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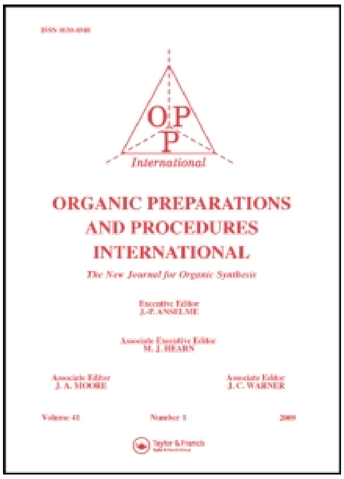

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PHOSPHORUS, ARSENIC, SILICON AND METAL DERIVATIVES OF THIOUREA. A REVIEW

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PHOSPHORUS, ARSENIC, SILICON AND METAL DERIVATIVES OF THIOUREA. A REVIEW

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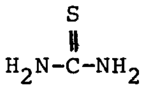
I. INTRODUCTION

The literature dealing with thioureas is quite voluminous. Several general reviews dealing with the chemistry of thioureas have appeared in recent years.[1-6] In addition, there have been specialty reviews on topics such as sulfanilyl- and sulfanylthioureas,[7] as well as the use of thioureas in the preparation of heterocyclic compounds.[8] This review will be concerned only with the synthesis and some reactions of phosphorus, arsenic, silicon and metal derivatives of thiourea. Chemical Abstracts was covered from volume 1, 1907 through volume 83, 1975. In addition, Current Abstracts of Chemistry - Index Chemicus was covered for the period of January 1964 through December 1974. Only those compounds forming a true bond from the metal or metalloid to an atom on the thiourea molecule will be included in this review: metal complexes are excluded.

Among the applications of these derivatives that have been found, and the metal bound to the thioureas are the following: bactericidals (mercury), fungicides (silicon, mercury), insecticides (phosphorus), lubricants (phosphorus) and antioxidants (silicon).

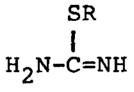
II. SHORT REVIEW OF THE PREPARATION OF THIOUREAS

One or more hydrogen atoms of thiourea 1 may be substituted by an aliphatic or an aromatic moiety. The S-substituted derivatives of thiourea (2) are known as isothioureas or pseudothioureas. Whereas thiourea is a very weak base, isothioureas are strongly basic and form isothiuronium salts



$H_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}NH_2$

1



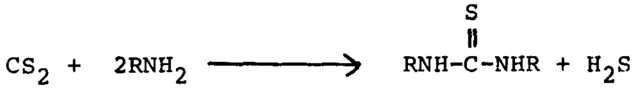
$H_2N\text{-}\overset{\overset{SR}{|}}{C}\text{=}NH$

2

R = alkyl,
aryl

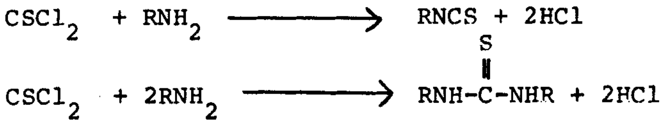
with acids. There are several standard ways of preparing thioureas. Some of these are summarized here. For greater detail, references 1-3 should be consulted.

The reaction of carbon disulfide with primary amines affords 1,3-disubstituted thioureas; secondary amines do not give the corresponding tetrasubstituted compounds.



$$CS_2 + 2RNH_2 \longrightarrow RNH\text{-}\overset{\overset{S}{\|}}{C}\text{-}NHR + H_2S$$

Thiophosgene may be reacted with primary amines to give either an isothiocyanate or a 1,3-disubstituted thiourea, depending upon the ratio of the reactants.



$$CSCl_2 + RNH_2 \longrightarrow RNCS + 2HCl$$

$$CSCl_2 + 2RNH_2 \longrightarrow RNH\text{-}\overset{\overset{S}{\|}}{C}\text{-}NHR + 2HCl$$

Secondary amines give only symmetrical thioureas.

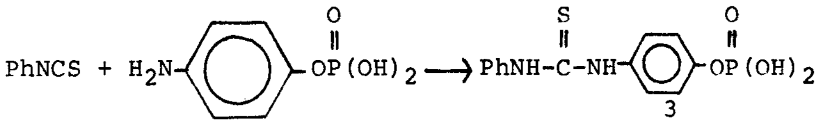
Unsymmetrical thioureas are most commonly prepared by the reaction of an isothiocyanate with an amine. Ammonia, primary or secondary amines may be used yielding 1-mono-, 1,1- or 1,3-di- or 1,1,3-trisubstituted thioureas, respectively.

The reaction of thioureas with alkyl, aralkyl and heterocyclic halides proceeds to give S-thiourea derivatives. Acylation of thioureas occurs initially at the sulfur atom upon being heated or sometimes standing at room temperature, the acyl group migrates to an N-position. Treatment of monoarylthioureas with an acyl halide gives the S-acyl-N-aryl derivative which upon heating is converted first to the 1-aryl-1-acyl- then to the 1-aryl-3-acylthiourea.

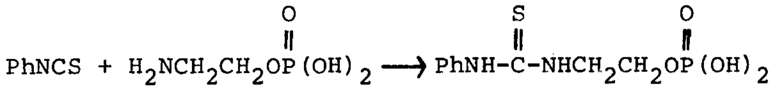
III. PHOSPHORUS DERIVATIVES

a. Preparation of Thioureas from Isothiocyanates

Esters of phosphoric acid containing a thiourea moiety (3) on the ester chain have been prepared by the condensation of *p*-aminophenyl esters of phosphoric acid with an aromatic isothiocyanate.[9] Aminoalkyl ester derivatives 4 have also been prepared by the reaction of the appropriate phosphoric acid ester with an aromatic isothiocyanate.[10,11]



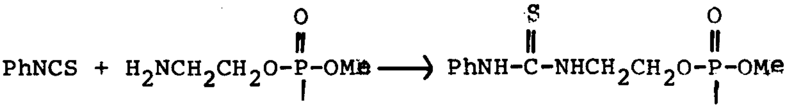
3



$$\mathrm{PhNCS} + \mathrm{H_2NCH_2CH_2O\overset{\overset{O}{\|}}{P}(OH)_2} \longrightarrow \mathrm{PhNH\text{-}\overset{\overset{S}{\|}}{C}\text{-}NHCH_2CH_2O\overset{\overset{O}{\|}}{P}(OH)_2}$$

4

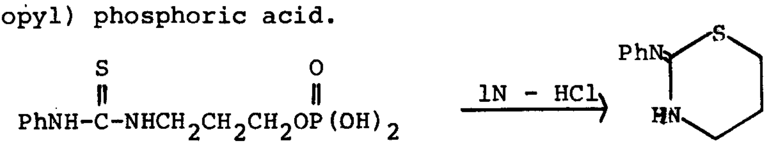
Phosphonate derivatives of thiourea (5) have been synthesized in a similar fashion.[11]



$$\mathrm{PhNCS} + \mathrm{H_2NCH_2CH_2O}\text{-}\underset{\mathrm{Ph}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}\text{-}\mathrm{OMe} \longrightarrow \mathrm{PhNH}\text{-}\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{NHCH_2CH_2O}\text{-}\underset{\mathrm{Ph}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}\text{-}\mathrm{OMe}$$

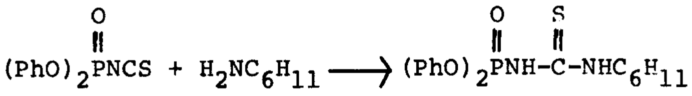
5

When O-[3-(phenylthiocarbamoylamino)propyl] phosphoric acid (6) is cleaved in 1 N hydrochloric acid, an intramolecular cyclization occurs to yield 2-(phenylimino)tetrahydro-1,3-thiazine (7).[12] The starting material is prepared by the condensation of phenyl isothiocyanate with O-(3-amino-1-propyl) phosphoric acid.



6 7

Kenner and co-workers prepared diphenoxyphosphinyl-3-cyclohexyl-2-thiourea (8) from diphenyl phosphoroisothiocyanatidate and cyclohexylamine.[13]

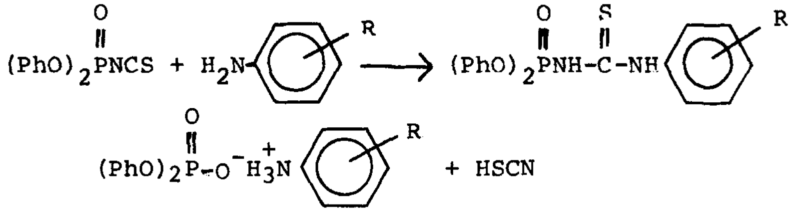


$$\mathrm{(PhO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{NCS} + \mathrm{H_2NC_6H_{11}} \longrightarrow \mathrm{(PhO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{NH}\text{-}\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{NHC_6H_{11}}$$

8

In a similar fashion, a variety of tolyl- and pyridylamines were condensed with the isothiocyanate.[14] These products are also known as derivatives of thiocarbamoylphosphoramidic acid. Thus, the latter thiourea derivatives may be called phenyl esters of N-tolyl- and N-pyridylthiocarbamoylphosphoramidic acid. Galstukova and co-workers[15] used this reaction to prepare a variety of derivatives containing cycloaliphatic and aromatic heterocycles.

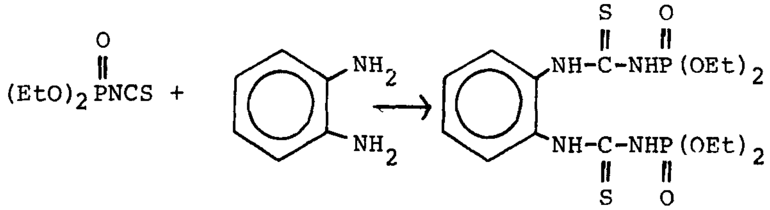
Elmore and Ogle[16] studied the condensation of diphenyl phosphoroisothiocyanatidate with aromatic amines in inert solvents to yield the corresponding thioureas. They found that some of these diphenyl N-arylthiocarbamylphosphoramidates readily undergo hydrolysis to the corresponding anilinium diphenylphosphates and thiocyanic acid.



They thought this labile property to be due to the electron-attracting substituents, since use of butyl or cyclohexyl substituents afforded stable thiourea derivatives.

