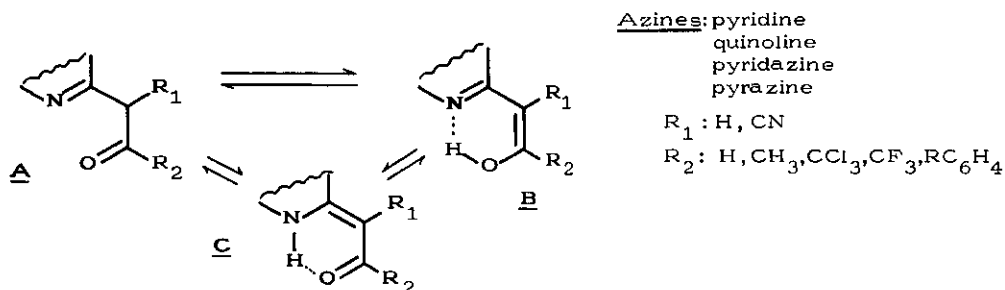


AZINYL-YLIDENE TAUTOMERISM OF ACYLMETHYL AZINES

S. A. Stekhova, V. V. Lapachov, O. P. Petrenko, V. P. Mamaev

Institute of Organic Chemistry, 630090 Novosibirsk, USSR

In the course of our systematic studies of azinyl-ylidene tautomerism¹, we have investigated the tautomerism of a wide range of acylmethyldiazines on the basis of multi-nuclear NMR approach (¹H, ¹⁴N and ¹⁷O nuclei).



Equilibria $A \rightleftharpoons B$ and $A \rightleftharpoons C$ (which are slow in the NMR time scale) were studied by ¹H and ¹³C NMR. Fast equilibria $B \rightleftharpoons C$, numerous reports of which are contradictory^{2,3}, were studied by ¹⁴N and ¹⁷O NMR (Bruker CXP-300 and WH-400 instruments).

The analysis of oxygen and nitrogen chemical shifts has been carried out for a series of model compounds containing iminoenole and enaminecarbonyl fragments (tautomers B and C, respectively). The solvent and substituent effects on equilibria are discussed. Electron accepting substituents (CF₃, CCl₃, CN) are shown to cause an almost complete shift of equilibrium towards the NH-tautomer C. The tendency of various azines to be transformed to ylidene form has been analysed by the PMO method. The results of this analysis are in good agreement with the experimental data, which show 3-pyridazine and 4-pyrimidine derivatives as the most liable and 2-pyrimidine derivatives as the least liable to produce the ylidene tautomer C.

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