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Reactions of Diarylphosphines, Their Oxides and Sulfides with Isothiocyanates and Thiocyanic Acid

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N-Substituted thiocarbamoyldiarylphosphine oxides and sulfides were prepared by the addition reaction of diarylphosphine oxides and diphenylphosphine sulfide with isothiocyanates. Diarylphosphine oxides and diphenylphosphine reacted with ammonium thiocyanate under hydrogen chloride stream to produce diarylphosphinyl- and diarylthiophosphinyl-substituted bis(iminomethyl) sulfides, which are a new type of sulfide. Diphenylphosphine also reacted with thiocyanic acid in ether to give thiocarbamoyldiphenylphosphine and bis(diphenylphosphinyliminomethyl) sulfide. Mechanisms for formation of these bis(iminomethyl) sulfides have been discussed.

In recent years, some attempts have been made to introduce the carbamoyl or thiocarbamoyl group to phosphines and phosphites.[1-3] Issleib and Harzfeld[3] prepared *N*-substituted thiocarbamoylphosphines by reactions of phosphines or their metal salts with isothiocyanates. *N*-Substituted thiocarbamoylphosphine oxides and sulfides were prepared by the reaction of the corresponding *N*-

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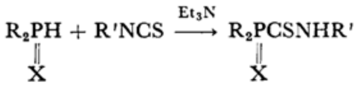
[1] T. Reetz, D. H. Chadwick, E. E. Hardy and S. Kaufman, *J. Am. Chem. Soc.*, **77**, 3813 (1955).

[2] R. C. Schulz and H. Hartmann, *Monatsh. Chem.*, **93**, 905 (1962).

[3] K. Issleib and G. Harzfeld, *Chem. Ber.*, **97**, 3430 (1964); *Z. anorg. allg. Chem.*, **351**, 18 (1967).

substituted thiocarbamoylphosphines with oxygen and sulfur, respectively.

We found that diarylphosphine oxides (I) and diphenylphosphine sulfide (I′, $R=C_6H_5$) as well as phosphines reacted with isothiocyanates in the presence of a few drops of triethylamine[4] at 70—80°C to give *N*-substituted thiocarbamoyldiarylphosphine oxides (II) and sulfides (II′) in good yields, respectively. These results are summarized in Table 1. The elemental analyses and spectral data of these compounds support the structures (see Tables 2 and 3).



$$\underset{\substack{\| \\ X}}{R_2PH} + R'NCS \xrightarrow{Et_3N} \underset{\substack{\| \\ X}}{R_2PCSNHR'}$$

I : X=O II : X=O
I′: X=S II′: X=S

As shown in Table 3, the UV spectra of II and II′ in ethyl alcohol displayed an intense band in the 290—350 mμ region, which presumably arises from the π–π^* transition in the C=S group. The n–π^* transition band appeared in the 390—450 mμ region.

TABLE 1. *N*-SUBSTITUTED THIOCARBAMOYLDIARYLPHOSPHINE OXIDES (II) AND SULFIDES (II′)

	R	R′	Mp (°C) (lit)	Yield (%)
IIa	C_6H_5	CH_3	190—191 (194)[3]	87
IIb*	C_6H_5	CH_2=$CHCH_2$	119—122	80
IIc*	C_6H_5	α-$C_{10}H_7$	181—183	67
IId*	C_6H_5	C_6H_5	163.5—164.5	75
IIe*	*p*-$CH_3C_6H_4$	C_6H_5	163—164	68.5
IIf*	*p*-$CH_3OC_6H_4$	C_6H_5	138—140	65
IIg*	*p*-ClC_6H_4	CH_3	225—226	90
IIh*	*p*-ClC_6H_4	α-$C_{10}H_7$	157—160	50
II′a*	C_6H_5	C_6H_5	126—128	75
II′b	C_6H_5	CH_3	98—100 (103)[3]	60
II′c*	C_6H_5	α-$C_{10}H_7$	128—130	95

