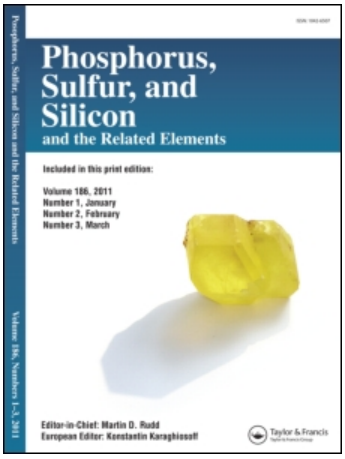

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Phosphorylation of Aminoheterocycles and Phosphorotropic Tautomerism

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PHOSPHORYLATION OF AMINOHETEROCYCLES AND PHOSPHOROTROPIC TAUTOMERISM

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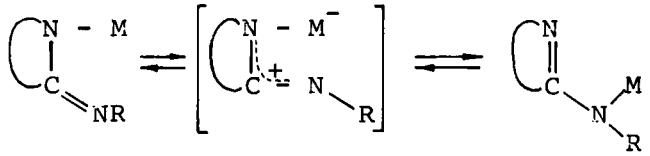
The reaction of phosphorylation of aminoheterocycles [aminodihydro(iminotetrahydro)-1,3-thiazines, amino(imino)-thiasoli(di)nes, amino(imino)pirroli(di)nes, isoindol(en)-ines] has been studied by means of NMR ^{1}H, ^{13}C, ^{31}P spectroscopy. The processes of intra- and intermolecular migrations of the phosphoryl groups P^{IV} between endo- and exocyclic nitrogens have been detected and examined.



M = $P(O)R^1R^2$, $P(S)R^1R^2$, $PR^1R^2R^3R^4$ $\Delta G^{\neq}$ 64 - 120 kJ/mol

Activation energies of migration of phosphoryl and trimethylsilyl groups in the isoindol(en)ines are comparable. It should have been expected that rapid phosphorotropic migrations must proceed also in the cyclic azoles, because silylotropic migrations proceed in these systems at extremely high rates. However, in phosphorylated pyrazoles and imidazoles degenerated phosphorotropic migrations have not been observed in the NMR time scale even at 200°C ($\Delta G^{\neq} \geqslant$ 100 kJ/mol). For the further study of the reaction mechanism of phosphorylation of aminoheterocycles the NMR ^{15}N spectroscopy has been employed.