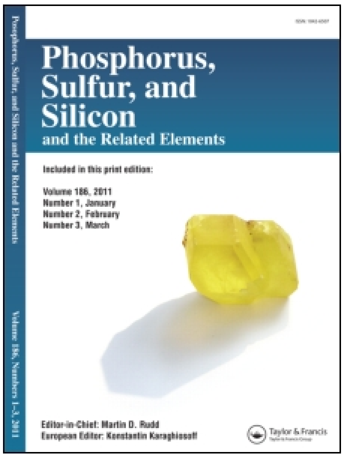

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INTERACTION OF PHOSPHORIC ANHYDRIDE WITH CH-, NH-, PH-, SH-ACIDS

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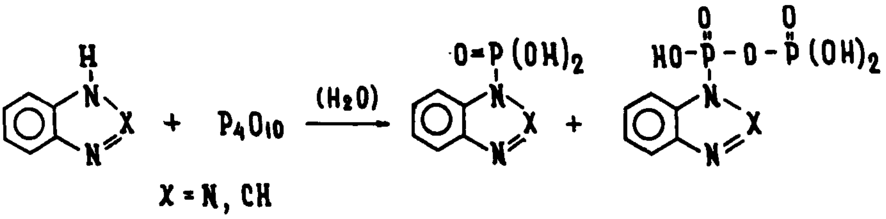
Abstract Phosphoric anhydride interacts with different CH-, NH-, PH-, SH-acids with the formation of corresponding amidophosphates and esters.

Phosphorus technology is one of the most unfavourable ecologically. Effective solution of the problem may be found in more active involving ecologically pure phosphoric anhydride in the technology.

There are several hundred articles published by now devoted to interaction of P_4O_{10} with organic substances. The majority of the described reactions occur due to its dehydrating ability. Only minority of the interactions result in phosphorylation of organic compounds: phosphoric anhydride interaction with different ethers, i.e. dialkyl-, ortho-, heteroatomic ethers, epoxides, amines, alkylphosphates, silanes, and some others. Little if any concideration has been given to analysis of phosphorus anhydride reactivity and its correlation with such variables as the nature of organic reagents, bond lability in reaction centre and conditions of the process.

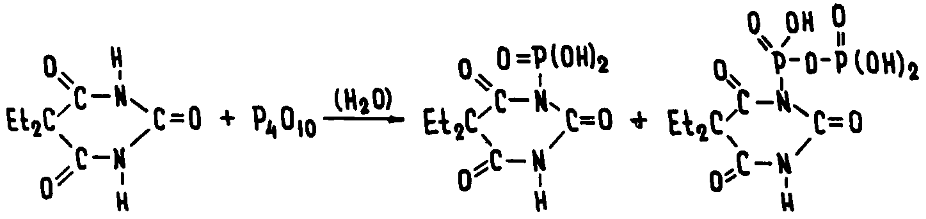
The purpose of the present paper is to broaden our outlook of synthetic possibilities of P_4O_{10} by its introduction into the reactions with CH-, NH-, PH-, SH-acids and some other compounds existing in different tautomeric forms such as keto-enol and amide-imide, and to detect the influence of tautomeric state on the selectivity of reactions.

Interaction of nitrogenheterocyclic compounds with P_4O_{10} is unknown by now. We have studied the reactions with NH-acids benzotriazole, benzimidazoles, and indole. Phosphoric anhydride reacts directly with benzotriazole and benzimidazoles to form corresponding phosphates and pyrophosphates. Interaction of P_4O_{10} with benzotriazole takes place at lower temperature and in less polar solvents than with benzimidazoles.

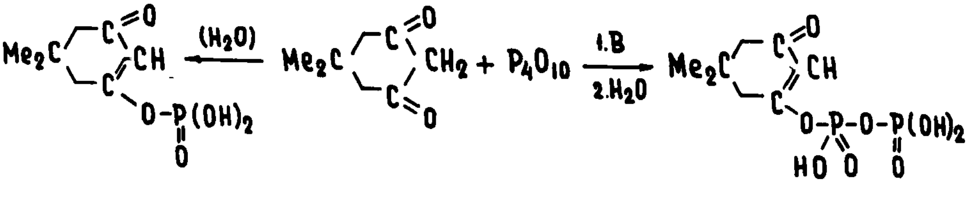


Indole does not react with P_4O_{10}, but its salt forms pyrophosphate.