* New compound

TABLE 2. ANALYTICAL DATA FOR II AND II′

	R	R′	Elemental analyses* (%)				
			C	H	N	S	Cl
IIa	C_6H_5	CH_3	60.92 (61.09)	5.32 (5.09)	4.86 (5.09)	11.97 (11.64)	
IIb	C_6H_5	CH_2=$CHCH_2$	63.59 (63.79)	5.75 (5.32)	4.57 (4.65)	10.63 (10.63)	
IIc	C_6H_5	α-$C_{10}H_7$	71.12 (71.32)	4.86 (4.65)	3.70 (3.62)	8.45 (8.27)	
IId	C_6H_5	C_6H_5	67.69 (67.66)	5.01 (4.75)	4.24 (4.15)	9.52 (9.49)	
IIe	*p*-$CH_3C_6H_4$	C_6H_5	68.72 (69.04)	5.61 (5.48)	3.88 (3.84)	8.78 (8.76)	
IIf	*p*-$CH_3OC_6H_4$	C_6H_5	63.54 (63.48)	5.31 (5.04)	3.34 (3.52)	8.27 (8.06)	
IIg	*p*-ClC_6H_4	CH_3	48.77 (48.86)	3.73 (3.51)	4.22 (4.07)	9.32 (9.31)	20.60 (20.49)
IIh	*p*-ClC_6H_4	α-$C_{10}H_7$	60.68 (60.53)	3.45 (3.51)	3.29 (3.07)	7.11 (7.02)	15.32 (15.57)
II′a	C_6H_5	C_6H_5	64.50 (64.59)	4.60 (4.53)	4.22 (3.97)	18.41 (18.13)	
II′b	C_6H_5	CH_3	57.87 (57.73)	4.93 (4.81)	4.86 (4.81)	22.06 (21.99)	
II′c	C_6H_5	α-$C_{10}H_7$	68.34 (68.49)	4.39 (4.47)	3.38 (3.48)	15.88 (15.88)	

* Values in parentheses show the calculated values.

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[4] R. B. Fox and D. L. Venezky, *J. Am. Chem. Soc.*, **78**, 1661 (1956).

TABLE 3. UV AND IR SPECTRA OF II AND II′

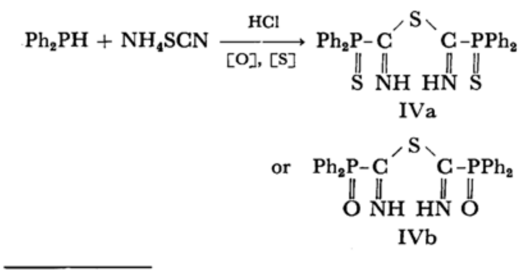
	λ_{max}^{EtOH} (mμ)		ν^{Nujol}		
	π-π^* (ε)	n-π^* (ε)	ν_{N-H}	" Amide II "	$\nu_{P=O}$
IIa	291 (6970)	395 (83)	3160	1520	1190
IIb	292 (7970)	401 (84)	3150	1515	1185
IIc	343 (6930)	436 s (154)	3060*	1480	1180
IId	330 (13000)	443 (120)	3060*	1530	1180
IIe	329 (12000)	441 (150)	3050*	1495	1170
IIf	328 (12900)	442 (115)	3070*	1490	1165
IIg	290 (7190)	394 (80)	3150	1520	1190
IIh	335 (5780)	388 s (67)	3050*	1490	1190
II′a	333 (11300)	447 (101)	3150 3100	1530	
II′b	280 (7500)	400 (68)	3230 3180	1515	
II′c	352 (7340)	446 s (127)	3180*	1500	

