quantity of acetic anhydride, b. p. 139–140°, d^{20}_{20} 1.075, $n^{20}D$ 1.3918, accompanied the formation of acetic acid.

Pure acetyl sulfide was produced in almost quantitative yield by merely refluxing thioacetic acid with twice its weight of acetyl chloride, then distilling the product *in vacuo*. When distilled at atmospheric pressure the product boiled at 155–158° and underwent partial decomposition, in agreement with the observations of Davies. The structure of the product was indicated by its conversion to acetaldehyde when refluxed in ethanol with Raney nickel.

Experimental Part

Acetyl Sulfide.—Thioacetic acid[4] (105 g.) and freshly distilled acetyl chloride (216 g.) were mixed in a one-liter flask equipped with a Friedrichs condenser under a calcium chloride tube. The mixture began spontaneously to reflux, then was heated under reflux for four hours. The crude mixture was distilled *in vacuo* through a short column containing a glass spiral. The main fraction, b.p. 63–64° (20 mm.), weighed 147 g. (90%). The product was redistilled without the column, b. p. 62–63° (20 mm.), and a middle cut taken for analysis, d^{20}_{20} 1.124, $n^{21}D$ 1.4810.

Anal. Calcd. for $C_4H_6O_2S$: C, 40.65; H, 5.12; S, 27.10. Found: C, 40.83, 40.68; H, 5.23, 5.08; S, 26.75.

Desulfurization.—Acetyl sulfide (1.12 g.) was refluxed for four hours in ethanol (*ca.* 50 ml.) with Raney nickel (*ca.* 10 g.), using a water trap beyond the condenser to catch as much acetaldehyde as possible. About half the mixture was then distilled, keeping the condenser tip below the surface of distillate to minimize the loss of acetaldehyde. The distillate was heated with excess 2,4-dinitrophenylhydrazine in dilute sulfuric acid, and the crude acetaldehyde 2,4-dinitrophenylhydrazone collected; yield 1.40 g. (33%), m. p. 135°. After two recrystallizations from ethanol the product had m. p. 165°.

(4) Clarke and Hartman, THIS JOURNAL, **46**, 1731 (1924).

STANFORD UNIVERSITY
STANFORD, CALIF.

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Chloroaminopyrimidines

BY SCOTT J. CHILDRESS AND R. L. MCKEE

A mixture of phosphorus pentachloride and phosphorus oxychloride has been observed to convert barbituric acid into tetrachloropyrimidine. This substance was found to react with ammonia more readily than 2,4,6-trichloropyrimidine, and only two products, a diamino-dichloro- and an impure triamino-monochloropyrimidine were isolated from the reaction. Assuming non-reactivity of the 5-chlorine atom, the former must be 2,4-diamino-5,6-dichloropyrimidine (I) or 4,6-diamino-2,5-dichloropyrimidine (II), and the latter must be 2,4,6-triamino-5-chloropyrimidine. Compound I was prepared by chlorination of 2,4-diamino-6-chloropyrimidine and was found to differ from the product obtained from the above reaction, which must thus be II. In addition, the hydrolysis product of II, a hydroxydiaminochloropyrimidine was shown to differ from 6-hydroxy-2,4-diamino-5-chloropyrimidine, the product to be expected from the hydrolysis of I.

To validate the assumption of the non-reactivity of the 5-chlorine atom, a portion of the 2,4,6-triamino-5-chloropyrimidine was hydrogenated to the known 2,4,6-triaminopyrimidine. It is of interest that the conditions capable of dechlorinating various chloropyridines[1] were ineffective in this reduction.

Experimental

Tetrachloropyrimidine.—Barbituric acid (12.8 g., 0.1 mole) was mixed with 100 g. of phosphorus pentachloride and 50 g. of phosphorus oxychloride, allowed to reflux overnight, and poured onto crushed ice. The product was steam distilled, dried *in vacuo* and sublimed under 2 mm. pressure. The compound so obtained in 37% yield, alone and when mixed with an authentic[2] sample of tetrachloropyrimidine, melted at 66–68°.

Anal. Calcd. for $C_4Cl_4N_2$: N, 12.8. Found: N, 12.7.

2,4,6-Triamino-5-chloropyrimidine.—One gram of tetrachloropyrimidine was heated in a bomb to 100° for twelve hours with 17 ml. of concd. ammonium hydroxide. The resulting light yellow needles were recrystallized from water to give 0.5 g. of long white needles melting at 199–201°. Additional recrystallization from water raised the melting point to 201–203°.

