NEW EXAMPLE OF THE DIMROTH REARRANGEMENT

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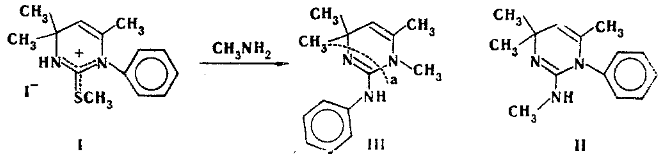
We have found that the isomeric 3,4,6,6-tetramethyl-2-phenylamino-3,6-dihydropyrimidine (III), instead of the expected product of substitution of the methylthio group by a methylamino group–4,6,6-trimethyl-3-phenyl-2-methylamino-3,6-dihydropyrimidine (II)–is formed in the reaction of 4,6,6-trimethyl-3-phenyl-2-methylthio-3,6-dihydropyrimidine (I) with methylamine in methanol at 100°C.

An analysis of the mass spectrum of III shows that the molecular ion undergoes fragmentation in two directions: 1) destruction of M^+ with respect to the "*a*" line with hydrogen migration to the nitrogen atom of the upper fragment, as a result of which fragments with m/e 118 and 112 are formed; 2) elimination of a methyl group from the 6 position with subsequent destruction of the $(M - CH_3)^+$ ion also with respect to the "*a*" line to give fragments with m/e 118 and 56. The precise empirical compositions of these ions, which can be formed only from isomer III, were confirmed by the high-resolution mass spectra.



I III II

The conversion of I to III is a new example of the Dimroth rearrangement [1], which apparently proceeds through a step involving the addition of methylamine (or water) to the C=C bond with subsequent ring opening and recyclization with migration of the N-phenyl fragment to the exocyclic position at the ring C_2 atom.

Compound II, with mp 97-98° (from hexane), was obtained in 65% yield. IR spectrum (mineral oil, ν, cm^{-1}): 1685 (C=C), 1625 (C=N), and 3395 (NH). UV spectrum: λ_{max} 262 nm (log ε 4.00). PMR spectrum ($CDCl_3$), δ, ppm: 1.09 (6H, s), 1.90 (3H, s, CH_3–C=), 3.20 (3H, s, NCH_3), 3.90 (1H, s, NH), 4.37 (1H, s, HC=), and 6.68-7.35 (5H, aromatic). The results of elementary analysis for nitrogen were in agreement with the calculated values.

LITERATURE CITED

1. M. Wahren, Z. Chem., 9, 241 (1969).

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