REACTION OF 2,6-DIAMINO-4-HYDROXYPYRIMIDINE WITH HYDROGEN PEROXIDE

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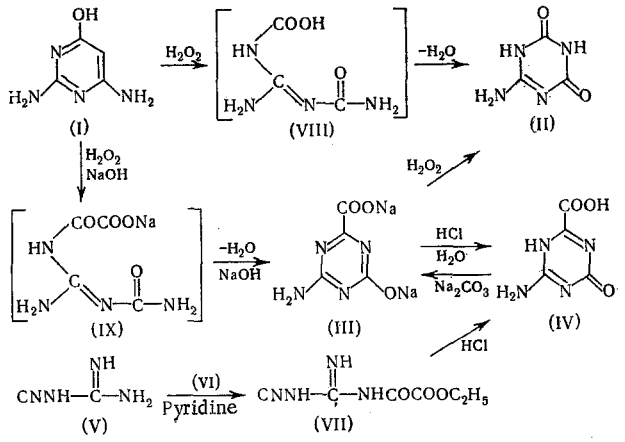
In a search for new methods of inserting functional groups in the 5 position of the 2,6-diamino-4-hydroxypyrimidine (I) molecule for the purpose of obtaining pteridine derivatives in this way, in the present paper we studied the reactions of (I) with H_2O_2 under various conditions



Ammelide (II)* is formed when (I) is reacted with perhydrol (20°C, 3 h). The reaction of (I) with alkaline H_2O_2 and subsequent treatment of the Na salt (III) with dilute HCl solution lead to 3-hydroxy-5-amino-s-triazine-1-carboxylic acid (IV), the structure of which was proved by reconversion to the Na salt (III) by heating with Na_2CO_3 solution, which was oxidized and decarboxylated to (II) under the influence of H_2O_2, and also by counter synthesis: by the acylation of dicyandiamide (V) with $ClCOCOOC_2H_6$ (VI) and subsequent cyclization of the oxalyldicyandiamide (VII) in conc. HCl medium. The transformations of (I) to (II) and (VI) can be depicted as being multistep processes, which include the oxidative cleavage of (I) and the cyclization of the intermediate N-carbamidoguanidine derivatives (VIII) and (IX). The formation of the 5-oxygen-containing (I) derivatives could not be detected in a single experiment.

EXPERIMENTAL METHOD

Reaction of (I) with H_2O_2. A suspension of 100 mg of (I) in 0.5 ml of 30% H_2O_2 solution was kept at ~20°C for 3 h, after which the precipitate was filtered, washed with water, and dried in the air. We obtained 80 mg (80%) of (II), decomposition point above 300°. Ultraviolet spectrum†: λ_{max} 221 nm. The IR spectrum‡ was identical with that given in [2]. The conversion of (I) to (II) was accelerated by catalytic amounts of $FeSO_4$.

* After the present study had been completed, there appeared a communication in which the formation of (II) from 2,5,6-triamino-4-hydroxypyrimidine under the influence of H_2O_2 is described [1].

† The UV spectra were taken in water on a Specord UV VIS instrument.

‡ The IR spectra were taken as KBr pellets on a UR-10 instrument.

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Reaction of (I) with Alkaline H_2O_2 Solution. A solution of 100 mg of (I) and 0.4 ml of 30% H_2O_2 in 1.25 ml of 2 N NaOH solution was kept at ~20° for 3 h, after which the precipitate was filtered and washed with water. We obtained 140 mg of (III), decomposition point above 300°. Ultraviolet spectrum: λ_{max} 250 nm; IR spectrum (ν, cm^{-1}): 3470, 3340, 1645, 1580, 1500, 1440, 1340, 825. Found: C 22.29; H 2.09; N 25.81; Na 20.83%. $C_4H_2N_4O_3Na_2 \cdot H_2O$. Calculated: C 22.02; H 1.84; N 25.69; Na 21.10%.

The obtained (III) was dissolved in 40 ml of water at 90-95°, acidified with 1:1 HCl solution, cooled to ~20°, and the precipitate was filtered, washed with water, and dried in the air. We obtained 90 mg (75%) of (IV), decomposition point above 280°. Ultraviolet spectrum: λ_{max} 250 nm; IR spectrum (ν, cm^{-1}): 3160, 1750, 1685, 1605, 1530, 1460, 1380, 1350, 930, 790. Found: C 29.06; H 2.91; N 34.44%. $C_4H_4N_4O_3 \cdot 1/2\ H_2O$. Calculated: C 29.09; H 3.03; N 33.94%.

Compound (IV) (100 mg) was dissolved in 10 ml of saturated Na_2CO_3 solution at 80-90°, cooled, and the precipitate was filtered. We obtained 100 mg (76%) of the Na salt, which in its IR spectrum was identical with the above described (III).

Conversion of (III) to (II). A mixture of 100 mg of (III) in 3 ml of 15% H_2O_2 solution was heated for 1 min at 50°, cooled, and the precipitate was filtered. We obtained 50 mg (85%) of (II).

Preparation of (IV) from (V). To a solution of 310 mg of (V) in 10 ml of absolute pyridine at 10° was added 500 mg of (VI), the mixture was stirred at ~20° for 4 h, and the precipitate was filtered and washed with $CHCl_3$ and ether. We obtained 360 mg of (VII), decomposition point above 220°. A solution of 100 mg of (VII) in 1 ml of conc. HCl was kept at ~20° for 24 h, and the precipitate was filtered and washed with water. We obtained 50 mg (30%) of (IV).

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CONCLUSIONS

Ammelide and 3-hydroxy-5-amino-s-triazine-1-carboxylic acid are formed respectively by the reaction of 2,6-diamino-4-hydroxypyrimidine with perhydrol and with alkaline H_2O_2 solution.

LITERATURE CITED

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2. W. M. Padgett and W. F. Hammer, J. Am. Chem. Soc., 80, 803 (1958).