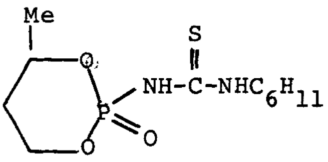
Levchenko and Sheinkman[17] found that the ester portion of the sodium salt of diethyl 3-hydroxy-4-carboxyphenylthiocarbamylphosphoramidate and other esters may also play a role in the stability of this type of compound. They demonstrated that an electron-donating group such as an alkyl substituent has a stabilizing influence. Structures for these adducts have been suggested on the basis of alcoholysis studies, infrared spectra and by analogy with previously studied systems.[18]

1-(3-Disubstituted phosphonothioureido)-2-(3-substituted thioureido)benzene derivatives (9) were prepared by the reaction of 1,2-diaminobenzene derivatives with dialkyl phosphoroisothiocyanatidates.[19]



9

Stereoisomeric derivatives of thiourea were prepared through the reaction of cyclohexylamine with diastereoisomeric 2-isothiocyano-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes to give the N-cyclohexyl-N'-(4-methyl-1,3,2-dioxaphosphorinan-2-yl)-p-oxide thioureas.[20] The *cis* P-oxide and *trans* P-oxide are shown as 10 and 11, respectively



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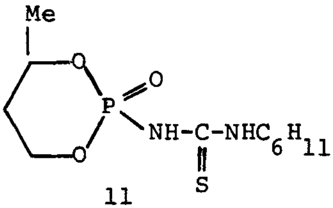
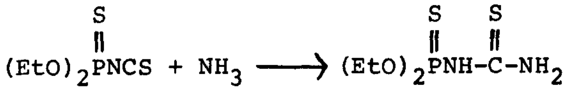
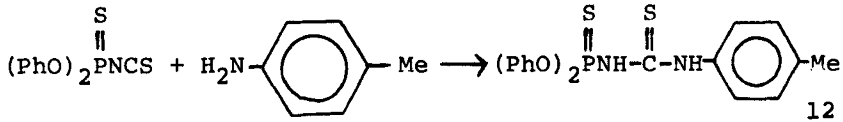


11

Dialkyl thionophosphorylthiocarbimides react in a similar fashion to their oxygen analogs with ammonia, primary or secondary amines to yield the thiourea derivatives.[21,22] Aleksenko and co-workers[23,24] reported the condensation of aryl amines with diphenoxy thionophosphoroisothiocyanatidate to yield the corresponding thiourea, an N-aryl-N'-diphenoxythiophosphonothiourea (12). This com-



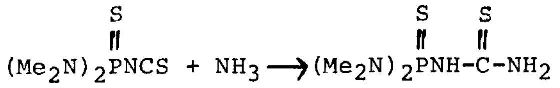
$$(EtO)_2\overset{S}{\overset{\|}{P}}NCS + NH_3 \longrightarrow (EtO)_2\overset{S}{\overset{\|}{P}}NH-\overset{S}{\overset{\|}{C}}-NH_2$$



12

pound forms complexes with cobaltous chloride.

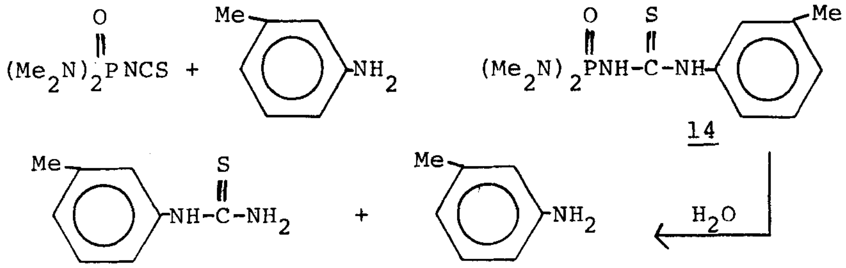
Dimethylamidothiophosphorous isothiocyanate (13) reacts similarly with ammonia yielding the corresponding thiourea.[25]



$$(Me_2N)_2\overset{S}{\overset{\|}{P}}NCS + NH_3 \longrightarrow (Me_2N)_2\overset{S}{\overset{\|}{P}}NH-\overset{S}{\overset{\|}{C}}-NH_2$$

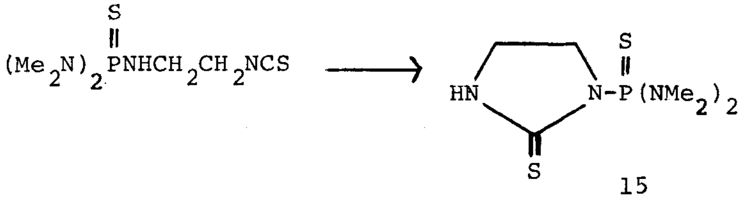
13

N-Aryl (alkyl)-N'-tetramethyldiamidophosphonothioureas (14) are prepared by treating dimethylamidophosphorous isothiocyanate with the appropriate amine.[26] The resulting thioureas undergo hydrolysis in aqueous acid or alkali losing their phosphorus moieties.



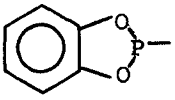
14

Imidazolidine-2-thione-N-phosphoramides (15) were prepared by cyclization of the corresponding isothiocyanates of the triamide derivative of thionophosphoric acid.[27]

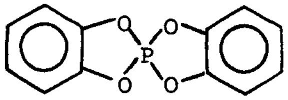


15

Barnikow and Gabrio[28,29] prepared a series of thiourea derivatives containing cyclic phosphorus groups by reaction of the appropriate amine with the cyclic phosphorus derivative of an isothiocyanate. If the isothiocyanate is represented by RNCS, then R = 1,3,2-benzodioxaphosphol-2-yl (16), 2,2'-spiro(1,3,2-benzodioxaphosphol)-2-yl (17), 2-oxo-1,3,2-benzodioxaphosphol-2-yl (18) and 2-thiono-1,3,2-benzodioxaphosphol-2-yl (19) groups.



16



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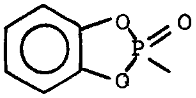

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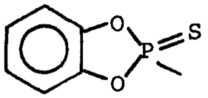
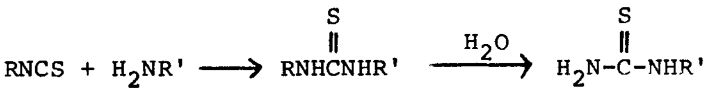


19

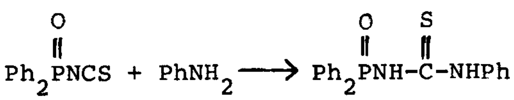
These compounds readily undergo hydrolysis affording the thiourea without the phosphorus radicals. The overall scheme may be represented as follows:



$$\mathrm{RNCS} + \mathrm{H_2NR'} \longrightarrow \mathrm{RNH}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\mathrm{NHR'} \xrightarrow{\mathrm{H_2O}} \mathrm{H_2N}\text{-}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\text{-}\mathrm{NHR'}$$

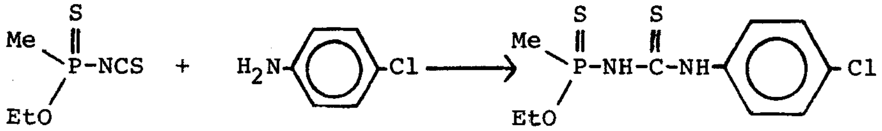
R is the phosphorus group depicted in 16 - 19.

Phosphinic acid thioureides are prepared in a similar fashion by the reaction of amines with phosphinyl isothiocyanates.[31,31]

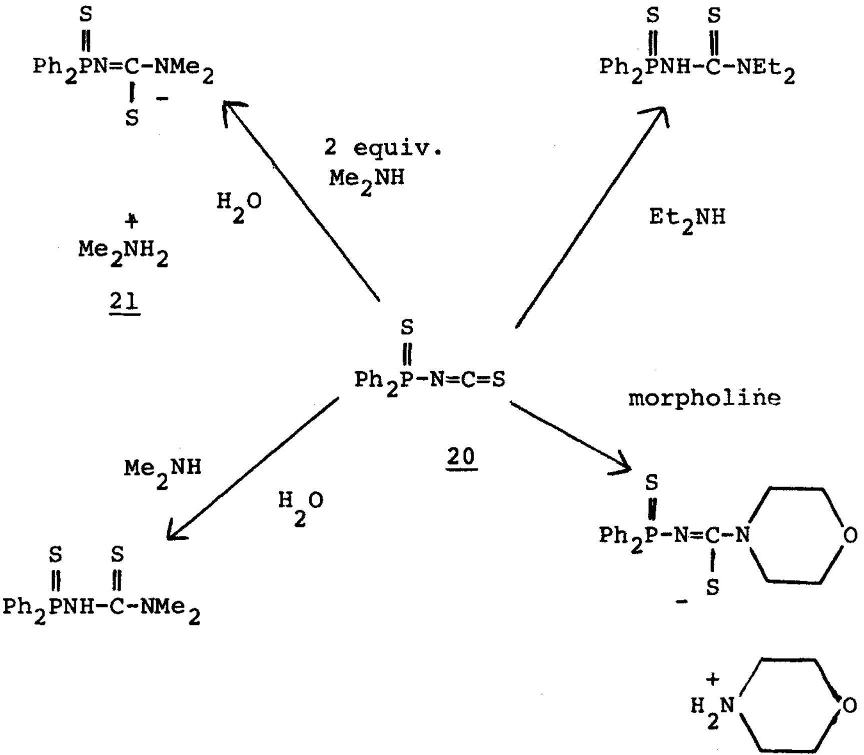


$$\mathrm{Ph_2}\overset{\overset{\displaystyle O}{\|}}{\mathrm{P}}\mathrm{NCS} + \mathrm{PhNH_2} \longrightarrow \mathrm{Ph_2}\overset{\overset{\displaystyle O}{\|}}{\mathrm{P}}\mathrm{NH}\text{-}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\text{-}\mathrm{NHPh}$$

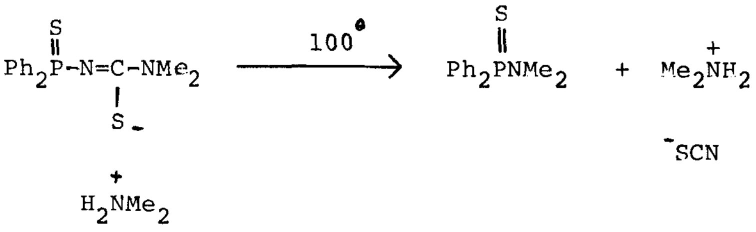
Alkylalkoxythionophosphinyl isothiocyanates were converted into the corresponding thioureas by reaction with amines.[32]



Diphenylphosphinothioyl isothiocyanate (20) reacts with amines via addition of the amine to the isothiocyanate group to yield diphenylphosphinothioylthioureas or their ammonium salts, depending upon reaction conditions.[33]



Schmidpeter and Groeger[34] studied the formation and reactions of compound 21, and found that it underwent thermal decomposition at 100° to give 22 and 23.



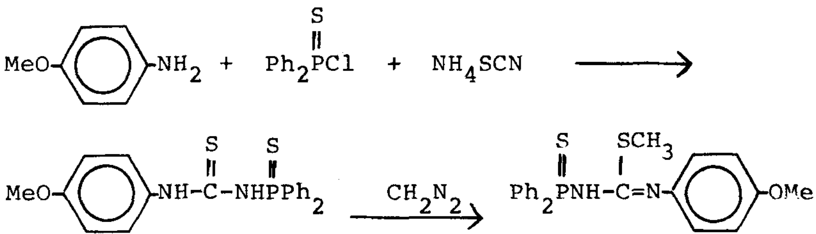
$$\mathrm{Ph_2\overset{\overset{S}{\|}}{P}-N{=}\underset{\underset{\overset{+}{H_2NMe_2}}{S^-}}{C}-NMe_2} \xrightarrow{100^\circ} \mathrm{Ph_2\overset{\overset{S}{\|}}{P}NMe_2} + \mathrm{Me_2\overset{+}{N}H_2}\ {}^{-}\mathrm{SCN}$$

21 22 23

Compound 21 was found to be methylated exclusively at the sulfur atoms, with preference for the sulfur bound to the carbon atom.

