2-tert-Butyl-5-methyltetrazole (IIa). bp 74°C (17 mm Hg), n_d^{20} 1.4447. PMR spectrum: 2.44 (3H, s, Me), 1.70 ppm (9H, s, t-Bu). Yield 69%.

2-tert-Butyl-5-phenyltetrazole (IIb). bp 90°C (0.1 mm Hg), n_D^{20} 1.5337. PMR spectrum: 8.08-8.18 (2H, m, o-H), 7.46-7.56 (3H, m, m,p-H), 1.78 ppm (9H, s, t-Bu). Yield 98%.

2-tert-Butyl-5-trifluoromethyltetrazole (IIc). bp 56°C (13 mm Hg), n_D^{20} 1.3855. PMR spectrum: 1.79 ppm (9H, s, t-Bu). Yield 85%.

Elemental analytical data for C, H, and N agreed with that calculated. The PMR spectra of Ia, IIa-c were recorded in acetone-d_6 (100 MHz).

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CHICHIBABIN AMINATION OF 1,3-DIMETHYLLUMAZINE

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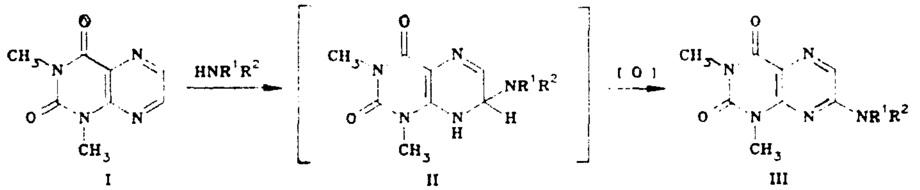
It is known that 1,3-dimethyllumazine (I) reacts with nucleophiles, in particular with alkali [1], hydrazine [2], and amines [3] at the amide $C_{(2)}=O$ and $C_{(4)}=O$ atoms with opening of the uracil nucleus. We now report the first example of nucleophilic substitution of hydrogen in the pyrazine ring of I with retention of the uracil fragment. It is shown that 1,3-dimethyllumazine (I) undergoes oxidative amination to give the 7-amino- and 7-alkylamino derivatives III in 20-35% yields.

A suspension of I in alkylamine (tert-butylamine, piperidine, morpholine) at 10-15°C was treated portionwise over 2-4 h with $[Ag(C_5H_5N)_2]MnO_4$ oxidant [4]. $KMnO_4$ cannot be used because of its insolubility in the indicated amines. Excess alkylamine was distilled off, the residue extracted with chloroform, and the product separated by column chromatography. The same reaction could not be carried out using liquid ammonia, evidently because of its low boiling point. However, amine IIIa could be prepared using potassium amide in liquid ammonia with oxidation of the adduct IIa using potassium permanganate.



a $R^1=R^2=H$; b $R^1=H$, $R^2=C(CH_3)_3$; c NR^1R^2=piperidinyl; NR^1R^2=N-morpholinyl

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Compound IIIa: mp >330°C (from alcohol), yield 32%. **Compound IIIb**: mp 262-264°C (from alcohol), yield 35%. **Compound IIIc**: mp 217-219°C (from alcohol), yield 29%. **Compound IIId**: mp 242-245°C (from alcohol), yield 21%.

Elemental analytical data and IR and PMR spectra agreed with the proposed structures.

The 7-amino and not the 6-amino structure is proposed for III on the basis of the quantum mechanically calculated data. The positive π-charge in molecule I on atom $C_{(7)}$ (+0.125) is significantly higher than on atom $C_{(6)}$ (+0.057). Compound IIIa has been obtained before [5] but IIIb-d are reported for the first time.

As might be expected, compound I participates in the Chichibabin reaction with greater difficulty than the 6-aza analog [6] due to its low electrophilicity. In addition, the lower yield of amination products may be due to the significantly poorer solubility of 1,3-dimethyllumazine in amines and, therefore, the lower concentration of the covalent adduct II. Nonetheless, the reaction described can serve as an alternative method for synthesizing III which was previously prepared by nucleophilic substitution of the 7-halogeno or 7-hydroxy groups in the difficult-to-obtain 7-X-lumazines [7].

In contrast to I, pteridine and its alkyl derivatives are aminated in ammonia and alkylamines at position 4, i.e., in the pyrimidine ring. Under conditions of thermodynamic control (10°C), unsubstituted pteridine gives the 6,7-diamino-5,6,7,8-tetrahydro adduct which could not be oxidized [8].

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