* In hexachlorobutadiene

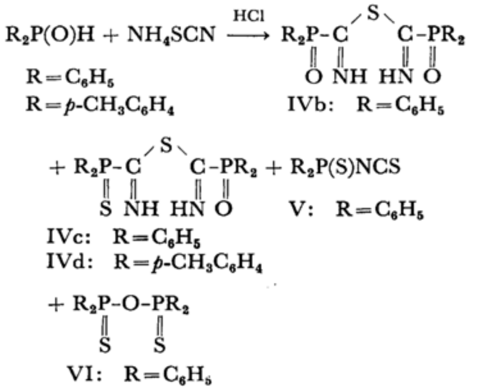
Lately, Vaughan and Lindsey, Jr., reported[5] that carbamoyldiphenylphosphine was prepared by the addition reaction of diphenylphosphine with isocyanic acid in benzene. Papp and Buckler also prepared it by the addition of aqueous potassium cyanate to the mixture of diphenylphosphine and acetic acid.[6]

We extended the addition reaction of I and I′ with isothiocyanates to the syntheses of thiocarbamoyldiphenylphosphine (IIIa) and its oxide (IIIb) by the reaction of diphenylphosphine and its oxide with thiocyanic acid. First, thiocyanic acid was generated *in situ* from the reaction of ammonium thiocyanate with dry hydrogen chloride analogously to the synthesis of diphenylthiourea from diphenylamine.[7]

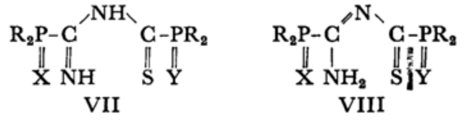
Diphenylphosphine was allowed to react with ammonium thiocyanate and dry hydrogen chloride in chlorobenzene under nitrogen atmosphere at 80—85°C. However, bis(diphenylthiophosphinyliminomethyl) sulfide (IVa), which is a new type of sulfide, was obtained in 20% yield, instead of the expected IIIa. In benzene at 50°C, the corresponding phosphinyl compound (IVb) was obtained in 20% yield. The oxygen atoms in IVb might be taken in during column chromatography on alumina, and the sulfur atoms in IVa might be taken in from some sulfur compound during the reaction. These reactions have not been known in the case of secondary amines.



A similar reaction of diphenylphosphine oxide in refluxing benzene gave the bis(iminomethyl) sulfides, IVb and IVc, in 28% and 13% yields, respectively. However, in chlorobenzene at 100°C, only IVc was obtained in 25% yield. In some cases, diphenylthiophosphinyl isothiocyanate (V) and diphenylthiophosphinic anhydride (VI) were obtained in 3—10% yield. A similar reaction of di-*p*-tolylphosphine oxide gave IVd (analogous to IVc) in 7—10% yield.



The structures of IVa, IVb, IVc, IVd, V and VI were supported by elemental analyses, IR, NMR and mass spectra. These data, however, can not exclude the possibility of structures VII or VIII, which are isomers of IV. II and II′ are yellow



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[5] L. G. Vaughan and R. V. Lindsey, Jr., *J. Org. Chem.*, **33**, 3088 (1968).

[6] G. P. Papp and S. A. Buckler, *ibid.*, **31**, 588 (1966).

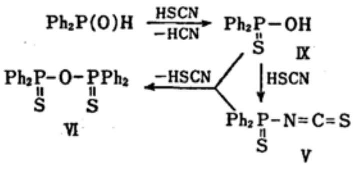
[7] H. Passing, *J. prakt. Chem.*, **153**, 1 (1939).

TABLE 4. UV AND IR SPECTRA OF IIIa, IIIb AND IIIc

	$\lambda_{\max}^{\text{EtOH}}$ (mμ)				ν^{Nujol} (cm^{-1})		
	π-π*	(ε)	n-π*	(ε)	$\nu_{\text{N-H}}$	"Amide II"	$\nu_{\text{P=O}}$
IIIa	292	(8720)	376	(135)	3300 3260 s 3130	1605	
IIIb	295	(5770)	406	(38)	3260 3170 s 3030*	1640	1160
IIIc	290	(5940)	412	(41)	3250 3200 s 3100*	1590	

