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FORMATION OF PERHYDROPYRROLO[3,2-c]PYRIDINES IN THE TROFIMOV REACTION

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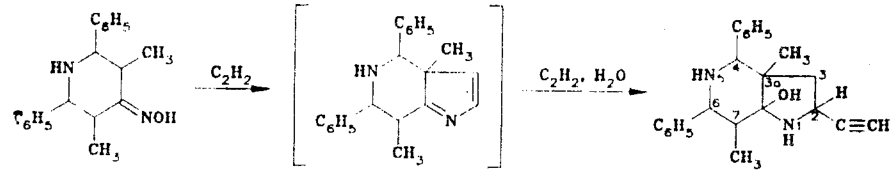
The condensation of 1,3,5-trimethyl-4-piperidinone oxime with acetylene in a superbase medium gave 2,4,5-trimethyl-1,2,3,4-tetrahydropyrrolo[1,2-c]pyrimidine, which is formed as a result of [1,3]-sigmatropic rearrangement of the primary reaction product 3*a*,5,7-trimethyl-3*a*H-4,5,6,7-tetrahydropyrrolo[3,2-c]pyridine [1].

The heterocyclization of 3,5-dimethyl-2,6-diphenyl-4-piperidinone oxime with acetylene at 80-90°C and an initial pressure of 15 atm in the presence of potassium hydroxide is accompanied by significant resinification. Chromatography of the reaction products gave three individual substances: Ia with mp 112-114°C and R_f 0.15; Ib with mp 155-157°C and R_f 0.31; Ic with mp 143-145°C and R_f 0.53 [all of the R_f values were determined with Silufol and ethyl acetate—hexane (1:3) as the eluent]. A fraction containing a mixture of Ic and Id was also isolated. Compounds Ia-d are a mixture of 3*a*,7-dimethyl-4,6-diphenyl-2-ethynyl-7*a*-hydroxyperhydropyrrolo[3,2-c]pyridine isomers; they were obtained in ~10% overall yield. Their structures were established from their ^{1}H and ^{13}C NMR spectra.



I a-d

Low-intensity molecular-ion peaks with m/z 346 (1-3%), corresponding to their empirical formulas, are observed in the mass spectra of Ia-d. Splitting out of water to give fragment ions with m/z 328 (2-4%) is characteristic for the fragmentation of the M^+ ions. The IR spectra (CCl_4) of Ib, c contain bands of vibrations of, respectively, OH and NH groups at 3610 and 3420 cm^{-1}. In addition, a band of a bonded hydroxy group at 3420 cm^{-1} is present in the spectrum of Ib.

According to the ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz), the Ia and Ib pair is isomeric to the Ic and Id pair with respect to the ring fusion, which is responsible for the difference in the chemical shifts (CS) of the $C_{(7a)}$ atom: 96.83 (Ia), 96.59 (Ib), 107.06 (Ic), and 106.82 ppm (Id). In turn, the Ia and Ic and Ib and Id pairs differ with respect to the configuration of the substituents in the five-membered ring. The cross peaks from the pairs of 2-H and 3*a*-CH_3 protons with coordinates 0.91-4.68 and 0.97-4.76 for isomers Ib and Id, respectively, that are observed in the two-dimensional NOESY spectra ($CDCl_3$, 400 MHz) indicate a trans configuration of the ethynyl group attached to the $C_{(2)}$ atom and the methyl group attached to the $C_{(3a)}$ atom of the radicals. The absence of analogous cross peaks in the NOESY spectra of Ia and Ib attests to a cis configuration of the indicated substituents. The corresponding tetrahydropyrrolo[1,2-c]pyrimidine is not detected in the reaction products. Sigmatropic rearrangement of the intermediate 3H-tetrahydropyrrolopyridine is probably suppressed in the case of a large excess of acetylene. Compounds Ia-d are formed as a result of the addition of water and acetylene to the 3H-pyrrole ring.

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