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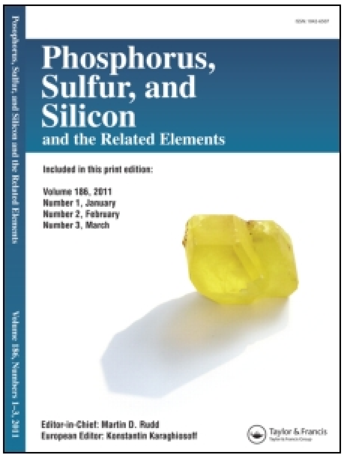

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INTERACTION BETWEEN PHOSPHORIC ANHYDRIDE AND ORGANIC COMPOUNDS WITH PROTOTROPIC PROPERTIES

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Abstract: Phosphoric anhydride has been shown to interact with organic compounds with prototropic properties, i.e. unsubstituted and monosubstituted amides, pyrimidinetriones, azoles and esters. Some products of phosphorylation have a tendency to exhibit phosphorotropy (1-3 and 1-4 shifts).

Key words: Phosphoric anhydride, phosphorylation, phosphorotropy.

The synthesis of various acidic phosphates is of high importance for medicinal and pharmaceutical chemistry as well as for industrial fire retardants, pesticides and photographic materials, etc. A variety of complicated and hazardous technological approaches are often used for the production of such compounds. Our study of the reactionof phosphoric anhydride with different types of organic compound has a potential for the development of a useful reagent for the preparation of acidic phosphates.[1-6]

Phosphoric anhydride reacts with many compounds which are able to tautomerise. The initial products are pyrophosphates but with careful hydrolysis of the residual phosphoric anhydride bonds it is possible to isolate phosphorylated products.

Cyclic compounds such as cyclohexane-1,3-diones are converted to the corresponding enol phosphates in satisfactory yields,[7] whereas pyrimidinetriones react with P_4O_{10} more readily forming N-phosphorylated amides.[8]

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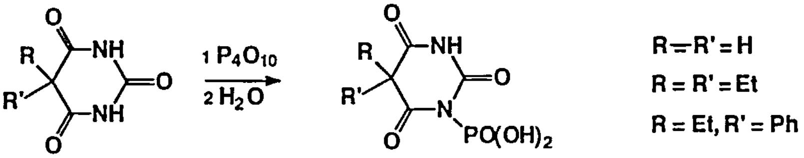
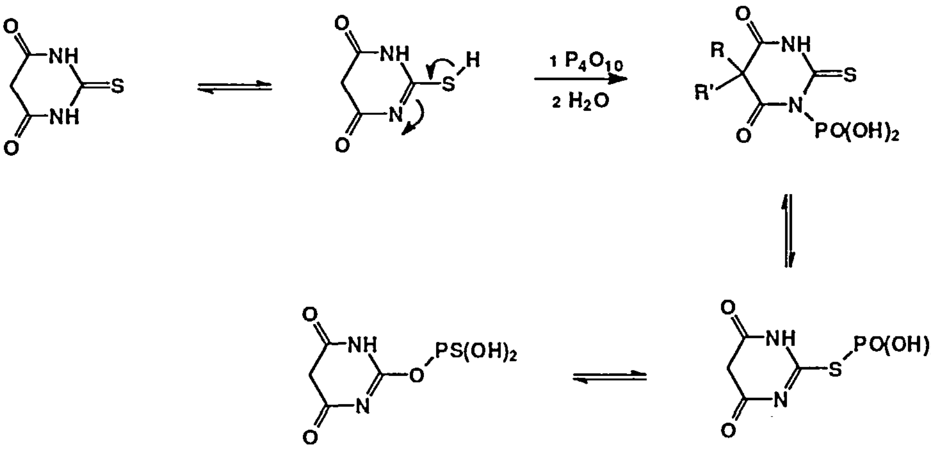
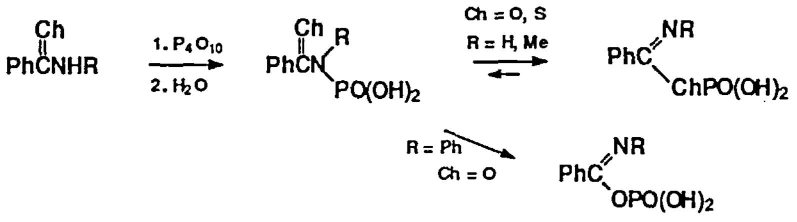


