### Tertiary Bases.

**Quinoline.**—A quantity of amorphous precipitate.

**Pyridine**—A red-black precipitate.

**Picoline.**—A chocolate-colored precipitate.

**Triethylamine.**—Transparent prismatic needles.

**Triisobutylamine.**—Cubes and spindle-shaped crystals.

**Triisoamylamine.**—Minute needles.

**Diethylaniline.**—A small amount of dirty brown precipitate.

**Tribenzylamine.**—Cubic masses and boat-shaped prisms.

Some of these compounds will be further investigated.

### Summary.

1. Diphenylureachloride reacts sluggishly with most bases; such reactions are promoted by sunlight or by heat.

2. Additive products are first formed; these yield by action of heat, water, etc., the $Ph_2NCO$-substituted products of the base.

3. Evidences for the nonionic nature of these reactions are given.

SEATTLE, WASHINGTON.

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[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

# THE COMPARATIVE BEHAVIOR OF THIOUREA AND UREA TOWARDS ACETIC ANHYDRIDE.

BY EDWARD F. KOHMANN.

Received July 5, 1915.

During the course of work in this laboratory, Professor Treat B. Johnson asked the author to determine whether there would be any formation of hydantoin if thiourea were used instead of ammonium thiocyanate in the reaction described by Johnson and Nicolet[1] for the preparation of 2-thio-3-benzoyl hydantoin.[2] Exactly the same conditions were employed, as well as the same reagents in the same proportions, as described for the preparation of the hydantoin, with the exception that the ammonium thiocyanate was replaced by an equivalent quantity of thiourea. Although no trace of a thiohydantoin was detected, a small amount of a substance was obtained which could be crystallized from water or alcohol in the form of colorless slender prisms. As this substance had a melting point of 165° it was concluded that it must be acetyl thiourea. In order to definitely establish this point it was decided to prepare acetyl thiourea for comparison and the method of Nenki[3] with slight modifications, was adopted.

Nenki assigned to this derivative a melting point of 11.5° which he

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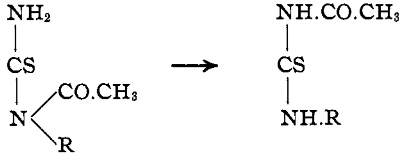
[1] THIS JOURNAL, **33**, 1973 (1911); *Am. Chem. J.*, **49**, 202 (1913).

[2] A discussion of this reaction and its application with anhydrides other than acetic will follow in a future paper by Bernard H. Bailey.

[3] *Ber.*, **6**, 599 (1873).

later[1] corrected to 165°. He stated that when thiourea was gently warmed with acetic anhydride it readily went into solution. On cooling, the solution solidified to a yellow crystalline mass which, after repeated crystallizations from water, finally yielded colorless prisms of acetyl thiourea.

Werner[2] found that when symmetrical diaryl thioureas were heated with acetic anhydride they yielded acetanilides and the corresponding mustard oils, whereas symmetrical dialkyl thioureas yielded the corresponding monoacetyl derivatives. Hagershoff[3] later made the observation that if the reaction mixture was heated to only 80° the expected monoacetyl derivative was obtained in all cases. From the monosubstituted thioureas, Hagershoff obtained in each case a labile and a stable monoacetyl modification. When the former was heated slightly above its melting point it soon solidified and rearranged into the latter modification. Wheeler[4] has shown that a molecular rearrangement of the following type takes place in this change:



It is interesting to note that in no case has a diacetyl derivative been obtained. Diacetyl urea has been prepared by several methods but not by the direct interaction of urea with acetic anhydride, whereas diacetyl thiourea is not known. Symmetrical dibenzoyl urea is also well known, whereas dibenzoyl thiourea has not been synthesized. It has now been found that thiourea forms a diacetyl derivative when heated with acetic anhydride although urea, under the same conditions, forms only the monoacetyl derivative. Curiously enough, diacetyl thiourea has a bright lemon-yellow color whereas monoacetyl thiourea is colorless.

In an attempt to prepare acetyl thiourea, pure reagents were used. Nevertheless, as was observed by Nenki, a yellow product resulted. This color was not changed by one crystallization from either water, alcohol or glacial acetic acid. As it seemed unreasonable that this color should be due to anything but the presence of a definite compound and as the product had a melting point of 150–155° instead of 165°, an analysis was made and the nitrogen content found to be 19.5%. This was evidence that the product was a mixture of mono- and diacetyl thioureas. As will be seen in the experimental part of this paper such a conclusion was correct and by crystallizing from acetic anhydride diacetyl thiourea

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[1] *Ber.*, **6**, 905 (1873).

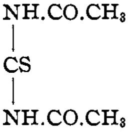
[2] *J. Chem. Soc.*, **59**, 396 (1891).

[3] *Ber.*, **32**, 3649 (1899).

[4] *Am. Chem. J.*, **27**, 270 (1902).

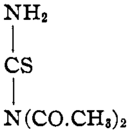
could be obtained. Under these conditions urea yielded only a monoacetyl derivative.

