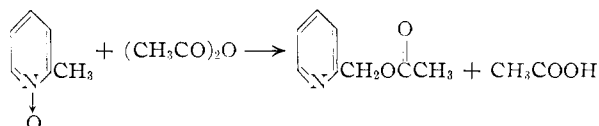
DEPARTMENT OF CHEMISTRY
CARSON-NEWMAN COLLEGE
JEFFERSON CITY, TENNESSEE

A New Synthesis of 1-(2-Pyridyl)-alkanols

BY O. H. BULLITT, JR., AND J. T. MAYNARD

RECEIVED DECEMBER 12, 1953

During an investigation of some of the reactions of pyridine N-oxides, a new rearrangement of alkyl-substituted pyridine oxides was encountered. The rearrangement is promoted by carboxylic acid anhydrides and results in the formation of an acylated 1-(2-pyridyl)-alkanol. For example, 2-methylpyridine oxide reacts with acetic anhydride to give 2-pyridylmethyl acetate



Proof of the proposed structure was provided by comparison of ultraviolet (Table I) and infrared spectra with those of known compounds, elementary analysis and preparation of the known picrate of the 2-pyridylmethanol obtained by saponification of the acetate.

(1) This research was supported in part by grants from the Damon Runyon Memorial Fund for Cancer Research and the National Institutes of Health, U. S. Public Health Service.

(2) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Auburn, Alabama, October 24, 1952.

(3) R. O. Roblin, Jr., J. O. Lampen, J. P. English, Q. P. Cole and J. R. Vaughn, Jr., *THIS JOURNAL*, **67**, 290 (1945).

(4) E. Klingsberg and D. Papa, *ibid.*, **73**, 4988 (1951).