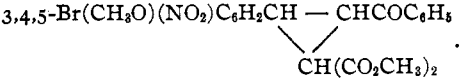
drolyzed to an ester acid, it is, doubtless, a cyclopropane derivative with a nitro-group in the nucleus.



The corresponding ester acid was obtained by hydrolysis with sodium methylate:

Calc. for $C_{20}H_{16}O_8NBr$: C, 50.2; H, 3.3.
Found: C, 50.8; H, 3.8.

## Summary.

1. The ring in (bromomethoxy-phenyl)-benzoyl-cyclopropane di-acid and its esters is more or less easily opened by reducing agents, halogen acids, bases, the Grignard reagent, and phosphorus pentachloride.

2. The various reagents open the ring in different positions; by using phosphorus pentachloride, bases, and reducing agents, it is possible to open the ring in three different ways.

3. The primary reaction between the cyclopropane derivative and a given reagent is similar to that between the corresponding ethylenic compound and the same reagent.

4. The cyclopropane derivative exhibits all the "peculiarities" of ethylenic compounds that contain conjugated systems; but it does not, like many ethylenic compounds, combine with the halogens or reduce permanganate.

CAMBRIDGE, MASS.

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

# RESEARCHES ON PYRIMIDINES. LXXXIV.

## THE TRANSFORMATION BY HYDROLYSIS OF SECONDARY PYRIMIDINE NUCLEOSIDES INTO IMIDAZOL COMBINATIONS.

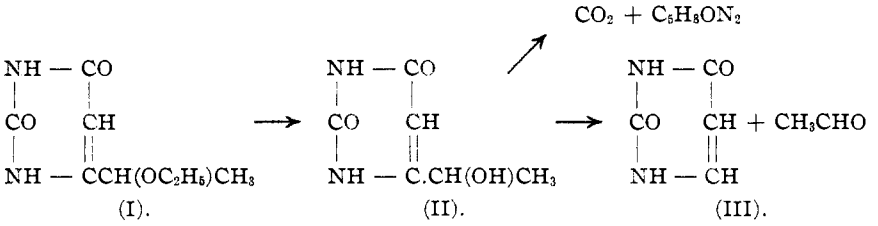
BY TREAT B. JOHNSON AND SIDNEY E. HADLEY.

Received May 16, 1917.

In the fourth paper from the Sheffield Laboratory on pyrimidine nucleosides, Johnson and Hadley[1] described an unique transformation which the ethyl ether of the secondary alcohol derivative of uracil (I) undergoes when it is subjected to hydrolysis by heating with aqueous hydrobromic acid. They showed that this pyrimidine is broken down by such treatment with evolution of ethyl bromide and carbon dioxide, giving a characteristic, crystalline compound having the formula $C_5H_8ON_2$. In other words, the secondary nucleoside (II) is apparently an intermediate product of the reaction but, being unstable in the presence of acid at high temperatures, gradually loses carbon dioxide and is transformed into the com-

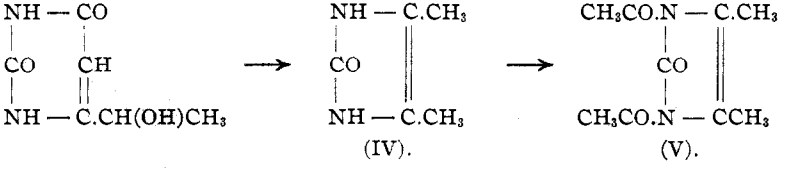
[1] THIS JOURNAL, 38, 1844 (1916).

pound $C_5H_8ON_2$ of unknown constitution. The products, which the writers expected to be formed by hydrolysis, namely, uracil (III) and acetaldehyde, were not obtained.[1]




At the time of publication of their paper Johnson and Hadley were unable to formulate definite conclusions regarding the structure of this interesting hydrolytic procuct on account of lack of experimental data. They emphasized, however, the significance of the unique result obtained and stated furthermore, that the substance agreed very closely in chemical and physical properties with 2-oxy-4,5-dimethylimidazol (IV) which had previously been synthesized by Kunne[2] and also Biltz.[3] This imidazol has now been synthesized by us and it is very gratifying to be able to state that it is identical with our hydrolytic product. In other words, we are dealing here with a new reaction suggesting genetic relationship between naturally occurring pyrimidines and imidazoles, and which on further investigation, we believe will be productive of experimental data of the greatest biochemical interest.

The identity of our hydrolytic product and the imidazol (IV) was established by the fact that both substances interact with acetic anhydride in the presence of sodium acetate, giving the same diacetyl derivative represented by Formula V. This compound has already been described by Biltz.[3]



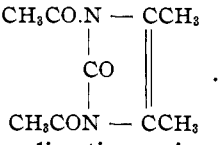

A discussion of the possible mechanism of this interesting reaction will be given in our next publication on pyrimidine nucleosides, in which we shall discuss the behavior of a thymine nucleoside on hydrolysis.

[1] A preliminary report of this work was given at the Fifty-Second Meeting of the American Chemical Society, held at the University of Illinois in Urbana-Champaign, April 17th to 21st, 1916.

[2] *Ber.*, **28**, 2040 (1895).

[3] *Ibid.*, 40, 4801 (1907).

## Experimental.

**Diacetyldimethylglyoxalone,**  . — This combination was prepared according to the directions given by Biltz[1] by treatment of our hydrolytic product, $C_5H_8ON_2$, with acetic anhydride. Five-tenths of a gram of the substance was digested with 5 cc. of acetic anhydride and 1 g. of anhydrous sodium acetate for 5 hrs., by heating in an oil bath. The resulting solution was then diluted with cold water, when a crystalline precipitate deposited. The compound was purified by crystallization from boiling alcohol, from which it separated on cooling, in the form of elongated prisms melting at 115–116° to a clear oil. The yield of purified material was 0.45 g. The imidazol used for comparison was made according to Kunne's method[1] and acetylated according to the directions of Biltz.[1] The diacetyl derivative obtained melted at 115–116° and we were unable to record a higher reading with the thermometers at our disposal. Biltz assigned to this compound a melting point of 117–118°. A mixture of the diacetyl derivative prepared from our hydrolytic product and Biltz's compound melted at 115–116°, showing that they were identical. A nitrogen determination gave:

Calc. for $C_9H_{12}O_3N_2$: N, 14.3. Found: N, 14.26.

NEW HAVEN, CONN.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

# REACTIONS OF PIPERIDINE WITH ORGANIC HALOGEN COMPOUNDS IN ETHER SOLUTIONS.

BY SARGENT G. POWELL AND WILLIAM M. DEHN.

Received May 26, 1917.

In common with other bases, piperidine reacts more or less readily with halogen compounds. If these reactions are carried out in aqueous alkaline solutions, nitrogen substitution products of piperidene are formed almost invariably. If the reactions are carried out in anhydrous media, however, as for example, in ether, the end products are found to be different. In the latter case the base and the halide unite to form a molecular compound, which subsequently may or may not undergo decomposition so as to yield the halogen-acid salt of piperidine and the nitrogen substituted homologue of piperidine.

These successive reactions may be illustrated by the equations:

[1] *Loc. cit.*