

hol as before we observed, however, a remarkable difference in behavior. The compound dissolved without difficulty in boiling absolute alcohol, but, on cooling, needles did not deposit as previously observed. Instead, the pyrimidine separated in characteristic blocks of rhombohedral habit. If recrystallized from 95% alcohol a mixture of needles and blocks was obtained in which the blocks predominated. In fact it was almost impossible to obtain needles alone by crystallization from alcohol. The pyrimidine base was synthesized a second time in November, 1914, and purified according to our original method. The base behaved exactly as the original preparation. We could obtain at will, by crystallization from 95% alcohol, the needle and prism modifications. Although the pyrimidine was purified by crystallization from absolute and 95% alcohol it still contained one molecule of water of crystallization. So firmly was this bound in the molecule that it could not be expelled by heating at  $100^{\circ}$ . At  $120^{\circ}$  it was removed with difficulty. At the same time the pyrimidine apparently underwent a partial hydrolysis, which accounts for the low analytical values obtained for nitrogen.

Water determination:

Calc. for  $C_{10}H_9ON_3 \cdot H_2O$ ,  $H_2O = 8.7$ ; found,  $H_2O = 8.31$ .

Nitrogen determinations in the anhydrous base:

Calc. for  $C_{10}H_9ON_3$ ,  $N = 22.4$ ; found,  $N = 22.1, 21.91$  and  $21.95$ .

**Hydrochloride**,  $C_{10}H_9ON_3 \cdot HCl \cdot H_2O$ .—This salt is easily obtained by dissolving the pyrimidine base in dilute hydrochloric acid and then allowing the solution to crystallize. It separated in the form of long, colorless needles which melted at  $274^{\circ}$  with decomposition. The salt was dried for analysis over concentrated sulfuric acid.

Calc. for  $C_{10}H_9ON_3 \cdot HCl \cdot H_2O$ ,  $N = 17.44$ ; found,  $N = 17.58$  and  $17.49$ .

The nitrate of 4-phenylcytosine is characterized by its property of crystallizing from water in two distinct forms. When it deposits from a hot, saturated aqueous solution it first separates in the form of needles. This form, however, is not permanent and as the solution cools the needles disappear and are replaced by characteristic prismatic crystals. The salt decomposes when heated above  $245^{\circ}$ .

NEW HAVEN, CONN.

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

## RESEARCHES ON HYDANTOINS. XXX. STEREOISOMERIC MODIFICATIONS OF BENZALHYDANTOIN.

BY TREAT B. JOHNSON AND JOSEPH S. BATES.

Received December 16, 1914.

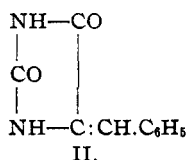
Benzalhydantoin (II) was first prepared by Ruhemann and Cunningham<sup>1</sup> by heating ethyl phenylpropiolate with urea in alcohol solution and in the

<sup>1</sup> *J. Chem. Soc.*, **75**, 958 (1899).

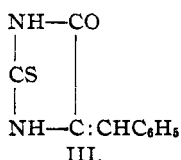
presence of sodium ethylate. They supposed the product of this reaction to be the ureide (I) and it was not until Ruhemann and Stapleton<sup>1</sup> later reinvestigated the reaction that it was shown that this conclusion was incorrect, and that the compound formed is really the hydantoin represented by Formula II. Thiourea and guanidine condense in an analogous manner, giving the corresponding cycles represented by Formulas III and IV, respectively.



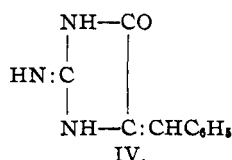
I.



II.



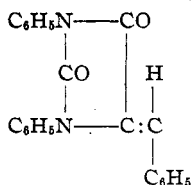
III.



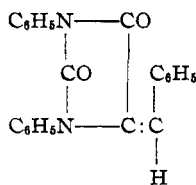
IV.

No attention was paid further to this hydantoin (II) until 1911 when Wheeler and Hoffmann<sup>2</sup> found that the same compound is obtained smoothly by condensing hydantoin with benzaldehyde. They assigned to the compound the same melting point as observed by Ruhemann and his co-workers, namely, 220°. Since this work of Wheeler and Hoffmann the hydantoin has been prepared a great many times by their method and in large quantities, but in no case has it hitherto been observed to melt otherwise than at the temperature mentioned.

Recently, Mr. Hadley, of this laboratory, has made the interesting observation that the aldehyde-condensation products of disubstituted hydantoins are capable of existing in isomeric modifications. For example, benzaldiphenylhydantoin (V and VI) occurs in two modifications<sup>3</sup> which melt at 152° and 192°, respectively. One form, however, the higher melting, represented the chief product of the reaction. With this result



V.



VI.

in hand it immediately became of interest to examine more carefully the products of the reaction when hydantoin undergoes condensation with benzaldehyde. This has now been done and we have made the interesting observation that Ruhemann and Stapleton's *benzalhydantoin* (II) likewise occurs in two isomeric modifications. Both isomers are formed by con-

<sup>1</sup> *J. Chem. Soc.*, 77, 246 (1900).

<sup>2</sup> *Am. Chem. J.*, 45, 368 (1911).

<sup>3</sup> Johnson and Hadley, *THIS JOURNAL*, 37, 171 (1914).

densing hydantoin with benzaldehyde. Ruhemann and Stapleton's<sup>1</sup> hydantoin melting at 220° is the chief product of the reaction as generally observed in our previous experiments.

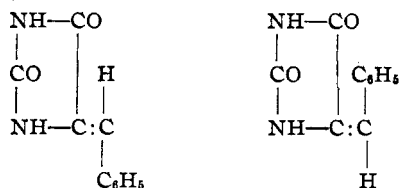
The isomeric modification (*trans*-benzalhydantoin) was identified in the alcoholic filtrates left after purification of the hydantoin melting at 220° (*cis*-benzalhydantoin). It deposited after concentration of these liquors, and was purified by a fractional crystallization from 95% alcohol. It separated from this solvent in burrs or aggregates of distorted prisms which melted at 246° to a clear oil. This modification is less soluble in alcohol than the isomer melting at 220°.

Calc. for  $C_{10}H_8O_2N_2$ ,  $N = 14.89$ ; found,  $N = 14.78$ .

The yield of this hydantoin melting at 246° is extremely small, being less than 1% of the theoretical. An attempt to prepare this modification by heating the isomer melting at 220° was unsuccessful. The latter was recovered unaltered after heating to the melting point of the higher modification (246°). In the case investigated by Johnson and Hadley<sup>1</sup> the higher melting modification of benzaldiphenylhydantoin (*trans*-form) was the chief product of the reaction. It is, therefore, a very interesting fact that benzaldehyde condenses with hydantoin in an anomalous manner, forming chiefly the lower melting modification of the hydantoin (*cis*-form melting at 220°).

### Summary.

Benzalhydantoin (II) occurs in two modifications melting at 220° and 246°, respectively:



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## THE ACTION OF CHLORAL, BROMAL AND BENZALDEHYDE ON THE POLYCYCLIC HYDROCARBONS IN THE PRESENCE OF ALUMINIUM CHLORIDE.

[PART II.]

BY G. B. FRANKFORDER AND W. KRITCHEVSKY.

Received December 14, 1914.

As has already been shown by us<sup>2</sup> when chloral is brought in contact with benzene or one of its derivatives in the presence of anhydrous aluminium chloride at the ordinary temperature, a violent reaction takes place,

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Bull.* 2, "Chemical Studies," University of Minnesota, also abstract, *THIS JOURNAL*, 26, 1511.