SIMPLE METHOD FOR THE SYNTHESIS OF 1,2-DIHYDROPYRROLIZINES

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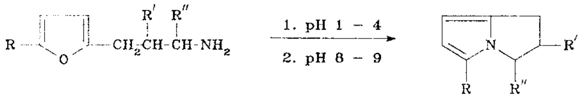
We have previously described the synthesis of 1,2-dihydropyrrolizines by catalytic dehydration of amines of the furan series in the gas phase [1]. We now present an intramolecular variant of the synthesis of dihydropyrrolizines in conformity with the scheme



I–IV

V–VIII

I, V R=R′=H, R″=CH$_3$; II, VI R′=R″=H, R=CH$_3$; III, VII R=R′=CH$_3$, R″=H; IV, VIII R=R″=CH$_3$, R′=H

In analogy with [2], it may be assumed that the first step in the transformation reduces to hydrolysis of the furan ring. The resulting intermediate (presumably a dicarbonyl compound) undergoes cyclization during liberation of the amino group by means of alkalization, as in the case of the intermolecular reaction of acetonylacetone with ammonia [2]. During the second step of the reaction the acidity of the medium increases and slows down markedly at pH 5 is approached. The proposed method for the synthesis of compounds of the V-VIII type is an alternative of the known method [1]. The reaction proceeds under mild conditions and ensures high purity of the transformation products. The first step in the transformation is realized by heating an acidic aqueous solution of the sulfate of amines II-IV (pH 1-2) in an argon atmosphere at 90-95°C for 20 min. In the second step the mixture is made alkaline to pH 8-9 with KOH solution and heated in a stream of argon at 85-95°C for 2.5 h while maintaining pH 6-8 by the periodic addition of alkali (the yields were 35-40% in the synthesis of VI and VIII). Similar results were obtained when the second step was modified as follows. A mixture with pH 8-9 was heated in an argon atmosphere in a sealed ampul at 100°C for 3 h, after which the product was extracted with ether at pH 4-5, the aqueous layer was made alkaline again, and the second step was repeated (the yield was 34% in the synthesis of dihydropyrrolidine VII). Compound V (15% yield) was obtained by heating an aqueous solution of the hydrochloride of amine I in the presence of a Prideau–Ward buffer mixture [3] (pH 4) at 80°C for 5 h. Alkalization gave a mixture of amine I and V, from which the latter was extracted with ether at pH 4. The structures of the compounds follow from the agreement between their constants and the values described in [1, 4] (V, VI, and VIII) and satisfactory analytical results and are confirmed by the PMR spectral data. Compound VII had bp 79°C (10 mm) and n_D^{20} 1.5103. PMR spectrum (without a solvent): 5.73 (6-H), 5.55 (7-H, $J_{6,7}$ = 3.2 Hz), 1.97 (5-CH$_3$), and 0.92 ppm (2-CH$_3$, J = 6.3 Hz).

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