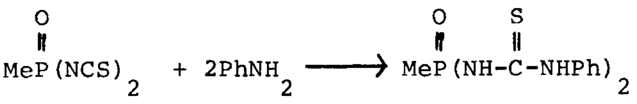
A patent[35] reports the reaction of dialkylthionophosphinyl thiocyanates with primary or secondary amines to form thiourea derivatives. It appears likely that isothiocyanates were used rather than the reported thiocyanates.

Bodeker prepared thiophosphinylthioureas (24) by the reaction of thiophosphinyl chloride with ammonium thiocyanate and the corresponding substituted aniline (the use of p-anisidine is illustrated below), without isolation of the intermediate isothiocyanate. When the thiophosphinylthiourea is reacted with diazomethane, the S-methyl derivative (25) and its tautomers are isolated.[36]



24 25

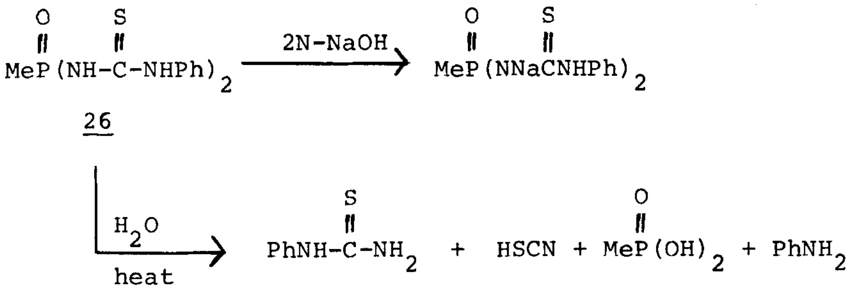
The reactions of diisothiocyanates of alkylphosphonic acids with two equivalents of amine in ether afforded the corresponding thiourea (26).[37,38]



$$\mathrm{Me\overset{O}{\overset{\|}{P}}(NCS)_2 + 2PhNH_2 \longrightarrow Me\overset{O}{\overset{\|}{P}}(NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}NHPh)_2}$$

26

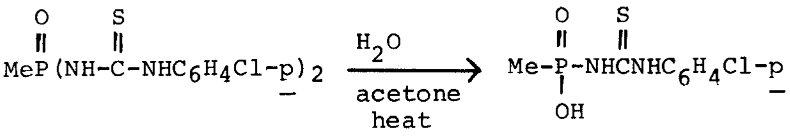
Compound 26 upon being heated in 2 N sodium hydroxide and cooled yielded its sodium salt. However, when these amides were heated in water, they could be hydrolyzed to arylthioureas, thiocyanic acid, methylphosphonic acid and aniline.



$$\mathrm{\underset{\underline{26}}{Me\overset{O}{\overset{\|}{P}}(NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}NHPh)_2} \xrightarrow{2N\text{-}NaOH} Me\overset{O}{\overset{\|}{P}}(NNa\overset{S}{\overset{\|}{C}}NHPh)_2}$$

$$\mathrm{\xrightarrow[heat]{H_2O} PhNH\text{-}\overset{S}{\overset{\|}{C}}\text{-}NH_2 + HSCN + Me\overset{O}{\overset{\|}{P}}(OH)_2 + PhNH_2}$$

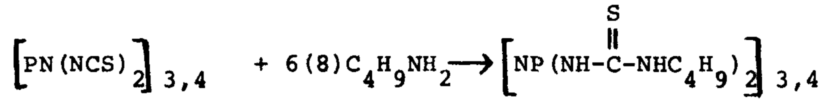
Alkylphosphonic acid dithiourea derivative 27, when heated in aqueous acetone until solution was complete and cooled, gave the mono-thiourea derivative 28.



$$\mathrm{Me\overset{O}{\overset{\|}{P}}(NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}NHC_6H_4Cl\text{-}p)_2 \xrightarrow[\text{acetone, heat}]{H_2O} Me\text{-}\underset{OH}{\overset{O}{\overset{\|}{P}}}\text{-}NH\overset{S}{\overset{\|}{C}}NHC_6H_4Cl\text{-}p}$$

27 28

Phosphonitrilic derivatives of thiourea were obtained by reacting phosphonitrilic isothiocyanates with ammonia, with aliphatic or aromatic amines. Thus, butylamine, for example, reacted with either triphosphonitrilic hexaisothiocyanate or tetraphosphonitrilic octaisothiocyanate to yield hexa (butylthioureido)-triphosphonitrile or octa(butylthioureido)-tetraphosphonitrile 29.[39]



$$\left[PN(NCS)_2\right]_{3,4} + 6(8)C_4H_9NH_2 \longrightarrow \left[NP(NH-\overset{\overset{\Large S}{\|}}{C}-NHC_4H_9)_2\right]_{3,4}$$

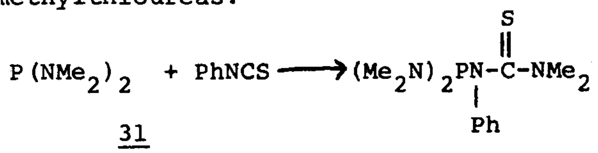
29

The tetraphosphonitrile upon reflux in ether afforded a white precipitate with the empirical formula of 30.

$$\left[PN(NCS)_2\right]_4 \cdot 6C_4H_9NH_2$$

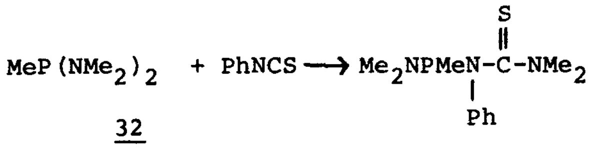
30

Alkyl and aryl isothiocyanates have been found to cleave the phosphorus-nitrogen bond in dimethylamidophosphorous or -phosphonic acids (31 and 32, respectively). The dimethylamino group is added to the carbon atom of the isothiocyanate with the formation of N-alkyl (aryl)-N,N'-dimethylthioureas.[18,40,41]



$$P(NMe_2)_2 + PhNCS \longrightarrow (Me_2N)_2P\underset{\underset{Ph}{|}}{N}-\overset{\overset{S}{\|}}{C}-NMe_2$$

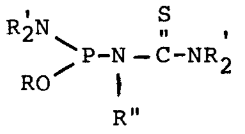
31



$$MeP(NMe_2)_2 + PhNCS \longrightarrow Me_2NPMe\underset{\underset{Ph}{|}}{N}-\overset{\overset{S}{\|}}{C}-NMe_2$$

32

The ester-amides of the "phosphorous" acid also gives similar products, i.e. compound 33.



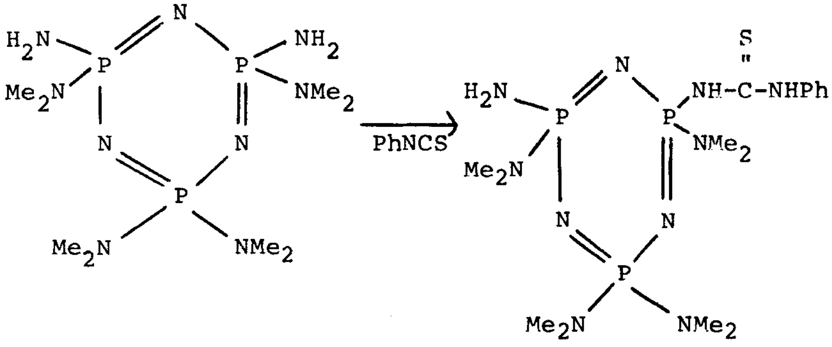
R = alkyl, aryl

R' = alkyl

R" = alkyl, aryl, acyl

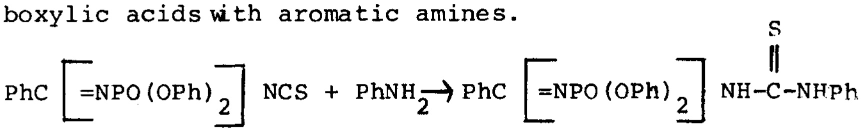
33

A mono-thiourea derivative of aminophosphonitriles 34 was prepared by the reaction of phenyl isothiocyanate with diaminotetradimethylaminophosphonitrile.[42]



34

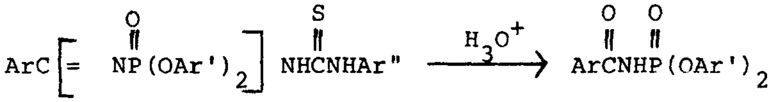
Derkach and co-workers[43] have prepared N'-aryl-N^2-(N^3-diaryloxyphosphoryliminoaroyl)thioureas (35) by the reaction of isothiocyanates of N-diaroxyphosphinyliminocarboxylic acids with aromatic amines.



$$PhC\left[=NPO(OPh)_2\right]NCS + PhNH_2 \rightarrow PhC\left[=NPO(OPh)_2\right]NH-\overset{S}{\overset{\|}{C}}-NHPh$$

35

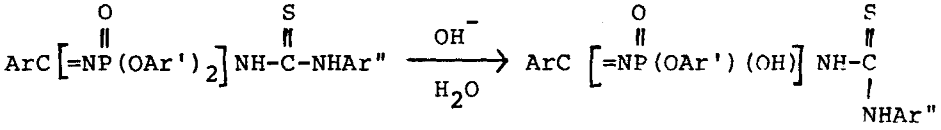
These compounds undergo hydrolysis in aqueous alcoholic solutions. Upon acidic hydrolysis, these compounds are hydrolyzed to diesters of acylamidophosphoric acid (36).



$$\text{ArC}\left[=\text{N}\overset{\text{O}}{\overset{\|}{\text{P}}}(\text{OAr}')_2\right]\text{NH}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{NHAr}'' \xrightarrow{\text{H}_3\text{O}^+} \text{Ar}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NH}\overset{\text{O}}{\overset{\|}{\text{P}}}(\text{OAr}')_2$$

36

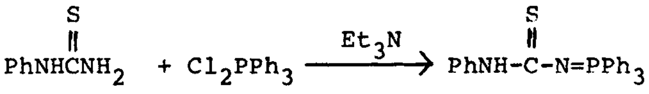
In alkaline solution, saponification of one aroxyl group bound to the phosphorus takes place with the amidine group remaining unchanged. This then yields N'-monoaroxymonohydroxyphosphinyl-N^2-(N^3-arylthiocarbaminyl)-arenamidines (37).



$$\text{ArC}\left[=\text{N}\overset{\text{O}}{\overset{\|}{\text{P}}}(\text{OAr}')_2\right]\text{NH-}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{-NHAr}'' \xrightarrow[\text{H}_2\text{O}]{\text{OH}^-} \text{ArC}\left[=\text{N}\overset{\text{O}}{\overset{\|}{\text{P}}}(\text{OAr}')(\text{OH})\right]\text{NH-}\underset{\underset{\text{NHAr}''}{|}}{\overset{\text{S}}{\overset{\|}{\text{C}}}}$$

