

Here,  $V_1Y + V_2X$  is the total amount of material added to tube number 0 and  $K = Y/X$ . Combining and rearranging we find that

$$p = KZ/(1 + KZ)$$

The probability,  $q$ , that the molecule will fail to advance to the next tube at the time of transfer is

$$q = 1 - p = 1/(1 + KZ)$$

The probability,  $P_{n,r}$ , that in  $n$  transfers the molecule under consideration will reach tube  $r$  is equal to the product of the probability of  $r$  successful transfers,  $n - r$  failures and the number of ways in which  $r$  successes and  $n - r$  failures can be combined.

$$P_{n,r} = \frac{n!}{r!(n-r)!} p^r q^{n-r}$$

If  $r$  and  $n - r$  are greater than five and if  $p$  is between 0.1 and 0.9, it is possible to express  $P_{n,r}$  with LaPlace's binomial approximation

$$P_{n,r} = \frac{1}{\sigma \sqrt{2\pi}} e^{-(r-r_m)^2/2\sigma^2}$$

where

$$r_m = np = \frac{nKZ}{1 + KZ}$$

and

$$\sigma = \sqrt{npq} = \sqrt{\frac{nKZ}{(1 + KZ)^2}}$$

By definition,  $r_m$  is the number of the tube in which the given molecule has the maximum probability of occurrence, and  $\sigma$  is the usual standard deviation of the distribution curve.

The general concentration distribution equation for a system containing  $g_0$  grams of solute then becomes

$$g_{n,r} = \frac{g_0}{\sqrt{2\pi} \frac{nKZ}{(1 + KZ)^2}} e^{-(r-r_m)^2/2(nKZ/(1 + KZ))^2}$$

For the special case where the volumes of the two phases are equal this general equation reduces to the final expression given by Williamson and Craig.

Illustrations of the precision of this equation under various values of  $p$ ,  $n$  and  $r$  are given by Fry.<sup>3</sup>

The properties of the distribution curve now can be employed to obtain information about the purity, homogeneity, identity and optimum separation conditions of the solutes under examination.

To find the conditions for optimum separation of multicomponent mixtures we plot  $\log KZ$  against  $r_m/n$ . From this plot it is apparent that optimum separation will occur if the  $\log KZ$  values for the components are symmetrically distributed about zero.

The position of the maximum,  $r_m = np$ , of an experimental concentration curve may be an

aid in establishing the identity of a component, by yielding the distribution coefficient

$$K = r_m/(n - r_m)Z$$

In addition, the geometry of the curve yields the standard deviation. The relation between  $\sigma$  and  $K$  is

$$K = \frac{\frac{n}{\sigma^2} - 2 \pm \sqrt{\frac{n^2}{\sigma^4} - 4 \frac{n}{\sigma^2}}}{2Z}$$

A test of homogeneity of sample can be made by normalizing the concentration curve and fitting it to a normal distribution curve, similar to the manner in which diffusion curves are treated.<sup>4</sup>

(4) Bevilacqua, Bevilacqua, Bender and Williams, *Ann. N. Y. Acad. Sci.*, **46**, 309 (1945).

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

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### A Convenient Synthesis of Acetyl Sulfide

BY WILLIAM A. BONNER

The literature records<sup>1</sup> conflicting claims in the preparation of acetyl sulfide. Several authors, using various methods of preparation, obtained a product boiling around 119°. On the other hand, by action of phosphorus pentasulfide on acetic anhydride, or of acetyl chloride on lead thioacetate, Davies obtained<sup>2</sup> mixtures which he fractionated into thioacetic acid, acetic acid and a liquid, b. p. around 157°. The latter gave an analysis close to that calculated for acetyl sulfide. Davies suggested that the samples previously reported to boil around 119° were largely acetic acid, but offered no proof of this point. A recent need for acetyl sulfide has prompted us to develop a new and convenient synthesis for this substance, to substantiate its structure by reductive desulfurization, and to demonstrate conclusively the correctness of Davies' claim that acetic acid had been obtained by previous workers.

An attempt was made to duplicate the preparation of Jacquemin and Vosselmann<sup>3</sup> using acetyl chloride and potassium sulfide. Regardless of the mode of mixing, moderate yields of a liquid, b. p. 118° on careful fractionation through a  $3/4 \times 24$  inch helix-packed column, were obtained, accompanied by extensive decomposition and tar formation. These findings accord with those of Jacquemin and Vosselmann. The main product was shown to be acetic acid by its boiling point,  $d_{20}^{20}$  1.041,  $n_{20}^{20}$  1.3728, its water solubility, and the fact that it produced benzylthiuronium acetate in the same yield as did pure acetic acid on reaction with benzylthiuronium chloride. When the reaction was conducted by adding potassium sulfide to refluxing acetyl chloride, a substantial

(1) Beilstein, "Handbuch der organischen Chemie," Vol. 2, p. 232 (101).

(2) Davies, *Ber.*, **24**, 3551 (1891).

(3) Jacquemin and Vosselmann, *Compt. rend.*, **49**, 372 (1859).

(3) Fry, "Probability and its Engineering Uses," D. Van Nostrand Company, Inc., New York, N. Y., 1928, p. 213.

quantity of acetic anhydride, b. p. 139–140°,  $d_{20}^{20}$  1.075,  $n_D^{20}$  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<sup>4</sup> (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,  $n_D^{20}$  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-chloropyrimi-

dine, 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 chloropyrimidines<sup>1</sup> 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<sup>2</sup> 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  $C_4H_6ClN_3$ : 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  $C_{10}H_9ClN_3O_7$ : 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).