UNEXPECTED FORMATION OF 1,3-DIMETHYL-5-DIAZOBARBITURIC ACID DURING THE OXIDATION OF 7-AMINO-8-BROMOTHEOPHYLLINE

A. F. Pozharskii, V. V. Kuz'menko,
and I. M. Nanavyan

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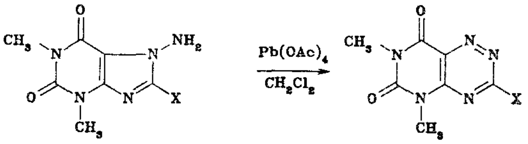
N-Aminobenzimidazoles are known to be oxidated by lead tetraacetate, forming the corresponding benzo-1,2,4-triazines after the intermediate formation of a nitrene [1]. We found that 7-aminotheophylline (Ia) undergoes a similar reaction, which results in the formation of 5,7-dimethyl-6,8-dioxopyrimido[4,5-e]-as-triazine (IIa), which is a structural isomer of the antibiotic fervenulin [2]. The yield of IIa is 74%, and the mp is 212°C (from butanol), in agreement with the data in [3]. This method for the synthesis of IIa is significantly simpler than that described in the literature [3].

However, when 7-amino-8-bromotheophylline (Ib) was oxidized under the same conditions, instead of the postulated 3-bromo derivative IIb, we isolated 1,3-dimethyl-5-diazobarbituric acid (IV), whose yield after purification was 54%. The melting point was 159-160°C (from methanol); according to the data in [4], mp 165-166°C. Compound IV is easily coupled to α-naphthol in an alkaline medium to form a reddish violet dye. The data from elemental analysis and IR, PMR, and mass spectroscopy are in complete agreement with structure IV.

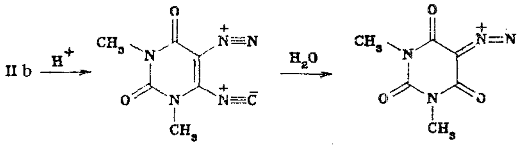


I a,b

II a,b

I, II a X=H, b X=Br

We suggest that the reaction takes place according to the following scheme:



III

IV

Compound IIb, which forms at first, undergoes ring opening with the limination of a bromide ion and the formation of the highly labile diazonium salt III under the action of the acetic acid appearing in the oxidation step. Upon hydrolysis, the isonitrile group in III undergoes nucleophilic substitution and is replaced by an hydroxyl group.

7-Amino-8-bromotheophylline (Ib), which has not previously been described, was obtained by the amination of 8-bromotheophylline by hydroxylamine-O-sulfonic acid. The yield was 25%, and the mp was 200-201°C (from ethanol).

LITERATURE CITED

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