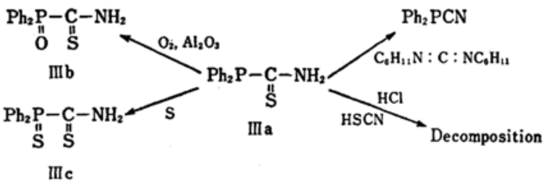
* In hexachlorobutadiene

crystals and display the intense π–π* and n–π* transition bands which arise from C=S group in their UV spectra(Table 3). However, compounds IVa—d are colorless and their UV spectra did not show any peaks due to π–π* and n–π* transitions of C=S group (see Experimental). Therefore, the structures of these compounds were determined to be IVa—d, which do not contain C=S group. Possible pathways for the formation of V and VI might be as follows, from separate experimental results (see Experimental).



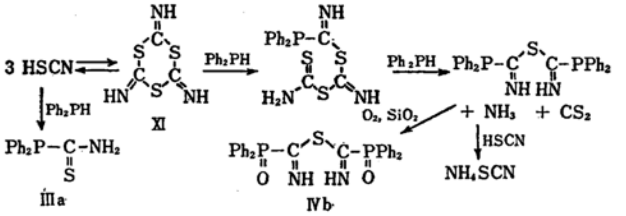
The formation of IVc or IVd from diarylphosphine oxide, ammonium thiocyanate and hydrogen chloride may be attributed to an oxygen-sulfur exchange reaction in P=O bond by thiocyanic acid during the course.

The compounds IVa, IVb and IVc were presumed to be formed by the condensation of IIIa or its oxide (IIIb) in the presence of hydrogen chloride. With this in mind, we let diphenylphosphine react with thiocyanic acid in ether[8] without hydrogen chloride under nitrogen atmosphere at room temperature for a week, and obtained IIIa (57%) and IVb (10%). The oxygen atoms in IVb might be taken in during column chromatography on silica gel. Thiocarbamoyldiphenylphosphine oxide (IIIb) and sulfide (IIIc) were prepared by the reaction of IIIa with oxygen and sulfur in 62% and 70% yields, respectively. These spectral data are listed in Table 4.



The condensation reaction of IIIa to IVa—c was attempted with hydrogen chloride or/and thiocyanic acid under various conditions. The expected condensation products (IVa—c) were not obtained, but only diphenylphosphine oxide and inorganic compounds (ammonium chloride or/and thiocyanate, from IR, respectively) were isolated. Namely, III decomposed in the presence of strong acid. This fact explains that no III could be obtained in the reactions of diphenylphosphine or diarylphosphine oxide with ammonium thiocyanate under hydrogen chloride at 50—100°C. This fact also made it certain that IV was not formed by the condensation of III.

Though the path of the formation of IV is not clear, one of possible paths is the addition of diphenylphosphine to a trimer (XI)*[1] of thiocyanic acid which is assumed to be present analogously to cyamelide form,[9] as shown below.



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8) R. Klason, *J. prakt. Chem.*, **35**, 407 (1887).

The reaction of IIIa with *N,N'*-dicyclohexylcarbodiimide as condensation reagent gave only diphenylcyanophosphine (X) in 71% yield, without any intermolecular condensation product, IV.

Experimental[*2]

Materials. Diphenylphosphine was prepared by the reduction of diphenylchlorophosphine with lithium aluminum hydride.[11] Bp 100—110°C/0.8—1.0 mmHg (lit 100—102°C/1.5 mmHg). Diphenylphosphine oxide was prepared by the hydrolysis of diphenylchlorophosphine.[12] Diarylphosphine oxides were prepared according to the directions of Grayson, Farley and Streuli.[13,14] $R_2P(O)H$: $R=C_6H_5$, mp 51—54°C (lit[12] 51—54°C); $R=p\text{-}CH_3C_6H_4$, mp 98—100°C (lit[14] 102—103°C); $R=p\text{-}CH_3OC_6H_4$, mp 121—124°C (lit[14] 125—126°C); $R=p\text{-}ClC_6H_4$, mp 130—133°C (lit[14] 131—133°C). Diphenylphosphine sulfide was prepared by the reaction of diphenylphosphine with sulfur.[15] Mp 96—97°C (lit[15] 95—97°C).