Thiobarbituric acid undergoes N-phosphorylation but this is not the terminal step of the reaction and the initial products rearrange reversibly to thiophosphate. ^{31}P NMR data indicated that the latter exists as an equilibrium of phosphorylthio-thiophosphoryl forms:

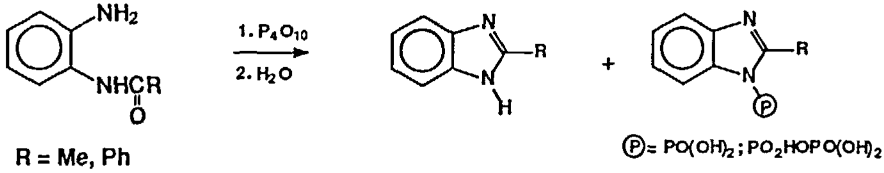


Whilst five-membered rings with the fragment NH-C(O) or NH-C(S), such as pyrrolidones and hydantoins are inert towards P_4O_{10}, thiohydantoin reacts with the formation of 3-N-(dihydroxophosphoryl)thiohydantoin for which no phosphorotropy was observed.

1-3 Shifts of the dihydroxyphosphoryl group is typical of phosphorylated non substituted amides.[1]. The process of phosphorylation followed by migration of the phosphorus group was monitored by means of ^{31}P NMR spectroscopy. Initial attack by P_4O_{10} was directed towards the more nucleophilic nitrogen atom. The primary products tend to be unstable and under the action of protic solvents or moisture rearrange to the corresponding O-phosphorylated amides. For benzamides and acetanilides N→O migration is reversible,[5] whereas phosphorylated benzanilides rearrange irreversibly:

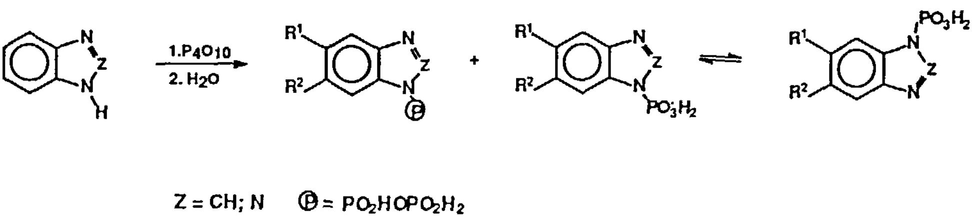


Acetanilides are reactive towards P_4O_{10} to give N-phosphorylated products. However, no intramolecular dehydration occurs[9] as observed in the reaction of N-acyl and N-benzoyl-o-phenylenediamines:[4]

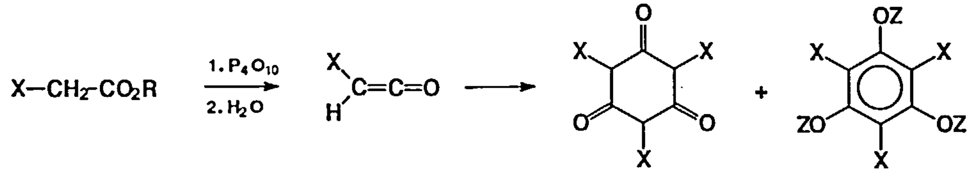


Benzoylhydrazine reacts with P_4O_{10} with phosphorylation of the terminal nitrogen. This is followed by a reversible rearrangement (1-4 shift) to give a mixture of O- and N-phosphorylated compounds:

Phosphorylated azoles[2] are produced readily from the corresponding parent compounds and P_4O_{10} :



The NMR data of phosphorylated 5,6-dimethylbenzotriazole supported the existence of facile phosphorotropy.[2] The reaction of P_4O_{10} and esters of monosubstituted acetic acid leads to the elimination of alcohol and gives monosubstituted ketenes that trimerise spontaneousely to give polysubstituted benzenes - 2,4,6-trisubstituted phloroglucinols and their derivatives:[3]



X = Ar, CN, NO_2; Z = H, $PO(OH)_2$, $PO(OH)OPO(OH)_2$

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