is strongly alkaline, pH = 11, and are free fatty acid films when pH = 3. Half-conversion to neutral soap occurs at pH = 5.1 for calcium and pH = 6.6 for barium solutions. These metallic constituents of the films have a profound effect upon the physical properties. They increase the rigidity of the films and affect the ease with which multimolecular films can be formed on metal or glass.

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[Contribution from the Chemistry Department of the College of Liberal Arts and Sciences of Temple University]

The Synthesis of 2-Amino-4-ethylpyrimidine

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In our synthesis of 6-amino-4-ethylpyrimidine recently reported, one of the steps involved the reduction of 2,6-dichloro-4-ethylpyrimidine by the action of hydriodic acid. In an analogous reaction with 2,6-dichloro-4,5-dimethylpyrimidine, Schlenker¹ reported that the chlorine atom in position 2 was replaced by hydrogen while that in position 6 was exchanged for an hydroxyl group as a result of hydrolysis.

While we believed that this reaction proceeded analogously with 2,6-dichloro-4-ethylpyrimidine, we thought it of interest to prepare 2-amino-4ethylpyrimidine in order to compare it with the 6-amino compound and to settle more definitely that the reduction had formed 6-oxy-4-ethylpyrimidine.

Furthermore, since the assumption of the presence of 6-amino-4-ethylpyrimidine in vitamin B_1 was based in part upon the nature of absorption bands in related compounds² and is still open to question as a result of other work,³ the synthesis of the isomeric 2-amino-4-ethylpyrimidine may be of interest in connection with the structure of this vitamin.

The synthesis of 2-amino-4-ethylpyrimidine was carried out by two different methods; one starting with 2-ethylmercapto-4-ethyl-6-oxypyrimidine, and the other with 2-amino-4-ethyl-6 oxypyrimidine prepared according to the method described by Jaeger⁴ for 2-amino-4-methyl-6-oxypyrimidine.

The syntheses are summarized by the formulas.

Experimental Part

2 - Ethylmercapto - 4 - ethyl - 6 - chloropyrimidine.— This compound was prepared in the usual manner by the

(2) Williams, Buchman, Ruchle, THIS JOURNAL, 57, 1093 (1935).
(3) Windaus, Tschesche and Grewe, Z. physiol. Chem., 237, 100 (1935).

(4) Jaeger, Ann., 262, 365 (1891).



action of 77 cc. of phosphorus oxychloride upon 32 g. of 2-ethylmercapto-4-ethyl-6-oxypyrimidine; b. p. 110-112° at 4-5 mm.; yield 24.3 g.

Anal. Calcd. for $C_8H_{11}N_2ClS$: Cl, 17.49. Found: Cl, 17.39.

2 - Ethylmercapto - 4 - ethylpyrimidine.—2 - Ethylmercapto-4-ethyl-6-chloropyrimidine (24 g.) dissolved in 100 cc. of ethanol and 80 cc. of water was reduced by the action of 50 g. of 90% zinc dust; b. p. 105-107° at 4 mm.; yield 16.1 g.

Anal. Calcd. for $C_8H_{12}N_2S$: N, 16.66. Found: N, 16.03.

2-Oxy-4-ethylpyrimidine Hydrochloride.—2-Ethylmercapto-4-ethylpyrimidine (15.8 g.) was hydrolyzed by the action of 50 cc. of concentrated hydrochloric acid. After recrystallizing the product from alcohol it melted at 211– 213° with decomposition, having begun to sinter in the neighborhood of 200°; yield 9.9 g.

⁽¹⁾ Schlenker, Ber., 34, 2823-2825 (1901).

Anal. Calcd. for $C_{6}H_{8}N_{2}O$ ·HC1: Cl, 22.08. Found: Cl, 22.22.

2-Chloro-4-ethylpyrimidine.—The above salt (9.7 g.) was refluxed for one and one-half hours with 30 cc. of phosphorus oxychloride. After removing 15 cc. of phosphorus oxychloride under diminished pressure, the residue was poured upon ice, made alkaline with potassium hydroxide and extracted with ether. Three grams of brown organic solid, soluble in hydrochloric acid and practically insoluble in alkali, remained after extraction with ether. This solid was not investigated further, since the desired product was found in the ethereal extract. After removal of the ether, this substance distilled at 89–91° at 7 mm. pressure, coming over as a clear, pale-yellow liquid with an odor resembling that of acetamide; yield 3 g.

