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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Tbiophosphoryl-3(5)-Amino-4-Cyano(Ethoxycarbon Yl)Pyrazoles: Synthesis, Structure and Phosphorotropic Equilibrium

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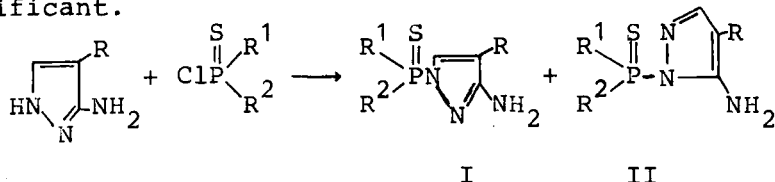
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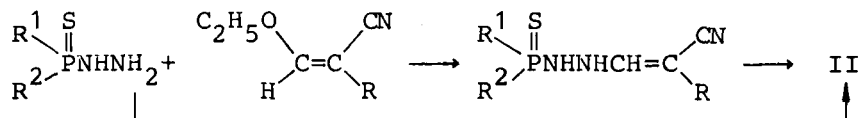
# THIOPHOSPHORYL-3(5)-AMINO-4-CYANO(ETHOXYCARBONYL) PYRAZOLES: SYNTHESIS, STRUCTURE AND PHOSPHOROTROPIC EQUILIBRIUM

L.V.RAZVODOVSKAYA, E.B.PUTSYKINA, M.V.ERIKOVA, N.A.KI-SELEVA, A.F.VASILYEV, A.F.GRAPOV, and N.N.MELNIKOV  
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 tecting Chemicals, Ugreshskaya 31, Moscow 109088, USSR

Methods of the synthesis of thiophosphorylated 3(5)-amino-4-cyano(ethoxycarbonyl)pyrazoles have been developed as a continuation of the work on phosphorylated aminoheterocycles. Two substitution products at the intracyclic N atom of the heterocycles, 3-amino-1-thiophosphorylpyrazoles (I) and 5-amino-1-thiophosphorylpyrazoles (II), are formed in the interaction of phosphoro- or phosphonothiochloridates with heterocycles; the yields of the products II are in-  
 significant.



The compounds II are obtained in high yields by intramolecular cyclization of  $\beta$ -(2,2-dicyanovinyl)- and  $\beta$ -(2-cyano-2-ethoxycarbonyl)hydrazidophosphorothioates and -phosphonothioates. The effect of structural factors on the cyclization process has been studied. The compounds II are also formed by direct condensation of the hydrazides of thio- phosphorus acids with ethoxymethylenmalononitrile or with ethoxymethylenecyanoacetic ester.



The presence of 1,2-phosphorotropic tautomerism I  $\rightleftharpoons$  II, catalyzed by thiophosphorylpyrazolium salts in the series of 3(5)-amino-1-thiophosphoryl-4-cyano(ethoxycarbonyl)-pyrazoles, was established by IR spectroscopy.