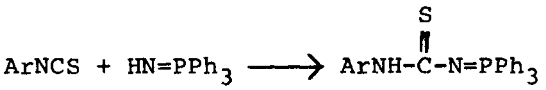
37

Triphenylphosphazo derivatives of thiourea (38) have been prepared either by the reaction of triphenylphosphic dichloride with a thiourea or by the reaction of its imide analog with an isothiocyanate.[44]

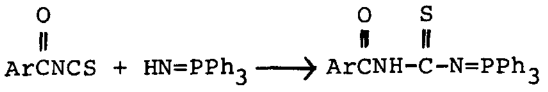


$$\text{PhNH}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{NH}_2 + \text{Cl}_2\text{PPh}_3 \xrightarrow{\text{Et}_3\text{N}} \text{PhNH-}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{-N=PPh}_3$$

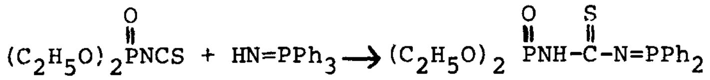
39



$$\text{ArNCS} + \text{HN=PPh}_3 \longrightarrow \text{ArNH-}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{-N=PPh}_3$$



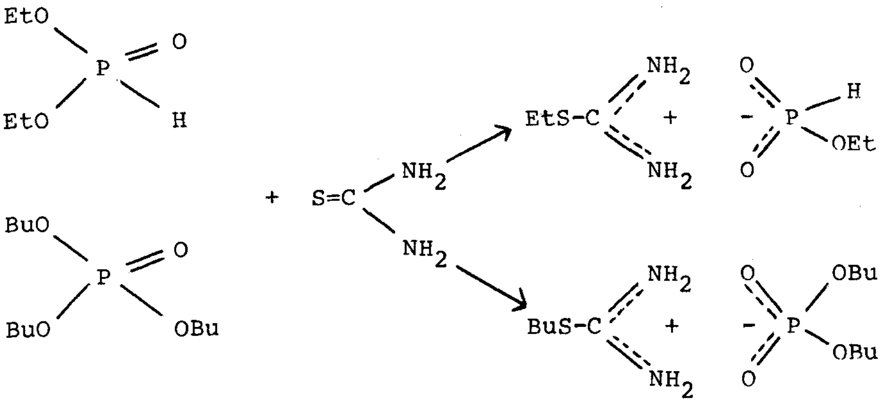
$$\mathrm{Ar\overset{O}{\overset{\|}{C}}NCS + HN{=}PPh_3 \longrightarrow Ar\overset{O}{\overset{\|}{C}}NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}N{=}PPh_3}$$



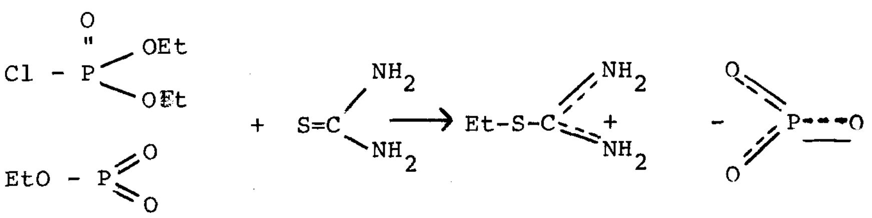
$$\mathrm{(C_2H_5O)_2\overset{O}{\overset{\|}{P}}NCS + HN{=}PPh_3 \longrightarrow (C_2H_5O)_2\,\overset{O}{\overset{\|}{P}}NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}N{=}PPh_2}$$

b. <u>Preparation and Reactions of Isothiuronium Salts</u>

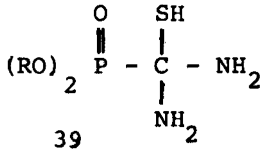
Dialkyl phosphonates and trialkyl phosphates react with thiourea to give the corresponding S-substituted products in quantitative yields.[45-47]



The reaction of thiourea with diethyl chlorophosphate or with ethyl metaphosphate affords S-ethylisothiuronium metaphosphate.[48]



Abramov[49] reacted thiourea with dialkyl hydrogen phosphites (phosphonates) $(RO)_2PHO$. He proposed structure 39 which would be obtained by addition at the

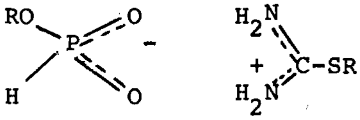


$(RO)_2\overset{O}{\overset{\|}{P}}-\underset{NH_2}{\overset{SH}{C}}-NH_2$

R = Alkyl

39

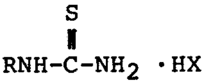
C=S bond. However, Miller and O'Leary[50], by studying infrared and nmr spectra of the products, established the correct structure to be that of an ionized adduct 40.



R=alkyl

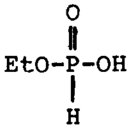
40

It is interesting to note that there is disagreement with S-alkylation of thiourea by dialkyl hydrogen phosphites, and by trialkyl phosphates. Parker and Smith[51] have proposed that the reaction affords N-alkylthiuronium alkyl phosphites and phosphates, respectively, and assigned the general structure 41 to the products where HX has structures 42 or 43.



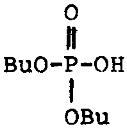
$RNH-\overset{S}{\overset{\|}{C}}-NH_2\cdot HX$

41



$EtO-\underset{H}{\overset{O}{\overset{\|}{P}}}-OH$

42

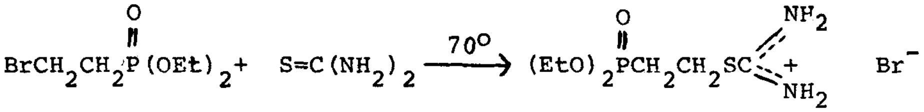


$BuO-\underset{OBu}{\overset{O}{\overset{\|}{P}}}-OH$

43

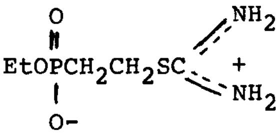
The assignment of this structure was based on a study of the precipitation products with uranyl nitrate and on infrared and ultraviolet spectroscopy, as well as variations in electrical conductivity in aqueous solution with changes in temperature. They noted that the C=S band was close to that in thiourea itself.

The reaction of diethyl 2-bromoethylphosphonate with thiourea at 70° yields the isothiuronium bromide 44.[48] When 44 is heated to 145°, the salt is transformed to the isothiuronium phosphonate 45.



$$\mathrm{BrCH_2CH_2\overset{O}{\overset{\|}{P}}(OEt)_2 + S{=}C(NH_2)_2 \xrightarrow{70^{\circ}} (EtO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2SC\overset{+}{\lesssim}\begin{matrix}NH_2\\NH_2\end{matrix}\quad Br^-}$$

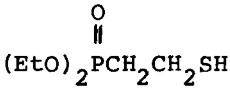
44



$$\mathrm{EtO\underset{O^-}{\underset{|}{\overset{O}{\overset{\|}{P}}}}CH_2CH_2SC\overset{+}{\lesssim}\begin{matrix}NH_2\\NH_2\end{matrix}}$$

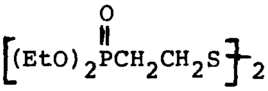
45

44



$$\mathrm{(EtO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2SH}$$

46



$$\mathrm{\left[(EtO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2S\right]_2}$$

47

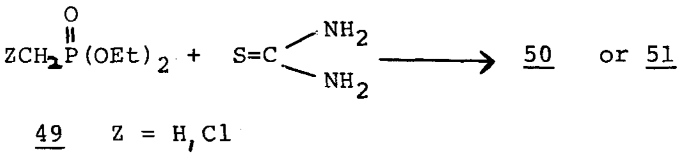
(A) Heat to 145°

(B) 20% NaOH

(C) Mohr's salt catalyst, 10% H_2O_2, 25% NaOH

When 44 is hydrolyzed in sodium hydroxide, the corresponding mercaptan 46 is formed. Compound 44 also undergoes oxidation in the presence of hydrogen peroxide and Mohr's salt catalyst under alkaline conditions yielding the disulfide 47.

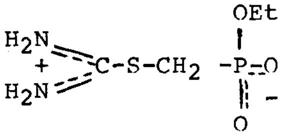
When diethyl methylphosphonate (48) or diethyl chloromethylphosphonate (49) is treated with thiourea, the product is the S-alkylated salt 50, where the ethyl group is derived from the phosphonate group.[52] When an excess of thiourea is used with the chloromethyl derivative, betaine 51 is obtained.



$$ZCH_2\overset{O}{\overset{\|}{P}}(OEt)_2 + S=C(NH_2)_2 \longrightarrow \underline{50} \text{ or } \underline{51}$$

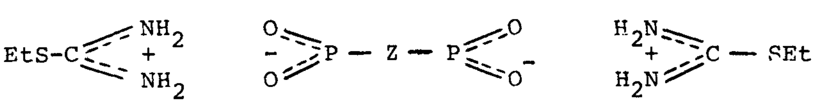
49 Z = H, Cl

50



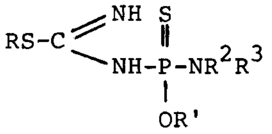
51

The derivatives $(EtO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(OEt)_2$ and $\left[(RO)_2\overset{O}{\overset{\|}{P}}\right]_2O$ where R = ethyl or propyl give the bis(isothiuronium) salts 52 upon reaction with thiourea.



52

Mel'nikov and co-workers[53] prepared phosphorylated S-alkylisothiuronium salts by treating hydrogen halide salts of S-alkylisothiourea with O-alkyl(O-aryl)-N-alkylphosphoramidothioic chloride in the presence of a hydrogen halide acceptor. The products have the structure 53.



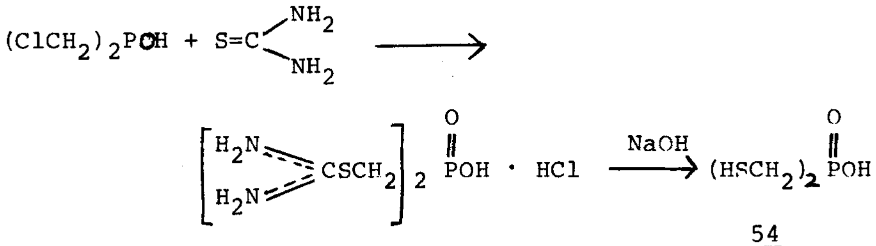
53

R = alkyl

R' = alkyl, aryl

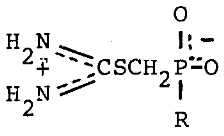
R^2 and R^2 = H or alkyl

Bis (mercaptomethyl)phosphinic acid 54 was prepared via the isothiuronium salt.[54] Thus, the phosphinic acid derivative was reacted with thiourea and the resulting isothiuronium salt was hydrolyzed to the mercaptan.



54

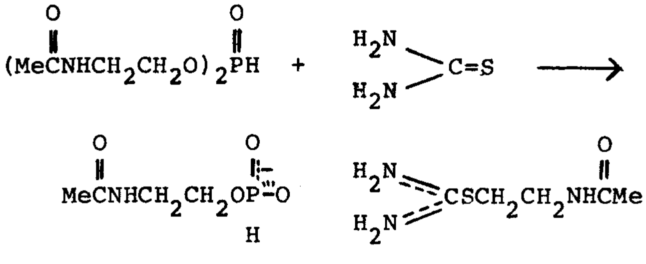
In a similar fashion, chloromethylphosphonic or -phosphinic acids reacted with thiourea to give the isothiuronium salts 55.[55] Hydrolysis of the salt, followed by acidification, yielded the mercaptan.