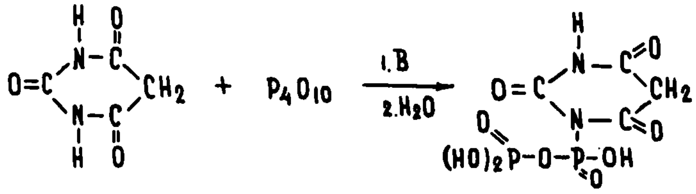
Barbital reacts with P_4O_{10} at low temperature at high rate to produce amidophosphate and some amidopyrophosphate.



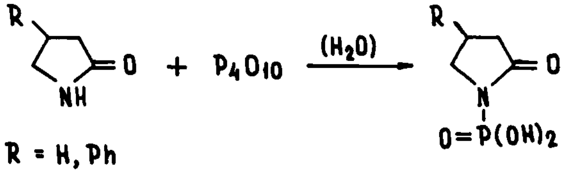
No O-phosphorylation product is registered. Cyclic β-diketones that can be represented as structural analogues of barbital undergo the reaction with P_4O_{10} only at high temperature and in polar solvents and form phosphates.



Introduction of corresponding salts in the reaction softens the conditions of the process and results in the formation of pyrophosphates with a high yield. Both tautomeric effects may occur in barbituric acid. Only its salt reacts with P_4O_{10} and produce pyrophosphates.

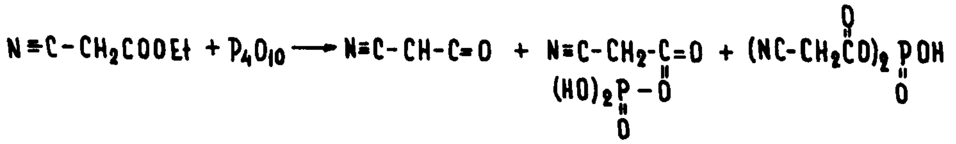


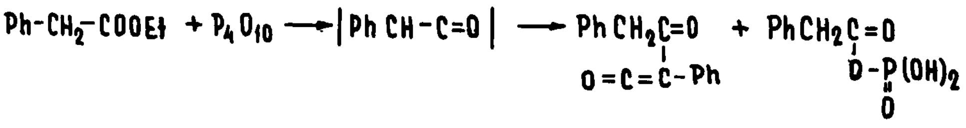
Pyrrolidones act in accordance with the regularity shown for barbital and barbituric acid.



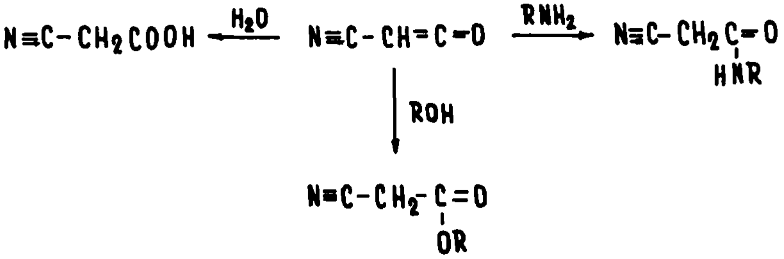
So the investigated heterocyclic compounds expose a tendency of N-phosphorylation by phosphoric anhydride and formation of corresponding pyrophosphates in the presence of bases. The acidic forms of organic reagents initiate further degradation of the pyrophosphates.

The reaction of P_4O_{10} with CH-acids, such as esters that contain CH_2-groups in α-position, is a specific one. At low temperature the reaction does not occur but the esters undergo dealcoholysis under heating and give rise to functional ketenes which easily go through secondary changes. The isolated products are listed below.





Formation of byproducts stands for the low yield of cyanoketene (30%) which was isolated in the form of colourless liquid (B.p.-34°C). Phenylketene was isolated in the form of dimer. In 1906 Diels described this kind of reactions for malonic ester which resulted in the formation of carbon suboxide. The method had not been extended since then. Cyanoketene exhibits the properties typical for ketenes but it is somewhat more chemically inert than carbon suboxide.



Interaction of P_4O_{10} with dialkylphosphites goes as deep as to formation of polyphosphates.

Under the action of P_4O_{10}, alkylthiols and their salts give rise to dialkyldisulphides whereas the salts of mercaptotetrazoles with phosphoric anhydride produce pyrophosphates.

$$2AlkSH \xrightarrow{P_4O_{10}} AlkS\text{-}SAlk$$