Anal. Calcd. for $C_4H_6ClN_5$: N, 43.9; Cl, 22.2. Found: N, 43.9; Cl, 21.3, 21.2.

The picrate decomposed above 300°, but on rapid heating melted at 315° with decomposition.

Anal. Calcd. for $C_{10}H_8ClN_8O_7$: N, 28.8. Found: N, 28.6.

4,6-Diamino-2,5-dichloropyrimidine (II).—One gram of tetrachloropyrimidine was heated at 80° for two hours with 15 cc. of concd. ammonium hydroxide. The product of this reaction was filtered and the filtrate discarded. The solid material was treated with 10 cc. of alcohol and filtered hot, the residue from this treatment consisting largely of the desired diamine. The filtrate was evaporated to dryness and the heating with ammonia and leaching with alcohol repeated. The residues thus obtained when combined with those from four identical reactions weighed 0.5 g. and melted at about 300°. After repeated recrystallization from alcohol, 0.13 g. of a white powder melting at 302–304° was obtained.

Anal. Calcd. for $C_4H_4Cl_2N_4$: N, 31.3. Found: N, 31.3.

2-Hydroxy-4,6-diamino-5-chloropyrimidine.—The above 4,6-diamino-2,5-dichloropyrimidine (125 mg.) was boiled for thirty minutes with 5 ml. of 1:1 hydrochloric acid. The product was precipitated with dilute ammonia, filtered and washed. The white powder so obtained weighed 100 mg. and failed to melt below 360°. For analysis, a portion of this material was redissolved in dilute hydrochloric acid, treated with Norite, precipitated while hot with ammonia, thoroughly washed with hot water, and dried *in vacuo* at 100°.

Anal. Calcd. for $C_4H_5ClN_4O$: N, 34.9; Cl, 22.1. Found: N, 34.9; Cl, 22.2.

The picrate decomposed when heated slowly above 300° but melted with decomposition at 325° with rapid heating.

Anal. Calcd. for $C_{10}H_8ClN_7O_8$: N, 25.2. Found: N, 24.9.

6-Hydroxy-2,4-diamino-5-chloropyrimidine.—Chlorine was passed through an aqueous solution of 0.9 g. of 6-hydroxy-2,4-diaminopyrimidine at 60° for five minutes. The solution was neutralized with ammonia, chilled and filtered. The product was recrystallized from water to

(1) Crouch and Lochte, THIS JOURNAL, **65**, 270 (1943); Pickard and Lochte, *ibid.*, **69**, 14 (1947).

(2) Ciamician and Magnaghi, *Ber.*, **18**, 3444 (1885).

yield 0.7 g. of white needles which underwent decomposition at 305°. Prior to analysis, the material was dried *in vacuo* at 100°, during which process the needles collapsed to a white powder.

Anal. Calcd. for $C_4H_5ClON_4$: N, 34.9; Cl, 22.1. Found: N, 34.6; Cl, 21.9.

The **picrate** decomposed slowly above 250°.

Anal. Calcd. for $C_{10}H_8ClN_7O_8$: N, 25.2. Found: N, 24.9.

2,4-Diamino-5,6-dichloropyrimidine (I).—2,4-Diamino-6-chloropyrimidine (1.5 g.) was dissolved in 25 ml. of dilute hydrochloric acid and treated with a rapid stream of chlorine for seven minutes (prolonged chlorination resulted in the complete loss of product). The solution was neutralized and filtered leaving 0.5 g. of material melting at 218–219°. After recrystallization once from alcohol and once from water, 0.2 g. of material melting at 218–220° was obtained.

Anal. Calcd. for $C_4H_4Cl_2N_4$: N, 31.3; Cl, 39.6. Found: N, 31.3; Cl, 39.6.

2-Amino-4,5,6-trichloropyrimidine.—Six grams of 2-amino-4,6-dihydroxypyrimidine was refluxed overnight with 45 g. of phosphorus pentachloride and 25 g. of phosphorus oxychloride. After pouring onto crushed ice, a solid formed which was removed and suspended in 50 cc. of water. It was then observed to liquefy and to resolidify. After filtration and sublimation, 1.5 g. of material melting at 234° was obtained.[3] Four recrystallizations from benzene yielded a product of constant melting point, 236–237°.

Anal. Calcd. for $C_4H_2Cl_3N_3$: N, 21.2; Cl, 53.6. Found: N, 21.2; Cl, 53.5.