55

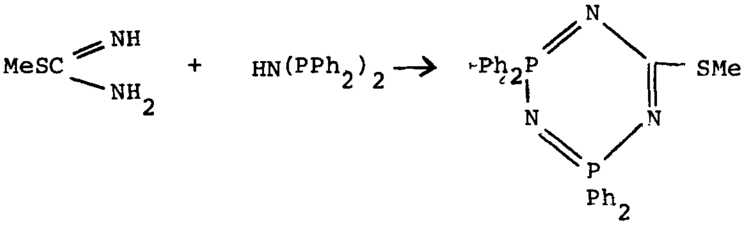
R = Ph, Et, OH

Di(2-N-acylaminoethyl)phosphites have been reported to alkylate thiourea according to the corresponding isothiuronium salts 56.[56]



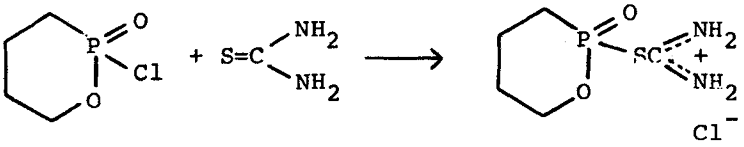
56

Bis(diphenylphosphino)amine was condensed with isothioureas to yield triazadiphosphorines 57.[57]



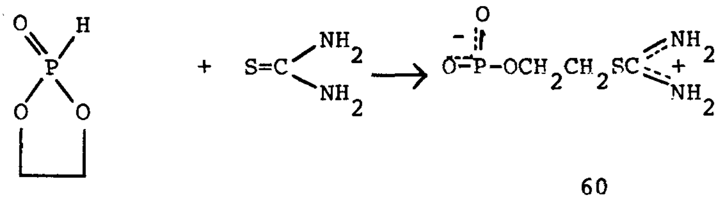
57

An S-phostone isothiuronium chloride (59) was prepared by reaction of 58 with thiourea.[58]



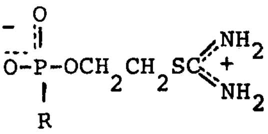
58 59

2-Hydro-2-oxo-1,3,2-dioxaphospholane reacts with thiourea to yield the zwitterion 60.



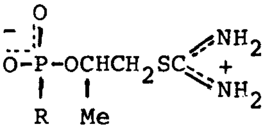
60

Mizrakh and co-workers[60] studied the reaction of thiourea with various 2-oxo-1,3,2-dioxaphospholanes. They found that the phospholanes bearing substituents such as Me, EtO or $ClCH_2$ on phosphorus gave 61 as products. Similar phospholanes containing substituents in the 4-position such as Me required higher temperatures and afforded products showing ring cleavage at the ester group formed by a primary alcohol structure. Thus, when R = EtO or Me the product 61 is formed. With the six-membered ring 2-ethoxy-2-oxo-1,3,2-dioxaphorinane still more drastic conditions were required, but a similar product, compound 63, was formed. The reaction of 2-hydro-2-oxo-1,3,2-dioxaphospholane with thiourea gave compound 64.



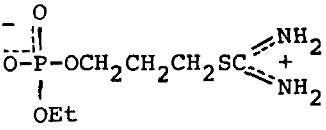
$^{-}O-\overset{O}{\underset{R}{P}}-OCH_2CH_2SC(NH_2)_2^{+}$

61



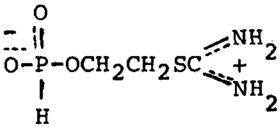
$^{-}O-\overset{O}{\underset{R}{P}}-OCH(Me)CH_2SC(NH_2)_2^{+}$

62



$^{-}O-\overset{O}{\underset{OEt}{P}}-OCH_2CH_2CH_2SC(NH_2)_2^{+}$

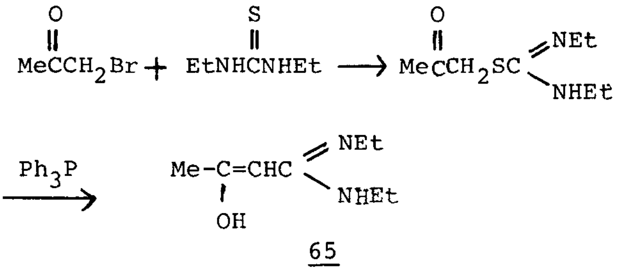
63



$^{-}O-\overset{O}{\underset{H}{P}}-OCH_2CH_2SC(NH_2)_2^{+}$

64

Phosphorus was also involved in the desulfurization of isothioureas to give β-ketoamidines (65).[61] The enol structure of

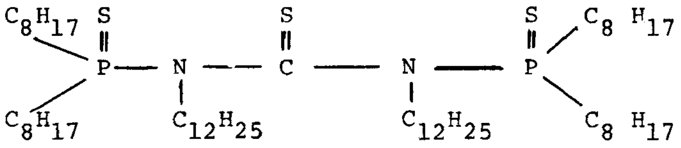


65

65 was established by nuclear magnetic resonance spectroscopy.

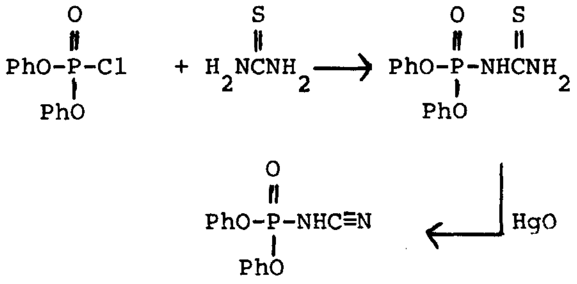
C. Miscellaneous Preparations of Thioureas

Phospho derivatives of thiourea have been prepared by reaction of a dialkyl halothiophosphate with primary amines in a molar ratio of 1:1. The product is then treated with carbon disulfide to form thiourea derivatives of thiophosphates.[62] Compound 66 is an example of such a derivative.



66

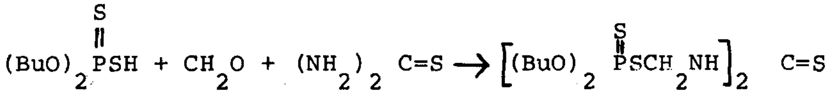
As part of an attempt to prepare creatinephosphoric acid diphenyl chlorophosphate was condensed with thiourea yielding diphenylphosphorylthiourea which was oxidized with mercuric oxide to afford diphenylphosphorylcyanamide.[63]



$$\mathrm{PhO{-}\overset{O}{\underset{PhO}{P}}{-}Cl + H_2N\overset{S}{C}NH_2 \longrightarrow PhO{-}\overset{O}{\underset{PhO}{P}}{-}NH\overset{S}{C}NH_2 \xrightarrow{HgO} PhO{-}\overset{O}{\underset{PhO}{P}}{-}NHC{\equiv}N}$$

Attempts to phosphorylate methylisothiourea with diphenyl chlorophosphate merely afforded methylisothiourea diphenylphosphate.

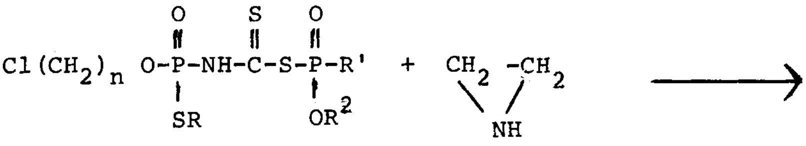
Dialkyl(dithiophosphatomethyl)thioureas (67) have been prepared by the reaction of the appropriate thiourea having an active hydrogen with formaldehyde and a dialkyl dithiophosphate.[64]



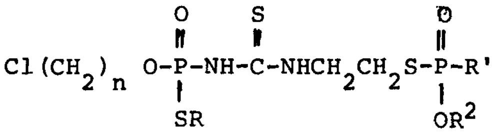
$$\mathrm{(BuO)_2\overset{S}{P}SH + CH_2O + (NH_2)_2\,C{=}S \longrightarrow \left[(BuO)_2\,\overset{S}{P}SCH_2NH\right]_2\,C{=}S}$$

67

The reaction of phosphorus derivatives of dithiocarbamates with ethylenimines to yield thiourea has also been reported.[65]



$$\mathrm{Cl(CH_2)_n\,O{-}\overset{O}{\underset{SR}{P}}{-}NH{-}\overset{S}{C}{-}S{-}\overset{O}{\underset{OR^2}{P}}{-}R' + \underset{NH}{CH_2{-}CH_2} \longrightarrow}$$



$$Cl(CH_2)_n\,O-\underset{SR}{\overset{O}{\overset{\|}{P}}}-NH-\overset{S}{\overset{\|}{C}}-NHCH_2CH_2S-\underset{OR^2}{\overset{O}{\overset{\|}{P}}}-R'$$

R = alkyl, aryl

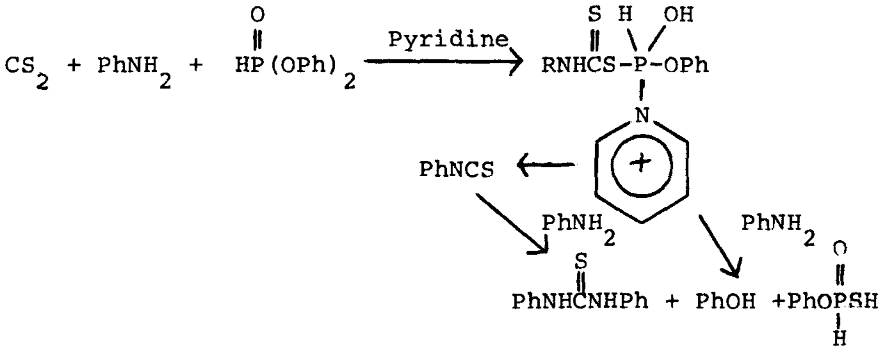
R' = aryl, aralkyl

R^2 = alkyl

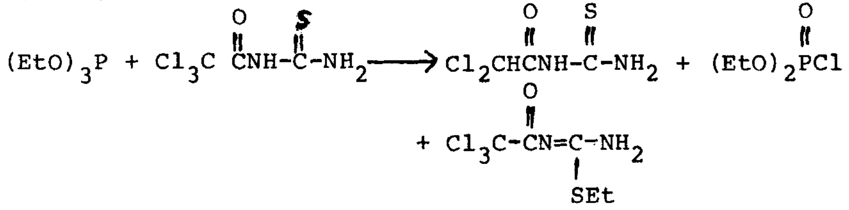
n = $\geq$ 2

D. Miscellaneous Reactions

Phosphite esters have been used in the synthesis of thioureas from amines and carbon disulfide.[66] Isothiocyanates are formed as intermediates.



