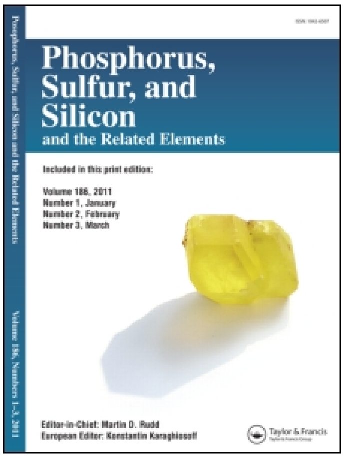

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NEW DIAZA AND THIAZADIPHOSPHETIDINES FROM THE DITHIOPHOSPHORIC ACID CHLORIDE BETAINE AND PRIMARY AMINES VIA MONOMETAPHOSPHATE ANALOGOUS INTERMEDIATES

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Abstract Under definite conditions the dithiophosphoric acid chloride pyridinium betaine reacts with primary amines, RNH_2, yielding four-membered rings. Depending on the electronic properties of R either diaza or thiazadiphosphetines are formed. An elimination-addition mechanism via imido dithiomonometaphosphate is discussed.

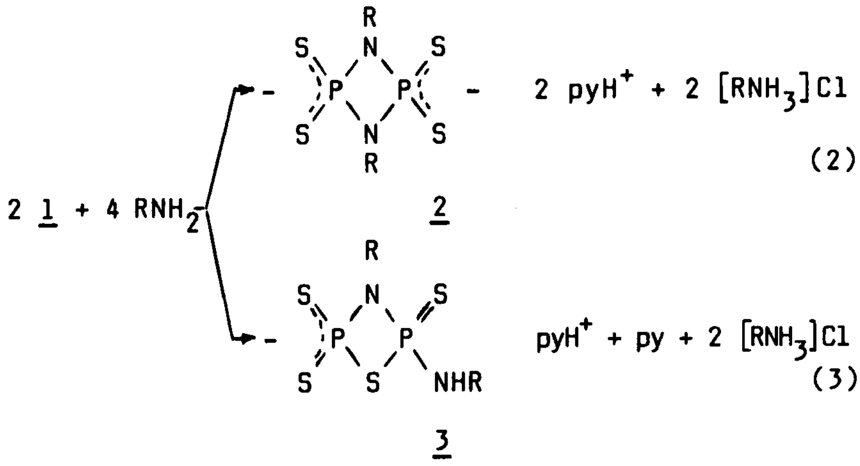
The dithiophosphoric acid chloride pyrididium betaine (1), $py \cdot PS_2Cl$ (py = pyridine) - a versatile and convenient intermediate[1-3] - reacts with an excess of primary or secondary amines to the corresponding diamido dithiophosphates:

$$\underline{1} + 4\ RR'NH \longrightarrow [RR'NH_2]\ [(RR'NH)_2PS_2] + [RR'NH_2]Cl \qquad (1)$$

In a completely other way the reaction occurs with primary amines in a molar ratio of amine:betaine = 2:1 or 1:1 in presence of e.g. triethylamine.

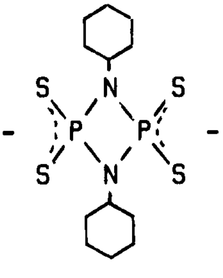
An extended study of this reaction has shown that depending on the amine used either preferably diaza or thiazadiphosphetidines of a new type are formed. It was found that aromatic or araliphatic amines give the diazadiphosphetidines (2) in high yields corresponding to equ. (2), whereas with aliphatic amines in general these compounds can be obtained only in small amounts.

The diazadiphospetidines were alkylated and then characterized by elemental analysis, NMR and mass spectrometry.