Neutralization of the original acidic filtrate from this reaction resulted in the separation of 2-amino-4,6-dichloropyrimidine, which after sublimation weighed 1.0 g. and melted at 220°.[4]

Dechlorination of 2,4,6-Triamino-5-chloropyrimidine.—One hundred and ten milligrams of 2,4,6-triamino-5-chloropyrimidine in 20 ml. of methanol containing excess sodium acetate was treated with hydrogen at 75° and 850 p. s. i. in the presence of palladium–charcoal catalyst containing a trace of Adams catalyst.[1] The solution was filtered, made distinctly basic with sodium carbonate, evaporated to dryness, and the residue extracted with 20 ml. of absolute ethanol. The residue from evaporation of the latter was sublimed *in vacuo* to give 30 mg. of triaminopyrimidine melting at 246° (dec.), alone and when intimately mixed with an authentic sample.[5]

(3) This product had a nitrogen content of 21.7% and was probably contaminated with 2-amino-4,6-dichloropyrimidine.

(4) Büttner, *Ber.*, **36**, 2227 (1903).

(5) Traube, *ibid.*, **37**, 4544 (1904).

THE VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

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A New Method for Ascertaining the Coördination Number in Choleic Acids

BY GIUSEPPE CILENTO

It is well known that desoxycholic acid forms molecular compounds, the so-called choleic acids, with a wide variety of organic derivatives. The method used for ascertaining the molar ratio of these compounds depends upon the nature of the acholic component.[1] A new method which may prove to be useful in many cases is reported in this paper. It consists in determining the ultraviolet or visible light absorption of alcoholic solutions of the choleic acid and of the pure acholic component. Provided both solutions have the same spectrum, from their concentrations and extinctions at a definite wave length, the percentage of the acholic component in the choleic acid—and thus the coördination number—can readily be ascertained.

Desoxycholic acid itself does not interfere with the method. Preliminary investigations have shown that it absorbs to some extent ultraviolet light of only very short wave length indicating that, working with a diluted (about 200 mg. per liter) solution of choleic acid, its absorption would be completely negligible above 230 mμ, when using a 1-cm. cell.

It is interesting to note that all investigations hitherto reported on the stability of choleic acids in alcoholic solutions indicate that the complex is practically or completely dissociated.[2–5] Actually one may expect that, independently of the extent of its dissociation, a solution of a choleic acid should show the same spectrum of the acholic component.

We decided to assay the method with the well-investigated choleic acid of naphthalene[6–9] and phenanthrene,[4,9,10] which can easily be prepared without being contaminated by the solvent (ethanol) choleic acid.

It has been found that naphthalene choleic acid shows the same ultraviolet spectrum as the pure hydrocarbon. Therefore we carried out the usual calculations and deduced, in agreement with earlier investigations[6–8] that naphthalene combines with two molecules of desoxycholic acid.

Phenanthrene choleic acid showed practically the same spectrum as the pure hydrocarbon below 300 mμ. However, above 320 mμ discrepancies were observed. The reason for those discrepancies is rather doubtful, though they may have been produced by some impurity. In spite of this fact, when the percentage of phenanthrene was com-

TABLE I

ABSORPTION DATA FOR DESOXYCHOLIC ACID IN ETHANOL
(c 14 g./liter; d 1.002 cm.)

λ, mμ	$\log_{10}(I_0/I)$	λ, mμ	$\log_{10}(I_0/I)$
230	0.116	270	0.013
240	.065	280	.011
250	.037	290	.008
260	.017		

(1) Harry Sobotka, "The Chemistry of the Sterids," The Williams and Wilkins Company, Baltimore, Md., 1938, pp. 118–120.

(2) H. Sobotka and J. Kahn, *Biochem. J.*, **26**, 898 (1932).

(3) H. Sobotka and J. Kahn, *Ber.*, **65**, 227 (1932).

(4) W. Marx and H. Sobotka, *J. Org. Chem.*, **1**, 275 (1937).

(5) E. Lorenz (quoted by L. F. Fieser and M. S. Newman), THIS JOURNAL, **57**, 1602 (1937).

(6) H. Wieland and H. Sorge, *Z. physiol. Chem.*, **97**, 24 (1916).

(7) E. Flume, Dissertation, Bonn, 1929, p. 26.

(8) P. Braun, Dissertation, Bonn, 1931, p. 34.

(9) P. Senise, *Bol. faculdade filosofia ciênc. letras. São Paulo Univ. XIV, Quimica No.* **1**, 35 (1942).

(10) L. F. Fieser and M. S. Newman, THIS JOURNAL, **57**, 1602 (1937).