

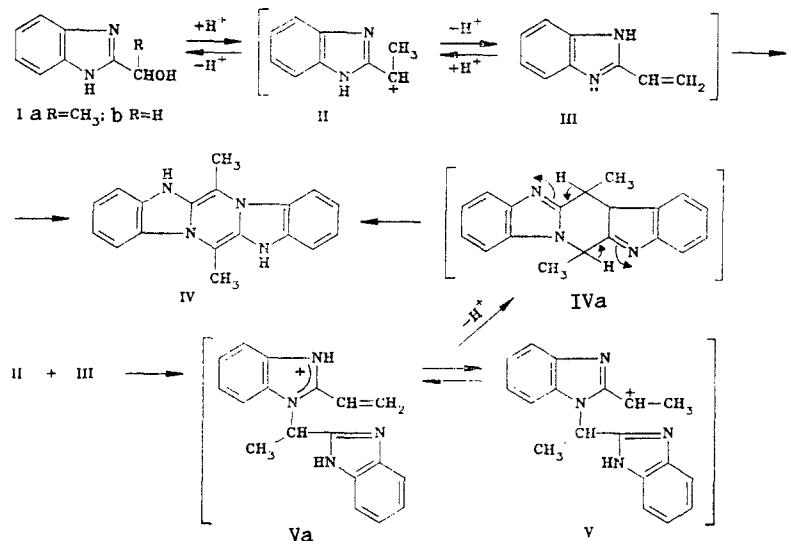
DEHYDRATION OF 2-(2-HYDROXYETHYL)BENZIMIDAZOLE. SYNTHESIS OF
6,13-DIMETHYL-5H,12H-PYRAZINO[1,2-*a*:4,5-*a'*]BISBENZIMIDAZOLE

I. I. Popov

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The acid-catalyzed dehydration of 2-(2-hydroxyethyl)benzimidazole (Ia) has been found to follow an unusual course. On heating the carbinol (Ia) in polyphosphoric (150-160°C, 3 h) or sulfuric acid (100°C, 48 h), there was unexpectedly formed 6,13-dimethyl-5H,12H-pyrazino[1,2-*a*:4,5-*a'*]bisbenzimidazole (IV) instead of 2-vinylbenzimidazole (III). Only in the initial stages of the dehydration of (Ia) in PPA were traces of (III) found, and these disappeared in the final stage. A control experiment showed that 2-vinylbenzimidazole dimerized completely on heating in PPA at 160-175°C to give (IV).

Since 2-hydroxymethylbenzimidazole (Ib) does not undergo similar reactions under these conditions, and is inert toward PPA even when the temperature is raised to 200-250°C, there is no reason for supposing that (IV) is formed by cyclodimerization of the carbocation (II), or by reaction of the latter with the starting carbinol (Ia). It appears that the 2-vinylbenzimidazole formed initially by dehydration of the carbinol (Ia) is attacked by the carbocation (II) under these reaction conditions to give the mesomeric cation (V), which then undergoes intramolecular cyclization to the dihydropyrazine (IVa). The latter isomerizes by prototropic rearrangement to the aromatic heterocycles (IV), the structure of which has been confirmed by its IR and PMR spectra.



The yield of (IV) was 76%, mp 155°C (from aqueous DMF). Its elemental analysis was in agreement with theory.

It is also noteworthy that dihydropyrazines are formed as by-products in the hydroxymethylation of 2,4(5)-dialkylbenzimidazoles [1].

LITERATURE CITED

1. M. Masui, K. Suda, M. Inone, K. Iizukura, and M. Yamauchi, Chem. Pharm. Bull., 22, 2259 (1974).