

3. Resorcinol condensed with acetylene to form ethylidene diresorcinol with linkage *ortho* and *para*, respectively, to the two hydroxyl groups.

4. Ethylidene diresorcinol gives off a molecule of water to form a new compound, dihydroxy-methylxanthene, which was oxidized to form hydroxymethylfluorone.

5. The di- and trihydroxy benzenes react with acetylene even more readily than does phenol.

6. The presence of negative groups as the nitro and sulfonic groups prevents the absorption of acetylene by the phenolic compound. As these groups, according to Crum Brown's rule, direct the entering group to a *meta* position, it appears that acetylene instead of entering in a *meta* position does not react at all. No cases have been observed where the acetylene substitutes in a *meta* position to another group.

7. The substitution of the hydrogen of the hydroxyl group of phenol by an ethyl group prevents reaction with acetylene.

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NEW METHODS OF SPLITTING PYRIMIDINES. III. THE ACTION OF IODINE SOLUTION ON PYRIMIDINES¹

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The discovery of the fact that the stable pyrimidine ring can be ruptured under mild conditions, such as moderate temperatures and in neutral or weakly alkaline solution, led to a search for other methods of producing this decomposition. The reagents which have already been applied are:³

(1) ferrous sulfate plus sodium bicarbonate plus air; (2) sodium pentacyano-aquo-ferroate plus oxygen or air; (3) ferrous sulfate plus oxygen; (4) ferrous sulfate plus hydrogen peroxide.

The observation of Pauly and Gundermann⁴ that indole is oxidized to indigo with a 40% yield by iodine solution in the presence of sodium bicarbonate, led us to a study of this reagent as a possible means of splitting pyrimidines. The investigation was attended by marked success, since we were able to split uracil, thymine, 5-ethyluracil, 4-methyluracil and cytosine into urea and other products.

In the case of thymine we were able to detect acetol, but no pyruvic

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³ Johnson and Baudisch, (a) *THIS JOURNAL*, **43**, 2670 (1921); (b) Pfaltz and Baudisch, *ibid.*, **45**, 2972 (1923).

⁴ Pauly and Gundermann, *Ber.*, **41**, 4002 (1908).

acid.⁸ The importance of this result from a theoretical standpoint will be discussed in a subsequent paper.⁵

Experimental Part

A solution of a weighed quantity of pyrimidine in distilled water was introduced into a 1 liter graduated flask with a weighed quantity of sodium bicarbonate. The total volume was increased to 500–600 cc. by the addition of distilled water. Iodine solution⁶ was then added gradually in order to observe the rapidity of decolorization. An excess of iodine solution was finally added and the reaction mixture was diluted to 1 liter. The solution was then allowed to stand overnight at room temperature. If it had not become decolorized, the excess of iodine was removed by a rapid stream of air or by warming it on a water-bath.

TABLE I

EXPERIMENTAL RESULTS

Nos. 1, 3, 4, 6–9, 11–17 were distilled; No. 5 was distilled with 4 g. of NaHCO_3 . Nos. 1, 4–9, 12, 15, 16 were decolorized by a stream of air; Nos. 2, 3, 10, 11, 13 by standing; Nos. 14, 17 on warming; No. 18 did not decolorize iodine solution.

No.	Pyrimidine G.	NaHCO_3 G.	Iodine solution Cc.	Products
Uracil				
1	0.4	30	100	Urea (20%)
2	.5	20	120	No urea
3	.5	20	120	Urea
4	.4	0	50	No urea
5	.4	0	50	No urea
6	.2	8	20	Urea
Hydro-uracil				
7	.2	8	20	No urea
Thymine				
8	.4	30	50	Urea (35%)
9	.5	30	80	Urea acetol
10	.4	20	20	No urea, no acetol
11	.4	20	20	Urea, acetol
12	.5	30	Ex. of Br_2	No urea, no acetol
4-Methyluracil				
13	.5	40	80	Urea, no acetol
5-Ethyluracil				
14	.1	20	20	Urea (30%)
15	.1	20	20	Urea (35%)
16	.5	30	70	Urea. No reducing compd. in dist.
Cytosine				
17	1.0	8	50	Urea
1,3-Dimethylthymine				
18	0.3	20	Did not decolorize iodine solution.	

⁵ Baudisch and Bass, *THIS JOURNAL*, **46**, 184 (1924).

⁶ Approximately decinormal (13 g. of I_2 and 20 g. of KI per liter).

The colorless solution was then distilled to a volume of 50–75 cc. and the residue was tested for urea according to the method of Fosse.⁷ In this test, after the addition of glacial acetic acid, the solution often turned red as a result of the liberation of iodine.

In experiments with thymine, tests were made for acetol⁸ in the distillate and for pyruvic acid⁹ in the residue. Strong tests for acetol were obtained, but in no case was it possible to detect any trace of pyruvic acid.

The results are summarized in the preceding table.

It was observed that, on gradual addition of iodine solution, decolorization took place very rapidly in experiments with uracil and with 4-methyluracil. Decolorization was slower with thymine and still slower with 5-ethyluracil. Hydro-uracil decolorized iodine solution, although no urea was formed in the reaction. 1,3-Dimethylthymine, however, did not decolorize iodine solution.

Summary

1. Pyrimidines with unsubstituted nitrogen atoms and with a double bond between carbon atoms 4 and 5 absorb iodine from solution in the presence of sodium bicarbonate. On distillation of the reaction mixtures, after removal of excess iodine, urea is found in the residues as a product of the split. No urea can be detected before the distillation.

2. Substitution of an alkyl group in Position 5 retards the rapidity of decolorization of iodine solution.

3. Hydro-uracil decolorizes iodine solution, but no urea is formed when the reaction mixture is distilled.

4. 1,3-Dimethylthymine does not decolorize iodine solution.

5. Thymine yields urea and acetol; no pyruvic acid is formed.

6. When bromine is substituted for iodine, the pyrimidine ring is not split under the conditions of the experiments.

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⁷ Fosse, *Ann. chim.*, [9] **6**, 13 (1916).

⁸ Baudisch, *Biochem. Z.*, **89**, 279 (1918).

⁹ Baeyer, *Ber.*, **15**, 2856 (1882).