Trichloroacetylthiourea was reacted with triethyl phosphate *via* the Perkow reaction.[67] Equimolar proportions of triethyl phosphite and trichloroacetylthiourea yielded dichloroacetylthiourea, diethyl phosphorochloridate, trimethyl phosphate and unchanged triethyl phosphite. In addition some S-ethyl-N-trichloroacetylisothiourea was formed.



$$(EtO)_3P + Cl_3C\,\overset{O}{\overset{\|}{C}}NH-\overset{S}{\overset{\|}{C}}-NH_2 \longrightarrow Cl_2CH\overset{O}{\overset{\|}{C}}NH-\overset{S}{\overset{\|}{C}}-NH_2 + (EtO)_2\overset{O}{\overset{\|}{P}}Cl + Cl_3C-\overset{O}{\overset{\|}{C}}N=\underset{SEt}{C}-NH_2$$

Resinous polymers of unknown structure have been obtained by condensation of organophosphonic acid diamides with thioureas.[68]

Hexachlorophosphazatriene reacts with thiourea to give trimetathiophosphimic acid.[69] In a similar fashion, octachlorophosphazatetraene yielded tetrametathiophosphimic acid (68) when treated with thiourea.

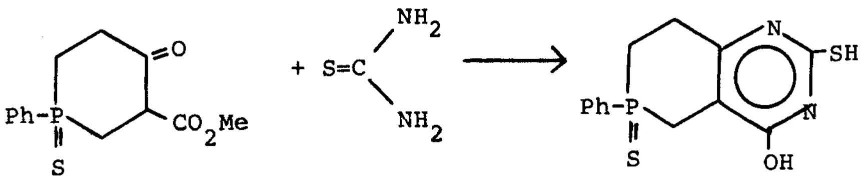
$$(PNCl\ )_4 + S{=}C(NH_2)_2 \longrightarrow (PN)_4\left[SC(NH_2)(=NH)\right]_8$$

$$\xrightarrow{NaOH} \left[PN(SH)_2\right]_4$$

68

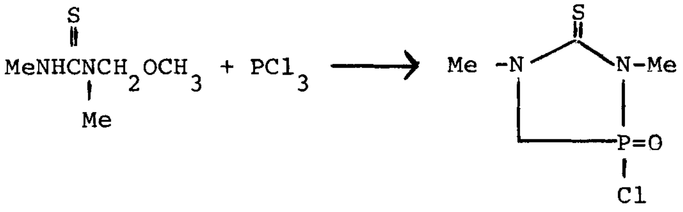
note: metaphosphimic acid is $\left[HOP(NH)\right]_n$ or $\left[(HO)_2P\ (=N)\right]_n$

Thioureas may be utilized for the synthesis of phosphorino [4,3-d] pyrimidines.[70] Thus, the condensation of thiourea with methyl 4-oxo-1-phenyl-3-phosphorinanecarboxylate 1-sulfide affords 5,6,7,8-tetrahydro-2-mercapto-6-phenylphosphorinol[4,3-d] pyrimidine-4-ol 6-sulfide (69).



69

The reaction of N-methylolthiourea derivatives and phosphorus trichloride yields 1,3,4-diazaphospholanes.[71] Thus, the reaction of N,N'-dimethyl-N-(methoxymethyl) thiourea with phosphorus trichloride affords 4-chloro-2,4-dioxo-1,3-dimethyl-1,3,4-diazaphospholane (70).



70

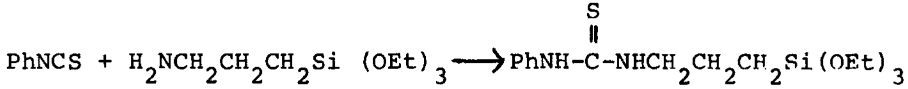
A thiourea derivative containing both phosphorus and silicon is mentioned in the section on silicon.[80]

A potential alkylating thiourea, N,N'- [[bis(2-chloroethyl)amino] phosphinylidene] bis [N'-phenylthiourea] was also prepared.[72]

IV. SILICON DERIVATIVES

a. Preparation of Thioureas from Isothiocyanates

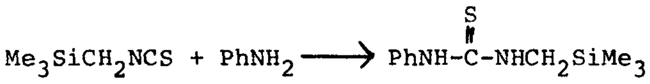
In a manner similar to their phosphorus analogues, an isothiocyanate may be treated with a silicon substituted amine to yield a silicon-containing derivative.[73] Thus, phenyl isothiocyanate may be condensed with 3-aminopropyltriethoxysilane to yield N-phenyl-N'-(3-triethoxysilylpropyl)thiourea (71).



$$PhNCS + H_2NCH_2CH_2CH_2Si(OEt)_3 \longrightarrow PhNH\text{-}\overset{S}{\overset{\|}{C}}\text{-}NHCH_2CH_2CH_2Si(OEt)_3$$

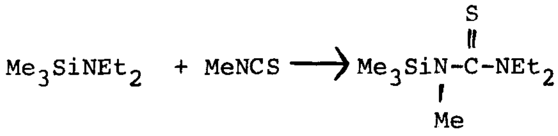
71

In a similar fashion, the reaction may take place with the isothiocyanate function being linked to the silicon-bearing group.[74,75]



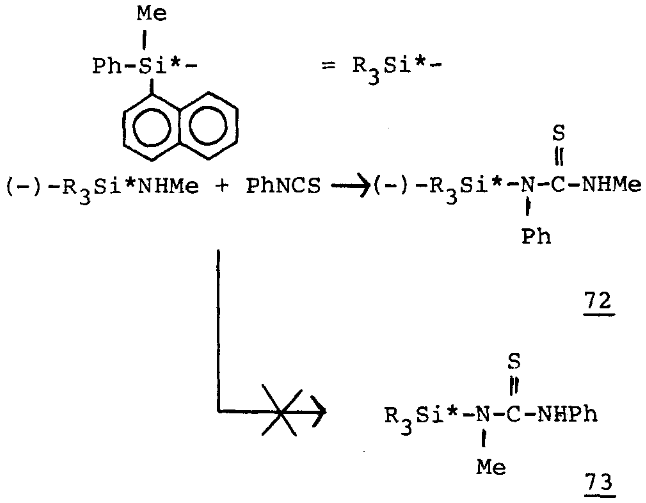
$$Me_3SiCH_2NCS + PhNH_2 \longrightarrow PhNH\text{-}\overset{\overset{S}{\|}}{C}\text{-}NHCH_2SiMe_3$$

Trialkylsilylamines react with isothiocyanates to yield the corresponding trialkylsilylthiourea.[41] This reaction takes place by insertion of the isothiocyanate between the silicon and nitrogen of the silylamine.



$$Me_3SiNEt_2 + MeNCS \longrightarrow Me_3Si\underset{\underset{Me}{|}}{N}\text{-}\overset{\overset{S}{\|}}{C}\text{-}NEt_2$$

Kaufman and co-workers prepared optically active thioureas by the reaction of optically active aminosilanes with an isothiocyanate.[76] Thus, (-)-N-(methylphenyl-1-naphthylsilyl)methylamine and -dimethylamine were condensed with phenyl isothiocyanate to form the corresponding thiourea with retention of configuration at the silicon atom. This reaction involves Si-N splitting rather than N-H splitting insofar as compound 72 was formed rather than compound 74.



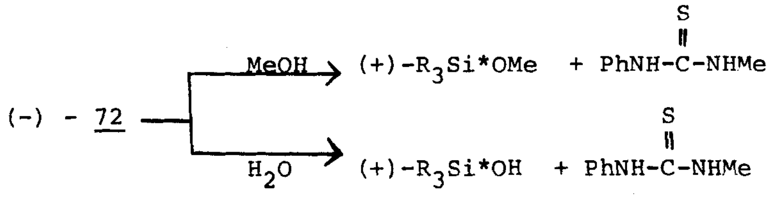
$$(-)\text{-}R_3Si^*NHMe + PhNCS \longrightarrow (-)\text{-}R_3Si^*\text{-}\underset{\underset{Ph}{|}}{N}\text{-}\overset{\overset{S}{\|}}{C}\text{-}NHMe$$

72

$$R_3Si^*\text{-}\underset{\underset{Me}{|}}{N}\text{-}\overset{\overset{S}{\|}}{C}\text{-}NHPh$$

73

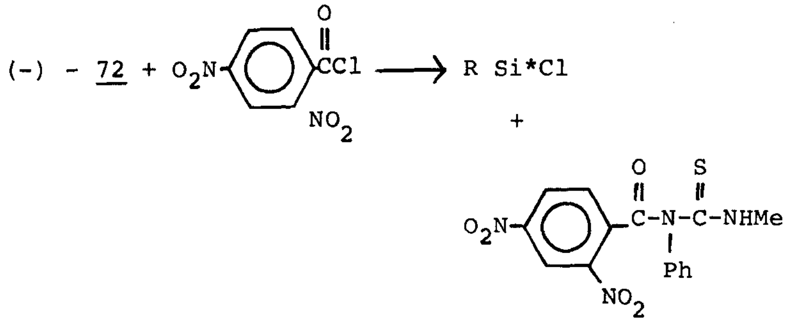
The silylthioureas undergo solvolysis with either water or methanol with inversion of configuration.



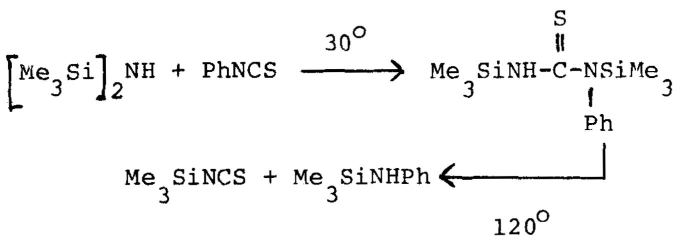
$$(-)\text{-}\underline{72} \xrightarrow{MeOH} (+)\text{-}R_3Si^*OMe + PhNH\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}NHMe$$

$$(-)\text{-}\underline{72} \xrightarrow[H_2O]{} (+)\text{-}R_3Si^*OH + PhNH\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}NHMe$$

In contrast to the N-silylureas which are inactive towards the halides of aromatic acids, N-silylthioureas are cleaved at the Si-N bond with retention of configuration when treated with 2,4-dinitrobenzoyl chloride.



Hexamethyldisilazane reacts with an equimolar amount of phenyl isothiocyanate at low temperatures to form N,N'-bis(trimethylsilyl)-N'-phenylthiourea (74) in poor yields.[77] When the ratio of hexamethyldisilazane-phenyl isothiocyanate was increased to 1:2 the yield was increased from 5-7% under the former conditions to 70% in the latter case. When the thiourea was heated to 120° formation of trimethylsilyl isothiocyanate and (trimethylsilyl)phenylamine took place. These products were also formed when hexamethyldisilazane and phenyl isothiocyanate were combined at 120°.

