BASIC PROTON EXCHANGE – A COMPETITIVE PROCESS UNDER KOST–SAGITULLIN REARRANGEMENT CONDITIONS

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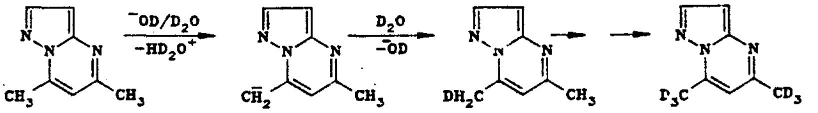
The conversions of pyrimidine ring systems, via the Kost-Sagitullin rearrangement, to give pyridine derivatives are known to be accompanied by competitive solvolysis processes, as well as decomposition and deamination reactions; in some cases, where the pyrimidine fragment of the molecule is not sufficiently active, or when there is very little excess electron density on the exocyclic carbon atom, these side reactions can become the dominating reaction pathways [1-3]. Thus, attempts to recyclize unsubstituted pyrazolo[1,5-a]pyrimidine led instead to the formation of 3-aminopyrazole, i.e., the molecule undergoes decomposition. 5,7-Dimethyl-5-methyl-7-phenyl- and 5-phenyl-7-methylpyrazolo[1,5-a]pyrimidines also do not undergo rearrangement [4].

We have found that basic proton exchange, as well as decomposition, can occur concurrently with recyclization, and thus can inhibit the course of recyclization in these systems. For instance, treatment of 5,7-dimethylpyrazolo[1,5-a]pyrimidine [1] with a solution of deuterated alkali led to the very rapid (over a period of several minutes) disappearance of the signals for the two methyl groups in the PMR spectra.



Isotopic exchange occurs in an analogous manner in unsubstituted pyrazolo[1,5-a]pyrimidine although here, as might be expected, the reaction takes place much less readily, due to the lower acidity of the ring CH bonds compared to the methyl groups. Based on analysis of the PMR spectra, we conclude that the pyridine ring proton located adjacent to the bridging nitrogen atom undergoes exchange first (the quartet at 9.09 ppm disappears as a result of deuterium exchange, and the quarter due to the 6-H proton is converted to a doublet as a consequence of the absence of spin–spin interaction between the 6-H and 7-H protons). After longer exposure to deuterated alkali, all the protons undergo exchange, but solvolysis also occurs to some extent. A similar type of basic proton exchange process has been noted previously in the case of N-substituted pyridines [5].

These types of reaction, leading to the formation of negative charge on the pyrimidine portion of the molecule, block direct nucleophilic attack on the pyrimidine ring, and thus inhibit isomerization, with which it acts as a competitive process.

LITERATURE CITED

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