Reaction of Diarylphosphine Oxides and Diphenylphosphine Sulfide with Isothiocyanates. A typical procedure is described for the reaction of diphenylphosphine oxide with phenyl isothiocyanate. A mixture of diphenylphosphine oxide (2.0 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) was heated without solvent in the presence of a few drops of triethylamine for 5 hr at 70—80°C. The crystalline product obtained was recrystallized from ethanol to afford 2.52 g (7.5 mmol, 75%) of *N*-phenylthiocarbamoyldiphenylphosphine oxide (IId), mp 163.5—164.5°C.

Physical properties and analytical data are shown in Tables 1—3.

Reaction of Diphenylphosphine with Ammonium Thiocyanate and Hydrogen Chloride. *a) In Chlorobenzene.* A solution of 18 g (89 mmol) of diphenylphosphine in 50 m*l* of chlorobenzene was vigorously stirred with 9 g (118 mmol) of dried ammonium thiocyanate powder under nitrogen atmosphere, and dry hydrogen chloride was passed through the mixture. After the initial exothermic reaction subsided, the reaction mixture was heated at 80—85°C for 1.5 hr. After removal of solvent under reduced pressure, the residue was chromatographed on alumina. Bis(diphenylthiophosphinyliminomethyl) sulfide (IVa) (4.2 g, 8.04 mmol, 20%) was eluted with dichloromethane and recrystallized from *n*-butyl alcohol; colorless needles, mp 221—222°C (dec.). IR(Nujol): 3370, 3230, 3150 (sh) (ν_{NH}), and 1525 cm^{-1} ($\nu_{C=N}$). $\lambda_{max}^{CH_3CN}$: 257(sh)mμ (ε=16000). NMR(DMSO): δ 8.16 (NH, doublet, J_{PCNH}=10.5 Hz). Mass spectrum (significant peaks): m/e=520 (M^+, 0.08), 488 (M^+-32, 14), 218 (Ph_2PSH^+, 86.5), 217 (Ph_2PS^+, 100), 185 (Ph_2P^+, 73), 140 ($PhPS^+$, 54.5), 108 (PhP^+, 50), 77 (Ph^+, 45.5), and 63 (PS^+, 50).

Found: C, 60.01; H, 4.34; N, 5.35; S, 18.47%. Calcd for $C_{26}H_{22}N_2P_2S_3$: C, 60.00; H, 4.23; N, 5.38; S, 18.46%.

b) In Benzene. When this reaction was carried out in benzene at 50°C for 2hr, the corresponding phosphinyl compound (IVb) was obtained in 20% yield by a similar treatment. Mp 228—229°C (dec.). The IR spectrum was identical with that of the product obtained from the reaction of diphenylphosphine oxide (described below).

Reaction of Diphenylphosphine Oxide with Ammonium Thiocyanate and Hydrogen Chloride. *a) In Benzene.* A solution of 10 g (49.5 mmol) of diphenylphosphine oxide in 100 m*l* of benzene was vigorously stirred with 3.5 g (46 mmol) of ammonium thiocyanate under dry hydrogen chloride stream. After the initial exothermic reaction subsided, the reaction mixture was heated under reflux for 5 hr and then chromatographed on alumina. Diphenylphosphine oxide (3.5 g, 35%) was recovered from a benzene eluate. Elution with ether afforded diphenylphosphinyliminomethyl diphenylthiophosphinyliminomethyl sulfide (IVc) (500 mg, 0.99 mmol. 13.4%), colorless prisms from isobutyl alcohol, mp 230—231°C (dec.). IR(Nujol): 3450, 3280, 3150(sh) (ν_{NH}), 1545 ($\nu_{C=N}$) and 1180 cm^{-1} ($\nu_{P=O}$). λ_{max}^{EtOH}: 253 (sh) mμ (ε=19700) and two weak shoulders in 260—275 mμ region. NMR(DMSO): δ 8.30 (NH, doublet, J_{PCNH}=10.5 Hz). Mass spectrum (significant peaks): m/e=504 (M^+, 3), 488 (M^+-16, 27), 472 (M^+-32, 3.3), 218 (Ph_2PSH^+, 61), 217 (Ph_2PS^+, 100), 202 (Ph_2POH^+, 23), 201 (Ph_2PO^+, 77), 185 (Ph_2P^+, 57) 140 ($PhPS^+$, 16), 124 ($PhPO^+$, 14), 108 (PhP^+, 25), 77 (Ph^+, 66), 63 (PS^+, 31), and 47 (PO^+, 20).

