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LETTERS TO THE EDITOR

NEW EXAMPLE OF THE ENAMINE REARRANGEMENT OF PYRIMIDINES

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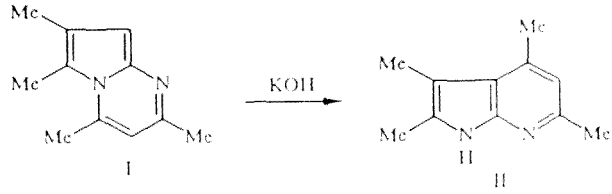
In the 1970s A. N. Kost and R. S. Sagitullin discovered the enamine rearrangement of pyrimidines and pyridines and showed that, provided a set of structural requirements were met and suitable nucleophiles were used, the iodomethylates of some 2-alkylpyrimidines and also substituted pyrimido[1,2-*a*]indoles and pyrazolo[1,5-*a*]pyrimidines rearranged to 2-methylaminopyrimidines [1, 2], α-carbolines [3] and pyrazolo[3,4-*b*]pyridines [4] respectively.

This report is concerned with the rearrangement of yet another condensed system — pyrrolo[1,2-*a*]pyrimidine into pyrrolo[2,3-*b*]pyridine. 2,4,6,7-Tetramethylpyrrolo[1,2-*a*]pyrimidine rearranges on heating in a sealed ampule for 25 h at 160-175°C in 20% aqueous alcoholic (1:1) potassium hydroxide to 2,3,4,6-tetramethylpyrrolo[2,3-*b*]pyridine (II) in 56% yield.



I II

Compound (II) ($C_{11}H_{14}N_2$), yellow crystals, mp 120-121°C (from aqueous ethanol), R_f 0.41 (3:1 benzene–acetone). ^{1}H NMR spectrum (DMSO-D_6): 2.25 (6H, s, 2-CH_3 and 3-CH_3), 2.35 (3H, d, J = 1.2 Hz, 6-CH_3), 2.48 (3H, s, 4-CH_3), 6.45 ppm (1H, m, 5-H).

The ^{1}H NMR spectra of the starting material (I) and the recyclized product (II) differ appreciably only in the weak field region. In particular while the spectrum of I in $CDCl_3$ has, along with signals from two pairs of methyl groups (2.17, 2.23 ppm and 2,55, 2.65 ppm), two singlets for the protons 3-H (6.17 ppm) and 8-H (6.08 ppm), whereas only the signal for the pyridine proton is observed at weak field for compound II.

It should be noted rearrangement was not observed with ethanolic sodium ethoxide whereas the rearrangement product was isolated with aqueous ethylammonium bisulfite but in low yield (16%). This confirms the role of water in opening the pyrimidine ring which had been noted previously [4]. We observed a reduction in the signals of the pyrimidine methyl groups in the ^{1}H NMR spectrum of compound I in CD_3OD on the addition of CD_3ONa which is apparently due to basic deuterium exchange caused deprotonation as a result of attack on the methyl group by the nucleophile. This process is concurrent with the rearrangement.

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