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SPONTANEOUS DEHYDROGENATION OF TETRAHYDRO-2,3-TRIMETHYLENEQUINAZOLINES AND -QUINAZOLONES

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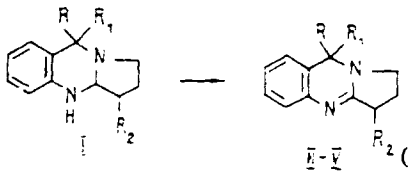
In a study of the mass spectra of dihydro derivatives of quinazoline and quinazalone alkaloids (I) and their deutero analogues [1, 2] we detected traces of dehydrogenation products in all the specimens (II), deoxypeganine; R = R_1 + R_2 = H; (III), peganine: R = R_1 = H, R_2 = OH; (IV), deoxyvasicinone, R_1(R)C=O, R_2=H, (V), vasicinone: R_1(R)C=O, R_2=OH. R_2 = OH. To find whether this process takes place spontaneously or under the action of electron impact, a sample of (I) was heated to the melting point. Heating was also carried out in amyl alcohol and in methanol in a sealed tube at 120°C. In all cases the formation of (II)-(V) was established with the aid of TLC and mass spectrometry. After samples of (I) in the form of bases had been stored for 2-5 years their mass spectra were recorded again.



Dihydrodeoxypeganine R = R_1 = R_2 = H
Dihydropeganine R = R_1 = H, R_2 = OH

Dihydrodeoxyvasicinone R_1(R)C=O, R_2 = H

Dihydrovasicinone R_1(R)C=O, R_2 = OH

(II). Deoxypenine R = R_1 = R_2 = H
(III). Peganine R = R_1 = H, R_2 = OH

(VI). Deoxypeganine R_1(R)C=O, R_2 = H

(V). Vasicinone R_1(R)C=O, R_2 = OH

The spectra showed the conversion of dihydropeganine (M^+ 190 into (III) by approximately 50%; of dihydrodeoxyvasicinone (M^+ 188) into (IV) completely; and of dihydrovasicinone (M^+ 204) into (IV) and (V) in equal proportions.

Among quinazoline derivatives similar transformations have been described previously only with the aid of oxidants (chromium trioxide [3] and potassium ferricyanide [4]) and only in the synthesis of the β-carbolinoquinazoline alkaloid evodiamine has the spontaneous dehydration of the tetrahydroquinazoline moiety of the molecule to the dihydroquinazolone analogue been observed [5].

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