DEALKYLATION DURING THE CYCLIZATION OF 2-PYRIDYLHYDRAZONES TO 3-METHYL-sym-TRIAZOLO[4,3-*a*]PYRIDINE

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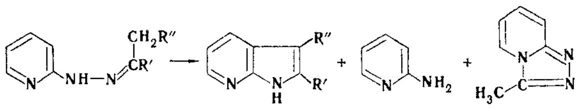
Investigations of the heterogeneous-catalytic synthesis of 7-azaindole on γ-Al_2O_3 and fluorinated aluminum oxide have shown [1] that the cyclization of acetaldehyde 2-pyridylhydrazone (Ia) under these conditions proceeds ambiguously: 3-methyl-sym-triazolo[4,3-*a*]pyridine (IV) is formed along with 7-azaindole (IIa) with 2-aminopyridine (III).



Ia-c IIa-c III IV

I, IIa R'=R''=H; b R'=CH₃, R''=H; c R'=R''=CH₃

On passing to acetone 2-pyridylhydrazone (Ib) and methyl ethyl ketone 2-pyridylhydrazone (Ic), we found that the same compound (IV) is formed as the sym-triazolo[4,3-*a*]pyridine derivative in all cases as a result of splitting out of a methyl or ethyl group, respectively.

The catalytic experiments were carried out under the conditions described in [1]. The benzene solutions of the catalyzates were evaporated, and the mixtures of products were subjected to chromatographic separation with a column filled with aluminum oxide (the separation was monitored by paper chromatography). Compounds I, II, and III were eluted with petroleum ether and diethyl ether, after which IV was eluted with chloroform. The yields of IV were 6-7% in all cases, and the product had mp 131-132°C. Found: C 63.0; H 5.2; N 31.3%. $C_7H_7N_3$. Calculated: C 63.1; H 5.3; N 31.6%. The trihydrate of IV had mp 58-59° (from benzene). The samples of IV did not depress one another's melting points nor the melting point of a genuine sample of IV obtained via the method in [2]. The IR spectra of all of the samples were identical.

Thus triazole ring closure of 2-pyridylhydrazones of aliphatic ketones is accompanied by C-dealkylation processes, which is apparently associated with the energetic advantageousness of the aromatic triazolopyridine system formed in the process.

LITERATURE CITED

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