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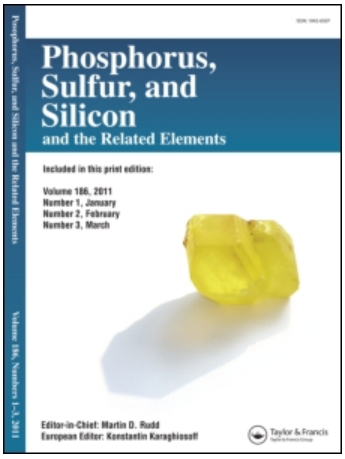

Phosphorus, Sulfur, and Silicon and the Related Elements

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Reactions of Phosphoryl and Thiophosphoryl Isocyanates and Isothiocyanates with Secondary Amines and Phosphines

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REACTIONS OF PHOSPHORYL AND THIOPHOSPHORYL ISOCYANATES AND ISOTHIOCYANATES WITH SECONDARY AMINES AND PHOSPHINES

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The addition of secondary amines and phosphines to a phosphorylated or thiophosporylated isocyanate or isothiocyanate group occurs according to equation (1) in a *reversible* equilibrium reaction.

$(PhO)_2P(X)NCY + HZR_2 \rightleftharpoons (PhO)_2P(X)\text{-}NH\text{-}C(Y)\text{-}ZR_2$ (1)

	1	2	3	4
X	O	O	S	S
Y	O	S	O	S

R = alkyl, aryl

Z = N, P

	5	6	7	8	9	10
X	O	O	S	S	O	S
Y	O	S	O	S	S	S
Z	N	N	N	N	P	P

The degree of the formation of the corresponding derivatives of phosphorylated ureas **5** - **10** depends on the electrophilic properties of the NCY group, on the nucleophilicity of HZR_2 as well as on the temperature.

1 and **3** form with dialkyl and diaryl amines **5** and **7**, respectively, in a nearly quantitative yield. The addition reaction of dialkylamines with **2** and **4** proceeds in most cases without any complication **6** and **8**, respectively, whereas diphenylamine reacts only in form of the potassium salt. The addition products **9** and **10** of diorganylphosphines (R= Ph, Et) with **2** and **4** have been isolated only at low temperature (-25 °C). The compounds $(PhO)_2P(O)\text{-}NH\text{-}C(O)\text{-}NMePh$, $(PhO)_2P(S)\text{-}NH\text{-}C(S)\text{-}NMePh$, and $(PhO)_2P(O)\text{-}NH\text{-}C(S)\text{-}PPh_2$ were characterized by x-ray crystal structure analysis[1, 2].

The shift of the equilibrium (1) in dependence on the temperature was studied by NMR spectroscopy. Solving well characterized pure samples

of **6** the signal of the educt **2** is observed. The dissociation increases with rising temperature. The equilibrium (1) is on the left side in case of the compounds **9** and **10**. Compounds of the type **8** are more stable. Signals of **4** are observed only after shaking solutions of **8** with diluted mineral acids.

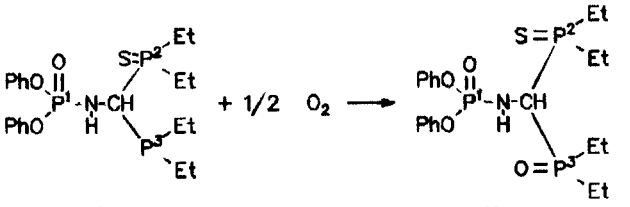
The compounds **9a** and **9b** and solutions of **9c** are not stable at room temperature. They undergo decomposition, and **11** is formed according to equation (2).

$$(PhO)_2P(O)\text{-}NH\text{-}C(S)PR_2 \xrightarrow{+\ HPR_2} (PhO)_2P(O)\text{-}NH\text{-}\underset{\displaystyle P(S)R_2}{\underset{|}{C}}H\text{-}PR_2 \qquad (2)$$

9a, 9b, 9c **11a, 11b, 11c**

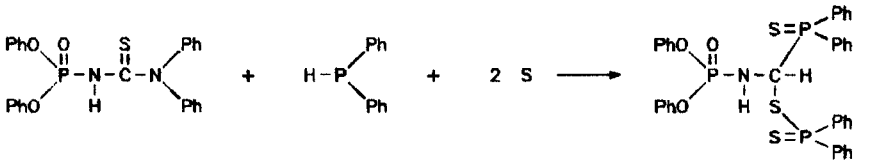
a: R = Ph, **b:** R = Et, **c:** R = Pr

Under the influence of air **12** reacts to **13**.



