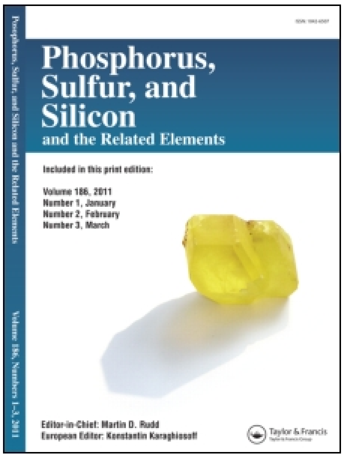

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New Investigation on the Reaction of $PhP(S)(NCS)_2$ and $C_6H_{11}P(S)(NCS)_2$ with Amines

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NEW INVESTIGATION ON THE REACTION OF PHP(S)(NCS)$_2$ AND $C_6H_{11}P(S)(NCS)_2$ WITH AMINES

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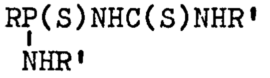
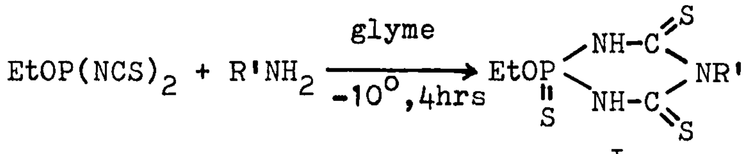
Abstract RP(S)(NCS)$_2$ reacting with R'NH$_2$ gave the corresponding substituted thioureas and new compounds with the general formular,



$$\underset{\displaystyle NHR'}{RP}(S)NHC(S)NHR'$$

where R = ph, C_6H_{11}; R' = i-C_3H_7, i-C_5H_{11}.

It has been reported in the previous paper(1) and the last symposium(2) that the reaction of O-ethyl(or O-phenyl) bis(isothiocyanatido)phosphorothioate, ROP(S)(NCS)$_2$(R= Et or ph), with primary aromatic amine gave the dithiourea derivatives, ROP(S)(NHC(S)NHR')$_2$, where R' = $-C_6H_4Cl$, $-C_6H_4OMe$, $-C_6H_4NO_2$ etc. and that similarly when O-ethyl bis(isothiocyanatido)phsophorothioate reacted with isopropyl- or isoamylamine in 1 to 2 moleculer ratio in glyme at low temperature cyclic compounds of type I were obtained in quite low yields (26-43%).



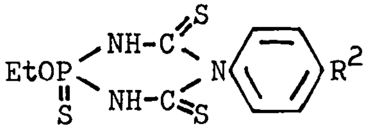
I

(1).

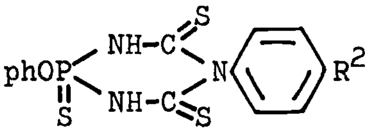
where R' = i-C_3H_7, i-C_5H_{11}

In order to synthesize more cyclic compounds I for searching new herbicides and to study further the reactions involved more work has been done.

O-Ethyl(or O-phenyl) bis(isothiocyanatido)phosphorothioate reacted with equimoleculer aniline and substituted anilines separetely in toluene at -60°C to room temp.. A number of new ethoxy and phenoxy cyclic compounds II and III were formed.



II

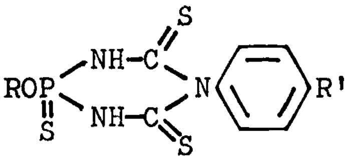


III

where R^2 = H, CH_3, Cl, Br.

The experimental results were listed in table 1 and some of their IR, ^{1}HNMR and MS given.

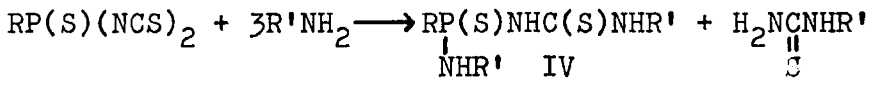
Table 1.



R	R'	m.p.(°C)	yield(%)
ph	H	111-2	98.1
ph	Me	110-1	92.3
ph	Cl	111-2	88.0
ph	Br	109-11	97.9
Et	H	79-80	65.9
Et	Me	92-4	61.3
Et	Cl	112-3	88.1
Et	Br	106-7	85.6

It seemed that at low temp.(-60° - 0°C) with toluene or MeCN as the solvent the aromatic amines gave better yields than the aliphatic such as isopropyl- or isoamylamine. For instance, compound II with $R^2 = H$ was formed in 65.9% yield when aniline was dropped slowly into the solution of O-ethyl bis(isothiocyanatido)phosphorothioate at -60°C. If the reaction temperature was raised to -20°- -15°C, the yield would be lowered to 43.5%.

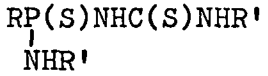
However, when the experiments were repeated with 1:3 molecular ratio of $RP(S)(NCS)_2$ and $R'NH_2$, where R = ph, C_6H_{11}; R' = $i\text{-}C_3H_7$, $i\text{-}C_5H_{11}$ in toluene at room temp.,



$$RP(S)(NCS)_2 + 3R'NH_2 \longrightarrow \underset{\displaystyle NHR'\quad IV}{RP(S)NHC(S)NHR'} + H_2N\underset{\underset{\displaystyle S}{\|}}{C}NHR' \qquad (2)$$

neither bis(thioureido)phosphorus compound nor the cyclic compound was obtained, but the corresponding substituted thioureas and new compounds with the general formula IV were resulted as shown in the reaction equation (2). See Table 2.

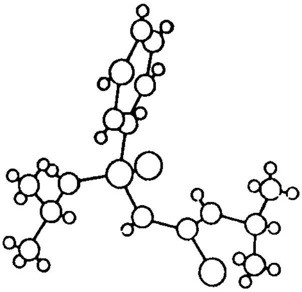
Table 2.



$$\underset{\displaystyle NHR'}{RP}(S)NHC(S)NHR'$$

R	R'	m.p.(°C)	yield(%)
ph	$i\text{-}C_3H_7$	94-5	57.1
ph	$i\text{-}C_5H_{11}$	oil	45.7
C_6H_{11}	$i\text{-}C_3H_7$	134-6	55.4
C_6H_{11}	$-C_6H_4CH_3$	38-41	65.2

The structure of the product IV was confirmed by X-ray diffraction(R = ph, R' = $i\text{-}C_3H_7$) in addition to the elemental analysis and ^{1}HNMR.



A view of the $PhP(=S)(NHC(=S)NHC_3H_7\text{-}i)(NHC_3H_7\text{-}i)$ molecule

Obviously in this reaction, the addition of the amine to one of NCS groups in the bis(isothiocyanatido)phosphonothioate goes first and then another NCS group was replaced by the amine via SN2 attack to thiophosphoryl group. A qualitative test was made to prove this mechanism. Red colour appeared immediately as soon as the solution of isopropylamine in glyme was added to the solution of phP(S)(NCS)$_2$ when a small amount of FeCl$_3$ was dropped in, and the colour faded away gradually after the addition of more isopropylamine. It indicated that one of the NCS groups in phP(S)(NCS)$_2$ was added and another substituted by amine with the formation of IV and H$^+$SCN$^-$ which reacted with the excess amine to form the corresponding thiourea.

REFERENCES

(1) Chen Ruyu; Yang Huazheng and Hu Shixian, Scientia Sinica (Series B), 26 (9), 917-30 (1983).

(2) Chen Ruyu; Hu Shixian, Phosphorus and Sulfur, 18, (1/2/3), 415 (1983).