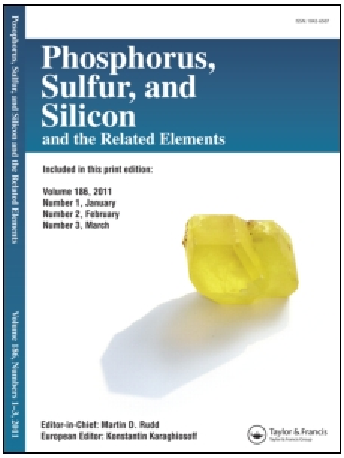

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REACTION OF DITHIOPHOSPHORIC ACID CHLORIDE BETAINE WITH BIFUNCTIONAL COMPOUNDS - A NEW ROUTE TO CYCLIC DITHIOPHOSPHATES

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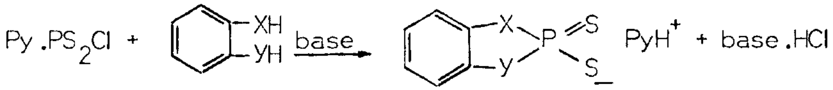
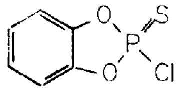
Dithiophosphoric acid chloride pyridinium betaine, Py.PS_2Cl (I)[1], can be widely used for the synthesis of various organophosphorus compounds.
I reacts in the presence of a base with an excess of nucleophiles like amines, alcohols or thiols to the corresponding disubstituted thiophosphoric acid derivatives[2-3].
In extension of this work it was found that a new synthetic approach to five membered cyclic dithiophosphates (II) is based on the reaction of bifunctional compounds like pyrocatechol or o-phenylenediamine with I in a molar ratio of 1:1 in the presence of a tertiary amine.



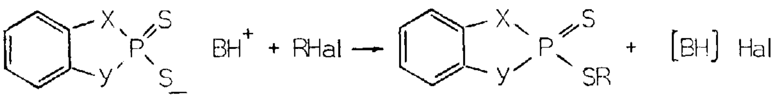
X = O, S, NH; Y = O, S, NH; Py = pyridine II

The phosphole derivatives II are obtained in 70-95 % yield. The 31P NMR chemical shifts of the phospholes are found in a range from 135 ppm to 95 ppm typical for dithiophosphoric acid derivatives.
The exchange of O by S and NH in II leads to an upfield shift of δ 31P which is caused by an increased shielding of the P nucleus.
The failure of the stretching frequencies of free OH, SH and NH_2 groups, respectively, in the infrared spectra of the compounds mentioned above evidences the proposed phosphole structure.
In the case of the reaction of I with pyrocatechol it has been proved that also an excess of nucleophile exclusively leads to the phosphole derivative besides unreacted pyrocatechol.

We did not find any indication for the formation of penta or hexacoordinated species as it was observed on the reaction of P_4S_{10} or  with pyrocatechol[4-5].

The phosphole derivatives II are stable crystalline, non-hygroscopic compounds which can recrystallized from alcohols. On treatment with water no hydrolysis of II takes place. In the presence of amines or ammonia only the pyridinium cation is exchanged.

Like most dithiophosphoric acid salts II can be converted into the corresponding S-alkylesters by reaction with alkyl halides and α-halogen carbonyl compounds, respectively:

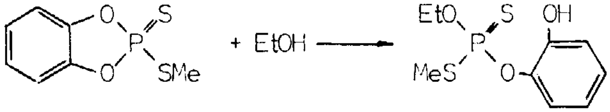


III

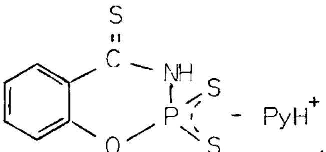
a: X = Y = O; R = Me
b: X = O; Y = NH; R = Me
c: X = S; Y = NH; R = Me
d: X = S; Y = NH; R = CH_2Ph
e: X = S; Y = NH; R = CH_2COPh
f: X = NH; Y = NH; R = Me

A comparison of the mass spectra showed that the compounds of type II and III, especially the S-alkylesters own a very similarity in the fragmentation pattern.

Considering the reactivity of the compounds of type III there are some differences. Whereas, e.g., III b and III c do not react in boiling MeOH or EtOH III a yields under ring cleavage the o-hydroxyphenyl-O-ethyl-S-methyl dithiophosphate:

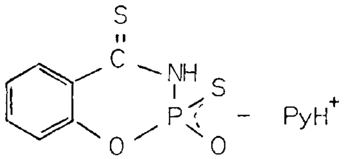


On melting salicylamide with I in different molar ratios two sixmembered cyclic thiophosphates are obtained:



IV

δ 31P + 88 ppm (d)

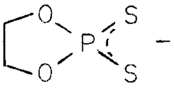
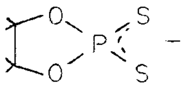
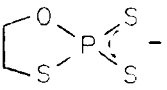
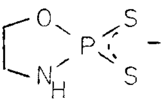
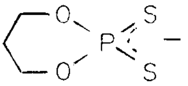
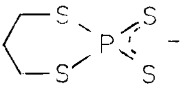


V

δ 31P + 39 ppm (d)

According to their infrared spectroscopic data both compounds contain the thiocarbonyl group. The sulfuration of the carbonyl group most likely occurs in the first stage of the reaction. The presumable mechanism consists in a primary interaction of the P-Cl group of I with the amido group of the salicylamide followed by oxygen-sulfur exchange and, finally, ring closure to V. By alkylation of IV with alkyl halides in acetone the corresponding S-alkylesters are obtained in 80-90 % yield.

TABLE I 31P NMR chemical shift of some cyclic dithiophosphates

compound	δ 31P (ppm)
	+ 130
	+ 121
	+ 125
	+ 121
	+ 110
	+ 77

Different to the biphilic aromatic compounds bifunctional aliphatic nucleophiles do not react exclusively with I to the corresponding cyclic thiophosphates. The ratio of cyclic and acyclic compounds formed by this reaction depends on the molar ratio of the starting components.

The best yields of cyclic compounds are obtained by reacting of I with an aliphatic biphile in a molar ratio of 1:1.

The 31P NMR chemical shifts (table I) show a similar dependence on the atoms attached to phosphorus as it was found for the aromatic derivatives. Furthermore an increasing shielding is observed on the transition from a five to a sixmembered ring system.

The structure of all prepared compounds has been confirmed by mass- and NMR-spectroscopic investigations.

Summarizing our results it can be stated that we have not found any restriction for the general applicability of this synthesis based upon ring closure reaction of biphiles with Py.PS_2Cl.

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