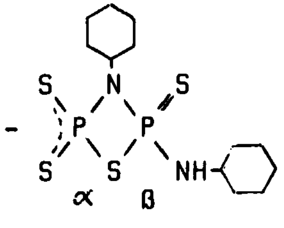
The methyl ester of the dibenzyl-diazaphosphetidine (1,3-dibenzyl-2,4-methylmercapto-2,4-dithioxo-1,3-diaza-2λ^5,4λ^5-diphosphetidine) is obtained as a mixture of two isomers, the crystal structure of which has been determinded.[4]

In the ^{31}P-NMR spectrum of the reaction product of 1 and cyclohexylamine in the presence of NEt_3 (molar ratio 1:1:2) a singlet (85,5 ppm) and two doublets are observed (74,3 and 46,1 ppm). The singlet is assigned to the diazadiphosphetidine 2a. Because of the same coupling constant the doublets are assigned to the diazadiphosphetidine 3a:



2a

^{31}P 85,5 ppm



3a

$^{31}P_{\alpha}$ 74,3 ppm; P_{β} 46,1 ppm

Reaction of cyclohexylamine with 1 in a 2:1 molar ratio leads only to 3a. The constitution of this compound has been confirmed by methylation, elemental analysis, the NMR and mass spectra of the methyl ester.

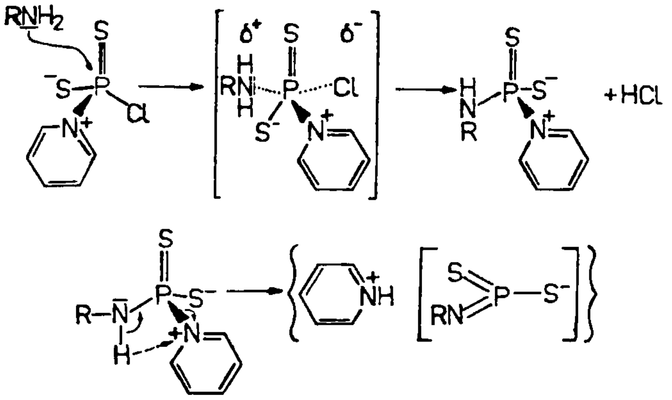
In a 2:1 molar ratio aliphatic amines preferably react to thiazadiphosphetidines (equ. (3)).

The following tendency of formation of thiazadiphosphetidines from aliphatic amines has been observed:

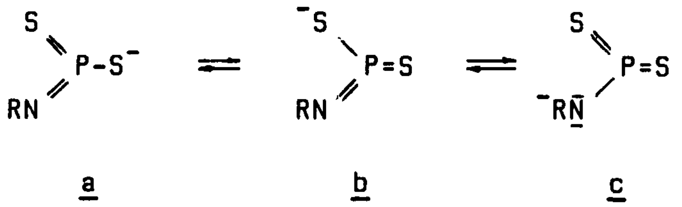
t-butyl > i-propyl > cyclohexyl > n-propyl

The tendency of formation of either diaza or thiazadiphosphetidines depends to a high degree on the amine used. Electron-withdrawing substituents (corresponding to decreasing basicity; R = aryl, benzyl) direct to the diazaphosphetidine ring, whereas electron-releasing groups (increasing basicity; R = alkyl) favor thiazadiphosphetidines. Steric effects also influence this reaction. Thus, the tendency of formation of 3 is also increased by bulky rests (R = t-butyl, i-propyl).

The presumable reaction mechanism consists in the primary formation of an amide betaine followed by an intramolecular proton migration yielding the tri-coordinated imido dithiomonometaphosphate, $RN = PS_2^-$

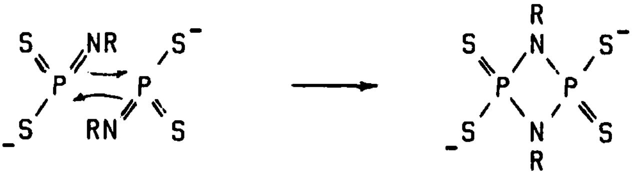


Depending on the substituent R at nitrogen several resonance structures of this intermediate are possible:



(4)

Electron-withdrawing groups favor the structures a and b and the stabilization of the reactive intermediate follows by /2+2/ cycloaddition at two P=N double bonds yielding diazaphosphetidines 2:



(5)

Electron-releasing substituents increase the basicity of nitrogen and so the amidate form c will appear in the equilibrium.

Thus, a /2+2/ cycloaddition at one P=N and one P=S bond will be possible yielding the thiazadiphosphetidine 3.

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