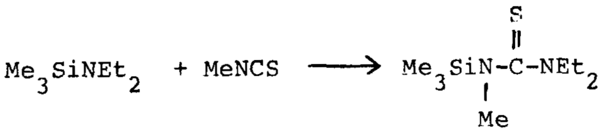


$$[Me_3Si]_2NH + PhNCS \xrightarrow{30^{\circ}} Me_3SiNH\text{-}\overset{\overset{S}{\|}}{C}\text{-}\underset{\underset{Ph}{|}}{N}SiMe_3 \xrightarrow{120^{\circ}} Me_3SiNCS + Me_3SiNHPh$$

74

$$[Me_3Si]_2NH + PhNCS \xrightarrow{120^{\circ}} Me_3SiNCS + Me_3SiNHPh$$

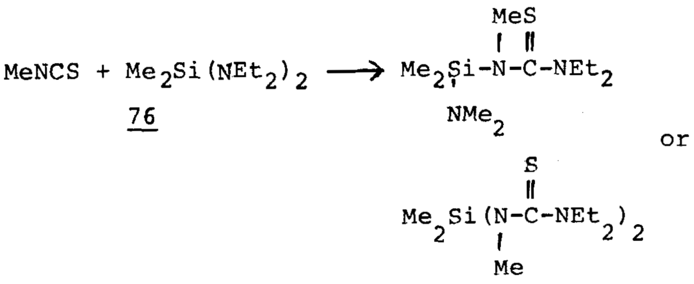
Another example of the cleavage of a silicon-nitrogen bond by an isothiocyanate is the reaction of methyl isothiocyanate with N-(trimethylsilyl)diethylamine (75).[18,41,78]



$$Me_3SiNEt_2 + MeNCS \longrightarrow Me_3Si\underset{\underset{Me}{|}}{N}\text{-}\overset{\overset{S}{\|}}{C}\text{-}NEt_2$$

75

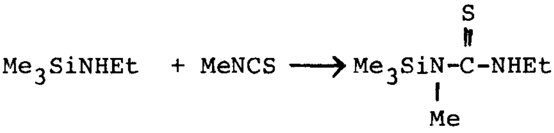
In a similar fashion, dimethylbis(N,N-diethylamino) silane (76) reacts with methyl isothiocyanate or with phenyl isothiocyanate affording one of two thioureas.

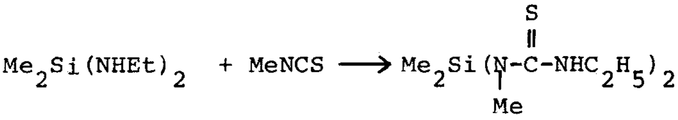


$$MeNCS + Me_2Si(NEt_2)_2 \longrightarrow \underset{\underset{NMe_2}{}}{Me_2Si}\text{-}\underset{}{\overset{\overset{Me}{|}}{N}}\text{-}\overset{\overset{S}{\|}}{C}\text{-}NEt_2 \quad \text{or} \quad Me_2Si(\underset{\underset{Me}{|}}{N}\text{-}\overset{\overset{S}{\|}}{C}\text{-}NEt_2)_2$$

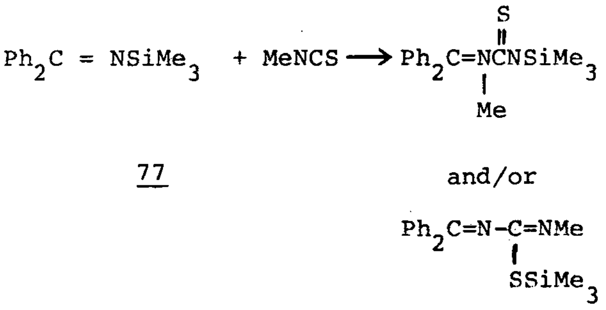
76

Other examples of this insertion reaction are shown below.[18]


$$\mathrm{Me_3SiNHEt + MeNCS \longrightarrow Me_3Si\underset{Me}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-NHEt}$$


$$\mathrm{Me_2Si(NHEt)_2 + MeNCS \longrightarrow Me_2Si(\underset{Me}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-NHC_2H_5)_2}$$

The silicon-nitrogen bond was also selectively cleaved in N-trimethylsilyl(diphenylmethylene)amine (77) by one molar equivalent of an isothiocyanate. The product being diphenylmethylenealkyl(aryl)trimethylsilylthiourea.[79] For example, using methyl isothiocyanate, the following reaction takes place.

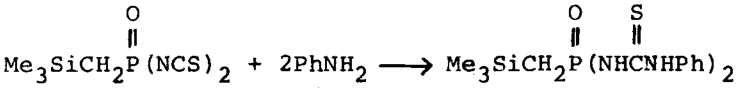

$$\mathrm{Ph_2C = NSiMe_3 + MeNCS \longrightarrow Ph_2C{=}N\overset{S}{\overset{\|}{C}}\underset{Me}{\underset{|}{N}}SiMe_3}$$

77

and/or

$$\mathrm{Ph_2C{=}N-\underset{SSiMe_3}{\underset{|}{C}}{=}NMe}$$

Thiourea derivatives containing both phosphorus and silicon were prepared by Liptuga and co-workers by reacting the corresponding phosphonyl isothiocyanate with an amine.[80]

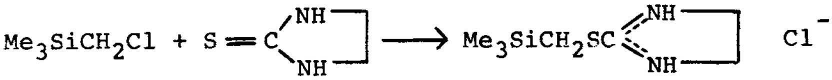

$$\mathrm{Me_3SiCH_2\overset{O}{\overset{\|}{P}}(NCS)_2 + 2PhNH_2 \longrightarrow Me_3SiCH_2\overset{O}{\overset{\|}{P}}(NH\overset{S}{\overset{\|}{C}}NHPh)_2}$$

b. Preparation and Reactions of Isothiuronium Salts

Thiourea was used as a co-reactant in the conversion of chloroalkylsilanes to the corresponding mercaptoalkyl derivatives.[81,82] An isothiuronium salt was the intermediate.

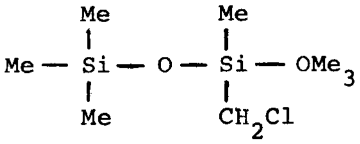
$$(EtO)_3\,Si(CH_2)_3Cl + S{=}C(NH_2)_2 \xrightarrow{\text{2 steps}} (EtO)_3Si(CH_2)_3SH$$

In other instances[83,84] the isothiuronium salts were isolated.



$$Me_3SiCH_2Cl + S{=}C(NH)(NH) \longrightarrow Me_3SiCH_2SC(NH)(NH)\quad Cl^-$$

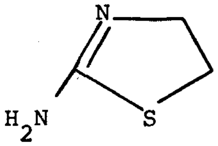
The reaction of thiourea with methylchloromethylpolysiloxane (molecular weight 1810) gave the corresponding polythiuronium chloride.[85] The same reaction also took place with the lower molecular weight compound 78. However, treatment of decamethyltetrasiloxane gave only unreacted material.



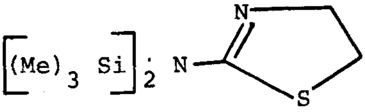
$$Me{-}Si(Me)_2{-}O{-}Si(Me)(CH_2Cl){-}OMe_3$$

78

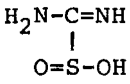
All of the N-bonded protons in a series of isothioureas were substituted by trimethylsilyl groups by using a mixture of trimethylchlorosilane-triethylamine.[86] Thus, compound 79 afforded 80. From isothiourea 81 was isolated compound 82 which was thermally unstable, affording the carbodiimide 83.



79

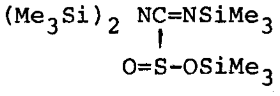


80



$$H_2N-\underset{\underset{O=S-OH}{|}}{C}=NH$$

81



$$(Me_3Si)_2\,N\underset{\underset{O=S-OSiMe_3}{|}}{C}=NSiMe_3$$

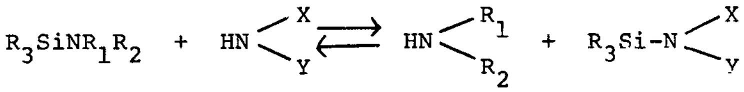
82

$Me_3SiN{=}C{=}NSiMe_3$

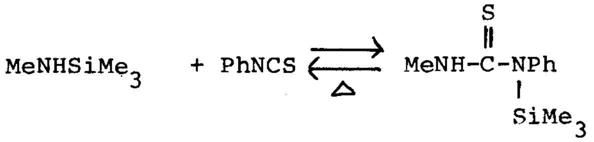
83

c. Miscellaneous Reactions

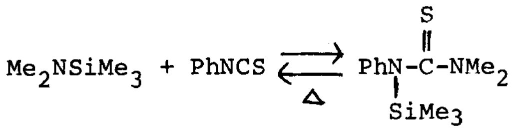
N-Silyl-substituted aromatic ureas and amides were found to be very powerful silyl donors.[87] N-Trimethylsilyldiphenylurea was used as the silylating agent to prepare N,N'-bis(trimethylsilyl) thiourea since the "conventional" silylation using hexamethyldisilazane did not afford product.



Secondary and tertiary silylamines react with isothiocyanates to give 1:1 adducts.[88] The thioureas that are formed revert to the starting material at elevated temperatures.



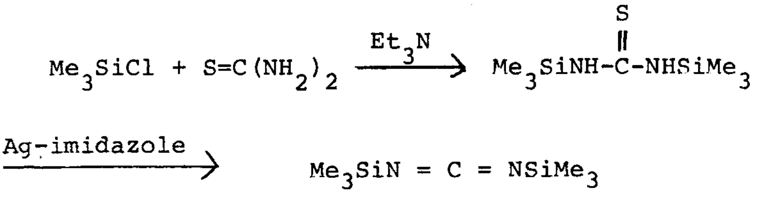
$$MeNHSiMe_3 + PhNCS \underset{\Delta}{\rightleftarrows} MeNH-\overset{\overset{S}{\|}}{C}-\underset{\underset{SiMe_3}{|}}{N}Ph$$



$$Me_2NSiMe_3 + PhNCS \underset{\Delta}{\rightleftarrows} Ph\underset{\underset{SiMe_3}{|}}{N}-\overset{\overset{S}{\|}}{C}-NMe_2$$

Attempts to obtain thioureas with two silyl substituents by reaction of silazanes with phenyl isothiocyanate failed.