11b **12b** (3)

9a reacts in benzene with sulfur forming **13** according to equ. (4)



9a **13** (4)

1,1-Diorganyl derivatives of urea react similar to equation (1) with **1**, **2**, **3** and **4** yielding the phosphorylated derivatives of the biuret.

$$(PhO)_2P(X)NCY + H_2N\text{-}C(O)\text{-}NR_2 \longrightarrow (PhO)_2P(X)\text{-}NH\text{-}C(Y)\text{-}NH\text{-}C(O)\text{-}NR_2 \qquad (5)$$

1, 2, 3, 4

	14	**15**	**16**	**17**
X	O	O	S	S
Y	O	S	O	S

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However, with phosphorylated isothiocyanates the reaction (5) occurs incompletely. Beside the addition reaction the substitution reaction (5) is observed in these cases and byproducts as e.g. **14** and **16** are formed.

$$(PhO)_2P(X)NCS + H_2N\text{-}C(O)\text{-}NR_2 \longrightarrow (PhO)_2P(X)\text{-}NH\text{-}C(O)\text{-}NR_2 + HSCN \longrightarrow$$

$$\xrightarrow[-\,[H_2NR_2]SCN]{} (PhO)_2P(X)NCO \xrightarrow{+\,H_2N\text{-}C(O)\text{-}NR_2} (PhO)_2P(X)\text{-}NH\text{-}C(O)\text{-}NH\text{-}C(O)\text{-}NR_2 \quad (6)$$

The phenoxy(thio)phosphoryl diisothiocyanates **18** and **19** react with secondary amines in three different ways (equation (7)-(9)):

$$(PhO)P(X)(NCS)_2 + 2\ HNR_2 \longrightarrow (PhO)P(X)(NH\text{-}C(S)\text{-}NR_2)_2 \quad (7)$$

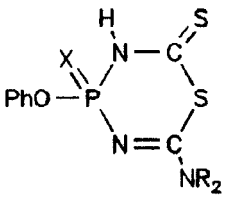
	18	**19**
X	O	S

20

$$(PhO)P(S)(NCS)_2 + 2\ HNR_2 \longrightarrow (PhO)P(S)(NCS)NR_2 + [H_2NR_2]SCN \quad (8)$$

R = alkyl **21**

$$(PhO)P(X)(NCS)_2 + HNR_2 \longrightarrow \quad (9)$$



22

It is possible to obtain all three types of compounds **20, 21** or **22** in good yields by variation of the reaction conditions and the kind of amine.

For X = S a compound of the type **20** can be synthesized with diphenylamine. With dialkylamines the corresponding dialkylammonium salts $(PhO)P(X)(NH\text{-}C(S)\text{-}NR_2)_2 \cdot HNR_2$ **23** are formed, which are however unstable. By standing for a longer time at room temperature from **23** (X = S) a compound $(PhO)_2P(S)(NR_2)\text{-}NH\text{-}C(S)\text{-}NR_2$, **24**, is yielded. The formation of **24** occurs via the substitution product **21**, which can be obtained separately according to equation (8), if the dialkylamine and

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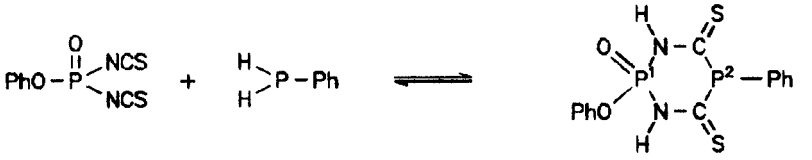
20 are used in the ratio 2:1. $(PhO)P(O)(NH\text{-}C(S)\text{-}PR_2)_2$, **24**, and $(PhO)P(O)(NCS)NH\text{-}C(S)\text{-}PR_2$, **25**, was observed in a reaction of diphenylphosphine with **18** , similar to equation (8).

With **18** compounds of the type **22** are obtained in a high yield. Dialkylamines form the corresponding ammonium salts. Their structures were determined by NMR spectroscopy and x-ray crystal structure analysis.

Phenylphosphine reacts with **18** and according to equation (10) the derivative **25** of a 1,3,2,5-diazaphosphorinane is formed.



(10)

25

The thiophosphorylated thioureas **8** are excellent extractants for weak metal ions. They form square planare complexes with nickel[3] and with copper(I) a complex $[Cu(PhO)_2P(S)NC(S)NR_2]$[4].

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