[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Catalytic Decomposition of Phenylhydrazine in the Presence of Uracils[1]

BY TREAT B. JOHNSON

Pyrimidines of the uracil type are unaffected by phenylhydrazine. All three of the oxypyrimidines—uracil, thymine and 4-methyluracil—can be recrystallized from this reagent and are recovered unchanged even after prolonged heating with phenylhydrazine. The author now finds, however, that extended digestion of uracil or 4-methyluracil with phenylhydrazine decomposes this reagent according to the equation

$$2C_6H_5NH{\cdot}NH_2 \rightleftarrows C_6H_5NH_2 + C_6H_6 + NH_3 + N_2$$

In other words, these pyrimidines act as organic catalysts in this reaction and are recovered unchanged in quantitative amounts. In this respect these cyclic ureides resemble certain inorganic salts. Cuprous halides,[2] cuprous cyanide,[3] and zinc chloride[4] promote decomposition of phenylhydrazine in a similar manner. Heating at 300° accomplishes the same result.[5]

It is interesting to compare this behavior of uracil and 4-methyluracil toward phenylhydrazine with their reaction with hydrazine. These pyrimidines and other cyclic ureides interact with hydrazine to give new heterocycles of the pyrazolone type, or are actually hydrolyzed with the formation of acyclic hydrazides. Well known instances of such transformations are as follows. From hydantoin and allantoin, Fosse, Hagene and Dubois[6] obtained the corresponding hydrazides; from uracil and thymine Fosse, Hieulle and Bass[7] obtained urea and pyrazolone,[8] and urea and methylpyrazolone,[8] respectively; from uridine Levene and Bass[9] obtained pyrazolone,[10] while from parabanic acid Fosse, Thomas and de-Gräeve[11] obtained oxalurhydrazide.

Experimental Part

Uracil.—One gram of this pyrimidine was dissolved in 20 g. of boiling phenylhydrazine and the mixture boiled for eight hours. The digestion unit was aerated to remove ammonia which was recovered as ammonium chloride. That nitrogen gas was evolved was shown by aeration with known volumes of air and noting the increase in volume. No attempt was made to determine the quantity of benzene formed.

After eight minutes, uracil began to deposit from the boiling liquid. This increased in quantity as the digestion was continued, and the quantity of aniline increased. Uracil is much less soluble in aniline than in phenylhydrazine. The digestion was continued at the boiling point for eight hours and then allowed to cool when the reaction mixture was extracted with ether to dissolve all aniline and phenylhydrazine, and the insoluble uracil dried and weighed. This was completely recovered and responded immediately to the Wheeler and Johnson[12] color test and underwent nitration to give 5-nitrouracil. The ether extract was subjected to distillation and pure aniline was obtained boiling at the correct temperature. The author obtained no evidence of the formation of any phenylpyrazolone derivative. The recovered aniline boiled at 182–190°. The ammonium chloride recovered from two digestion experiments weighed 4.45 and 4.0 g., respectively.

4-Methyluracil.—This experiment was carried out in the manner described for uracil, but using only 10 g. of phenylhydrazine for 1 g. of 4-methyluracil. The latter pyrimidine is more soluble in boiling phenylhydrazine than uracil, and crystallizes on cooling in prisms. The digestion with phenylhydrazine was discontinued after three hours of boiling. Ammonia was constantly evolved during the digestion. As in the previous experiment the author could detect no change in the 4-methyluracil and it was recovered practically quantitatively, there being no evidence of the formation of any phenylpyrazolone derivative. The recovered phenylhydrazine weighed 5 g. and boiled at 240–242°. The ammonium chloride recovery was 1.5 g.

Summary

1. When phenylhydrazine is digested with uracil, thymine or 4-methyluracil it is decomposed with formation of aniline, benzene, ammonia and nitrogen.

2. These three pyrimidines act as true organic catalysts and are recovered unaltered after hours of digestion with phenylhydrazine.

NEW HAVEN, CONNECTICUT

RECEIVED NOVEMBER 20, 1940

---

(1) Researches on Pyrimidines, CLXVIII.

(2) Arbusow and Tichwinski, *J. Russ. Phys.-Chem. Soc.*, **45**, 69 (1913); *Chem. Zentr.*, **84**, I, 1415 (1913).

(3) Struthers, *Chem. News*, **91**, 161 (1905).

(4) Fischer, *Proc. Chem. Soc.* (London), **21**, 95 (1905).

(5) Walther, *J. prakt. Chem.*, [2] **53**, 471 (1896).

(6) Fosse, Hagene and Dubois, *Compt. rend.*, **178**, 578 (1924).

(7) Fosse, Hieulle and Bass, *ibid.*, **178**, 811 (1924).

(8) These cycles were isolated and identified as *Xanthyl* derivatives.

(9) Levene and Bass, *J. Biol. Chem.*, **71**, 167 (1926).

(10) The authors obtained no evidence of the formation of a ribosepyrazolone, which they conclude is evidence that in uridine the linkage of ribose to uracil is in position-3 of the pyrimidine cycle.

(11) Fosse, Thomas and de Gräeve, *Compt. rend.*, **200**, 1260 (1935).

(12) Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).