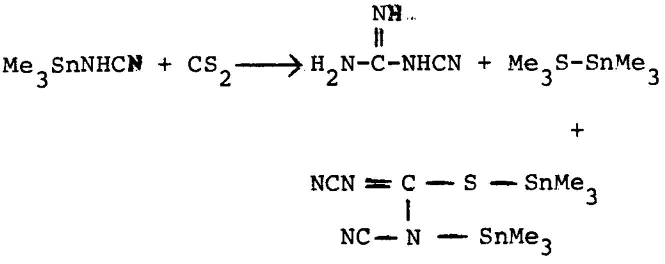
Trimethylchlorosilane in the presence of triethylamine was used to silylate thiourea yielding N,N'-bis(trimethylsilyl)thiourea.[89] The corresponding carbodiimide was prepared from the thiourea by reaction of the latter with the silver salt of imidazole.



$$Me_3SiCl + S{=}C(NH_2)_2 \xrightarrow{Et_3N} Me_3SiNH\text{-}\overset{\overset{S}{\|}}{C}\text{-}NHSiMe_3 \xrightarrow{Ag\text{-}imidazole} Me_3SiN = C = NSiMe_3$$

V. TIN DERIVATIVES

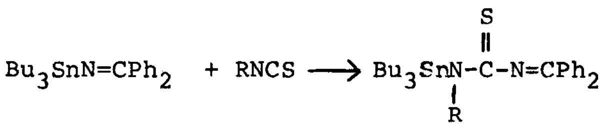
Triorganostannyl cyanamides react with carbon disulfide to yield the corresponding N,N'-dicyano-N'-triorganostannyl-S-triorganostannylisothiourea (84).[90]



$$Me_3SnNHCN + CS_2 \longrightarrow H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NHCN + Me_3S\text{-}SnMe_3 + \mathbf{84}$$

84

N-Tributylstannylbenzophenone imine (85) undergoes rapid reaction with methyl and phenyl isothiocyanate to give N-tributylstannyl-N-alkyl(aryl)-N'-benzhydrylideneaminothioureas (86) as the product.[91]

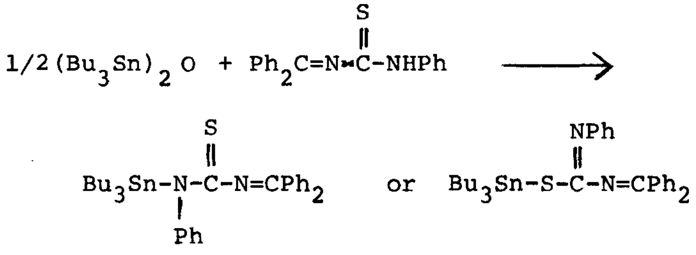


$$Bu_3SnN{=}CPh_2 + RNCS \longrightarrow Bu_3Sn\underset{R}{N}-\overset{S}{\overset{\|}{C}}-N{=}CPh_2$$

R = Me,Ph

85 86

Tributyltin oxide reacts with N-benzhydrylideneamino-N'-phenylthiourea to give the stannylated product 87 or 88. This reaction does not work with the corresponding methylthiourea derivative.



$$1/2(Bu_3Sn)_2O + Ph_2C{=}N{-}\overset{S}{\overset{\|}{C}}{-}NHPh \longrightarrow$$

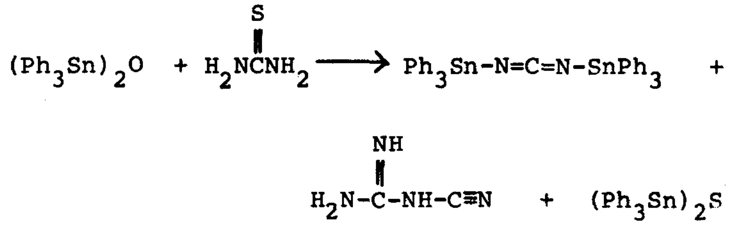
$$Bu_3Sn-\underset{Ph}{N}-\overset{S}{\overset{\|}{C}}-N{=}CPh_2 \quad \text{or} \quad Bu_3Sn-S-\overset{NPh}{\overset{\|}{C}}-N{=}CPh_2$$

87 88

An infrared spectrum of the product suggests that the stannylation takes place at the sulfur giving an Sn - S bond since the band attributable to C = S could not be observed.

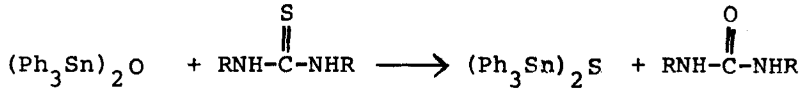
George and co-workers[92] report that infrared spectroscopy indicates that the product of aminostannylation of phenyl isothiocyanate is a thioureido-organostannane.

When bis(triphenyltin)oxide, $(Ph_3Sn)_2O$ was treated with thiourea the products were bis(triphenylstannyl)carbodiimide, dicyandiamide and bis(triphenyltin)sulfide.[93]



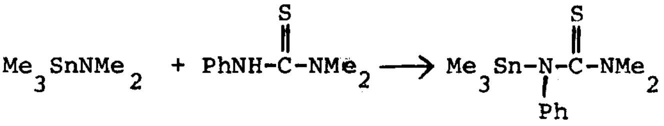
$$(Ph_3Sn)_2O + H_2N\overset{S}{\overset{\|}{C}}NH_2 \longrightarrow Ph_3Sn{-}N{=}C{=}N{-}SnPh_3 + H_2N{-}\overset{NH}{\overset{\|}{C}}{-}NH{-}C{\equiv}N + (Ph_3Sn)_2S$$

When the same reaction was conducted with 1,3-disubstituted thioureas, the products were bis(triphenyltin)sulfide and the corresponding 1,3-disubstituted urea.



$$(Ph_3Sn)_2O + RNH{-}\overset{S}{\overset{\|}{C}}{-}NHR \longrightarrow (Ph_3Sn)_2S + RNH{-}\overset{O}{\overset{\|}{C}}{-}NHR$$

Compounds such as trimethylstannyl-N,N-dimethyl-N'-phenylthiourea are formed by what are essentially insertions into the Sn-N bond.[94,95]



$$Me_3SnNMe_2 + PhNH{-}\overset{S}{\overset{\|}{C}}{-}NMe_2 \longrightarrow Me_3Sn{-}\underset{\underset{Ph}{|}}{N}{-}\overset{S}{\overset{\|}{C}}{-}NMe_2$$

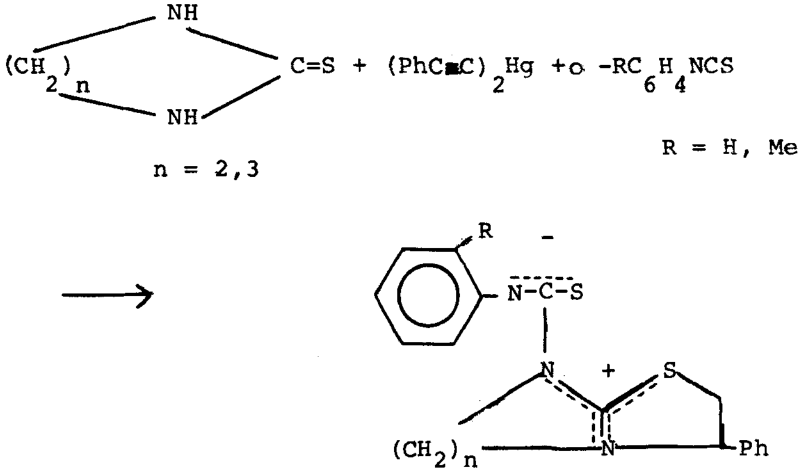
These tin (IV)-amino compounds are highly reactive and may be of value as synthetic intermediates for the synthesis of organometallic compounds.

VI. MERCURY DERIVATIVES

o-, m- and p-Carboxyphenylthioureas may be mercurated with mercuric acetate yielding the monoacetoxymercury derivatives.[96] Phenyl and the tolylthioureas give the di-mercurated products, while carboxyphenylthioureas afford the monomercurated product.

m-Bromophenylthiourea is monomercurated in the para-position by reaction with mercuric acetate.[97] The 4-chloromercury and 4-bromomercury analog is obtained by reaction of the product with sodium chloride or sodium bromide, respectively.

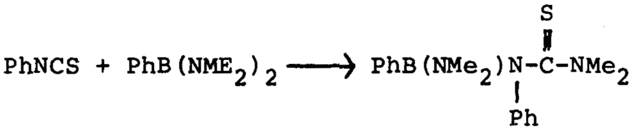
Cyclic thioureas react with bis (phenylethyanl)mercury and phenyl or o-tolylisothiocyanate to give betaines with an imidazothiazole or a pyrimidinothiazole structure.[98]



Not all reactions of thiourea with organomercury compounds lead to mercurated derivatives. Thus, the reaction of iodomercuriacetone (CH_3COCH_2HgI) with thiourea and alcoholic iodine leads to the formation of 2-amino-4-methylthiazole.[99]

VII. BORON, ARSENIC AND GERMANIUM DERIVATIVES

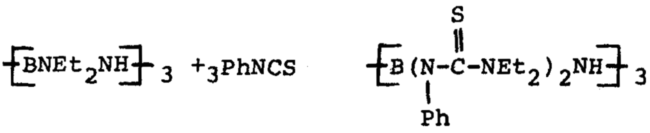
The aminoboration of phenyl isothiocyanate with alkylaminoboranes or -borazines afford acyclic thioureido derivatives.[100,101] Thus, the reaction of bis (dimethylamino)phenylborane reacts with phenyl isothiocyanate to yield N',N'-dimethyl-N-(phenylthioureido)phenylborane 89.



$$PhNCS + PhB(NME_2)_2 \longrightarrow PhB(NMe_2)\underset{\underset{\displaystyle Ph}{|}}{N}-\overset{\overset{\displaystyle S}{\|}}{C}-NMe_2$$

89

Tris-B-(diethylamino)borazine reacts with phenyl isothiocyanate to yield tris-B-(N',N'-diethyl-N-phenylthioureido) borazine 90.

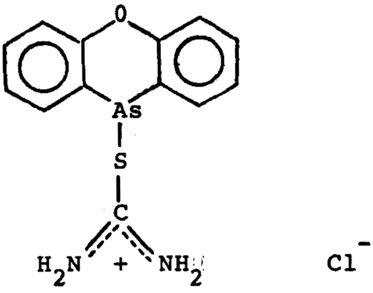


$$\left[BNEt_2NH\right]_3 \ {+}_3PhNCS \qquad \left[B(\underset{\underset{\displaystyle Ph}{|}}{N}-\overset{\overset{\displaystyle S}{\|}}{C}-NEt_2)_2NH\right]_3$$

90

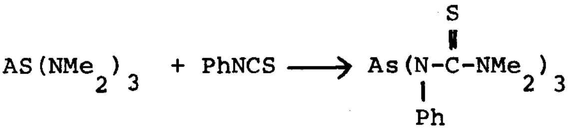
Similarly, the product $\left[B\ PhNC(S)NHBu\text{-}t\right]_3$ is obtained by the reaction of phenyl isothiocyanate with tris-(t-Butylamino)borane.

Thiourea was reacted with 10-chlorophenoxyarsine to yield S-(10-phenoxarsinyl)thiopseudourea hydrochloride 91.[102] Other similar arsenic derivatives were also prepared.



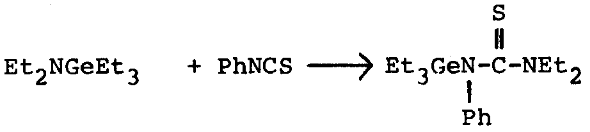
91

Alkyl and aryl isothiocyanates cleave the arsenic nitrogen bond in dimethylamidoarsenous acids. The arsenic-phosphorus bond in phosphonic acids may also be cleaved by these isothiocyanates.[40,41] The dimethylamino group is added to the carbon atom of the isothiocyanate with the formation of N-substituted-N'-dimethylthioureas.



$$AS(NMe_2)_3 + PhNCS \longrightarrow As(\underset{\underset{Ph}{|}}{N}-\overset{\overset{S}{\|}}{C}-NMe_2)_3$$

Alkylgermanium derivatives of thiourea were prepared by the cleavage of dialkylaminotrialkylgermanes with phenyl isothiocyanate.[103] The Ge-N bond is cleaved under these conditions.



$$Et_2NGeEt_3 + PhNCS \longrightarrow Et_3Ge\underset{\underset{Ph}{|}}{N}-\overset{\overset{S}{\|}}{C}-NEt_2$$

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