Diacetyl thiourea may be represented by any one of the following structural formulae, or even by the corresponding pseudo forms of (I) and (II):



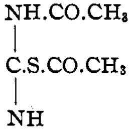
$$\begin{array}{l} NH.CO.CH_3 \\ | \\ CS \\ | \\ NH.CO.CH_3 \end{array}$$

(I).



$$\begin{array}{l} NH_2 \\ | \\ CS \\ | \\ N(CO.CH_3)_2 \end{array}$$

(II).



$$\begin{array}{l} NH.CO.CH_3 \\ | \\ C.S.CO.CH_3 \\ | \\ NH \end{array}$$

(III).

From analogy, according to Wheeler, (II), and according to Dixon and Hawthorn,[1] (III) should undergo molecular rearrangement, on being heated to their melting points, to yield (I). Diacetyl thiourea, however, when heated to the melting point, is apparently unchanged. If heated for some time at a somewhat higher temperature it assumes a darker color and undergoes a slow decomposition with the evolution of gas bubbles. On cooling, the viscous liquid is rather slow to solidify. Richter[2] states that monoacetyl thiourea may be obtained from thiourea and acetic anhydride or from cyanamide and thioacetic acid. The latter synthesis he states, argues in favor of a pseudo structure. But it is conceivable that a molecular rearrangement might easily take place under the conditions of this reaction and the normal derivative result. Hence Formula I seems the most reasonable to assign to diacetyl thiourea.

## Experimental Part.

**Preliminary Experiment.**—One and eight-tenths grams of thiourea were dissolved in 5 cc. of acetic anhydride by heating to boiling. The solution was yellow and the reaction was probably complete within a short time, but the heating was continued for one hour at 100° in a water bath. On cooling, yellow prisms separated. These crystallized from water, alcohol, or glacial acetic acid and melted at about 150–155°. The portion crystallized from glacial acetic acid was dried at 100° for analysis.

Calc. for $C_3H_6ON_2S$: N, 23.7; for $C_5H_8O_2N_2S$: N, 17.5. Found: 19.5.

**Monoacetyl Thiourea.**—One-half gram of the above product was dissolved in 10 cc. of boiling water and the solution heated for one hour at 100° in a water bath. On cooling, colorless prisms separated which melted at 165° to a clear colorless liquid.

Calc. for $C_3H_6ON_2S$: N, 23.7. Found: 23.5.

**Diacetyl Thiourea.**—One-half gram of the yellow product described above was dissolved in about 5 cc. of hot acetic anhydride and heated at 100° in a water bath for one hour. On cooling, clusters of transparent

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[1] *J. Chem. Soc.*, 91, 122 (1907).

[2] *Organische Chemie*, 1, 501 (1909).

pale yellow blade-like prisms separated which melted at 151–152° to a transparent yellow oil. These were dried in a current of air until free from the odor of acetic anhydride. They could then be heated to 110° without any loss of weight but meanwhile assumed a bright lemon yellow color. Nitrogen determination:

Calc. for $C_6H_8O_2N_2S$: N, 17.5. Found: 17.4. The analysis of a later preparation gave 17.6% and 17.5%.

If diacetyl thiourea is crystallized from a concentrated solution in acetic anhydride it separates in the form of a bright lemon-yellow product. If allowed to crystallize slowly from a dilute solution larger crystals are obtained which are pale yellow and transparent. On heating to 100° they assume a bright lemon-yellow color, losing nothing in weight and retaining their original form.

**Monoacetyl Urea.**—One gram of urea was dissolved in 10 cc. of acetic anhydride by boiling and the heating continued for one hour at 100°. On cooling, clusters of colorless prisms separated, melting at 212°. These were dried at 110° with no loss in weight.

Calc. for $C_3H_6O_2N_2$: N, 27.4. Found: 27.3.

URBANA, ILL.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

# RESEARCHES ON HYDANTOINS. XXXIII. THE CONDENSATION OF CINNAMIC ALDEHYDE WITH HYDANTOINS.[1]

BY TREAT B. JOHNSON AND RICHARD WRENSHALL.

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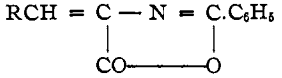
Erlenmeyer's method of synthesizing $\alpha$-amino acids, the first step of which involves the condensation of hippuric acid with an aldehyde giving an azlactone (I), has found a wide application for the preparation of amino



$$\begin{array}{l} RCH = \underset{|}{C} - N = \underset{|}{C}.C_6H_5 \\ \quad\quad\quad CO\text{———}O \end{array}$$

(I).

acids containing aromatic groups. The majority of the aromatic aldehydes which have been studied, have been shown to condense smoothly with hippuric acid giving good yields of the corresponding azlactones. Attempts to synthesize aliphatic $\alpha$-amino acids by application of Erlenmeyer's method with aliphatic aldehydes have been attended with very little success. Erlenmeyer and Kunlin[2] were the first to apply the method with an aliphatic aldehyde with the object of developing a new synthesis of leucine (V). They condensed isobutylaldehyde with hippuric acid

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[1] Part of a dissertation presented by Mr. Richard Wrenshall to the Faculty of the Graduate School of Yale University, 1915, in candidacy for the Degree of Doctor of Philosophy.

[2] *Ann.*, 316, 145 (1901).