Anal. Calcd. for $C_6H_7N_2C1$: Cl, 24.87. Found: Cl, 24.53.

2-Amino-4-ethylpyrimidine.—The above 2-chloro compound (2.9 g.) was heated in 200 cc. of saturated alcoholic ammonia at 120-130° for four hours. After removal of the alcohol under diminished pressure, the residue was treated with an excess of 25% potassium hydroxide and extracted with ether in which the compound was only moderately soluble. The ether was removed and the residue recrystallized from alcohol. The product consisting of white crystals with a faint odor suggestive of pyridine melted to a clear liquid at 140-141°. The material sublimes readily to form long white needles and may be distilled at ordinary pressure without decomposition; b. p. 229° (Siwoloboff's method); yield 1.3 g.

Anal. Calcd. for $C_6H_9N_3$: C, 58.49; H, 7.37; N, 34.14. Found: C, 58.62, 58.58; H, 7.31, 7.15; N, 33.89, 34.16.

The base forms an orange-yellow aurichloride, m. p. 97-98°; a pale-yellow picrate, m. p. 194.5-195.5°.

Anal. of the aurichloride. Calcd. for $C_6H_9N_8$ ·HAuCl₄: Au, 42.55. 0.1068 g. of the air-dried aurichloride gave 0.0453 g. Au, or 42.41%. 0.1294 g. of the aurichloride dried forty-eight hours in a desiccator, gave 0.0551 g. Au, or 42.58%.

2 - Amino - 4 - ethyl - 6 - oxypyrimidine.—Propionylacetic ester (29.3 g.) and guanidine carbonate (37.5 g.) were refluxed in 225 cc. of ethanol on a steam-bath for eight hours. Water (40 cc.) was then added and the heating prolonged for another two hours. After removal of the solvent, the residue was recrystallized from water, forming white crystals melting at $243-245^{\circ}$ with decomposition; yield 20 g.

Anal. Calcd. for $C_{\varepsilon}H_{\varepsilon}N_{\varepsilon}O$: N, 30.21. Found: N, 30.17.

2-Amino-4-ethyl-6-chloropyrimidine.—This compound was prepared by the method of Gabriel and Colman⁵ by refluxing 13.3 g. of the above compound with 27 cc. of phosphorus oxychloride for half an hour and then warming on a steam-bath for an additional hour and a half. After removing only 3 or 4 cc. of phosphorus oxychloride under diminished pressure, the residue was poured upon crushed ice, made alkaline with ammonia and the precipitate filtered off and recrystallized from alcohol. The white needles melted at 129–130° to clear liquid; yield 5 g.

Anal. Calcd. for C₆H₈N₈Cl: Cl, 22.50. Found: Cl, 22.91.

2-Amino-4-ethylpyrimidine.—Four and four-tenth grams of the above compound, 50 cc. of ethanol, 40 cc. of water and 25 g. of 90% zinc dust were refluxed for ninety minutes. After filtering from unchanged zinc, the filtrate and washings were evaporated, the residue treated with excess of 25% potassium hydroxide and extracted with ether. The residue, after evaporation of this extract, was recrystallized from alcohol, forming white crystals, with the same faint odor of pyridine; m. p. 139–141°; yield 1.2 g. of purified product.

This base formed an orange-yellow aurichloride, m. p. 98–99°; a pale-yellow picrate, m. p. 194.5–195.5°.

Anal. 0.1035 g. of the aurichloride gave 0.0441 g. of Au, or 42.60%.

Mixed melting points: free bases, 139-141°; picrates, 194.5-195.5°; aurichlorides, 98-99°.

The base does not affect red litmus, but forms a hygroscopic hydrochloride that reddens blue litmus.

Summary

2-Amino-4-ethylpyrimidine has been synthesized by two independent methods, corroborating the structure of the isomeric 6-amino-4-ethylpyrimidine previously prepared.

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(5) Gabriel and Colman, Ber., 32, 2922-2923 (1899).