Found: C, 61.82; H, 4.72; N, 5.58; S, 12.65%. Calcd for $C_{26}H_{22}N_2OP_2S_2$: C, 61.90; H, 4.36; N, 5.58; S, 12.75%.

Elution with ethyl acetate - ethyl alcohol (1 : 1) gave bis(diphenylphosphinyliminomethyl) sulfide (IVb) (2.0 g, 4.1 mmol, 27.6%), colorless prisms from isobutyl alcohol, mp 229—229.5°C (dec.). IR (Nujol): 3475(sh), 3250, 3150 (ν_{NH}), 1550 ($\nu_{C=N}$), and 1170 cm^{-1} ($\nu_{P=O}$) λ_{max}^{EtOH}: 253(sh) (ε=18300), 265(sh) (14800), and 272 (sh) mμ (11800). NMR($CDCl_3$): δ 9.93 (NH, doublet, J_{PCNH}=10.5 Hz). Mass spectrum (significant peaks):

[*1] Thiocyanic acid reversibly polymerizes to trimer or hexamer,[10] whose structures are not clear. Although we assumed the existence of "thiocyamelide"(XI), in so far as the polymer has $(\text{-S-}\overset{\overset{\text{NH}}{\|}}{\text{C}}\text{-})_n$ structure, III, IV, NH_3 and CS_2 can be formed through ring opening or chain cleavage reactions, analogously to the case of XI.

9) E. A. Werner and W. R. Fearon, *J. Chem. Soc.*, **117**, 1356 (1920); A. Senier and T. Walsh, *ibid.*, **81**, 290 (1902).

10) L. Birckenbach and E. Büchner, *Ber.*, **73**, 1153 (1940).

[*2] IR spectra were recorded on a grating spectrometer HITACHI Model EPI-G2. The NMR spectra were recorded on a JEOL Model JNM-C-60H using TMS as an internal standard. UV spectra were measured on a HITACHI Model EPS-3. Mass spectra were measured on a HITACHI Model RMU-6D. The melting and boiling points are not corrected.

11) W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).

12) L. D. Quin and R. Montgomery, *J. Org. Chem.*, **28**, 3315 (1963); R. C. Miller, *ibid.*, **24**, 2013 (1959).

13) R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952).

14) M. Grayson, C. E. Farley and C. A. Streuli, *Tetrahedron*, **23**, 1065 (1967).

15) G. Peters, *J. Am. Chem. Soc.*, **82**, 4751 (1960).

m/e=488 (M^+, 2), 472 (M^+-16, 16), 202 ($\mathrm{Ph_2POH}^+$, 60), 201 ($\mathrm{Ph_2PO}^+$, 100), 185 ($\mathrm{Ph_2P}^+$, 18), 124(PhPO^+, 10), 108 (PhP^+, 7), 77 (Ph^+, 56), and 47 (PO^+, 28).

Found: C, 63.72; H, 4.78; N, 5.70; S, 6.77%. Calcd for $\mathrm{C_{26}H_{22}O_2P_2S}$: C, 63.93; H, 4.51; N, 5.74; S, 6.56%.

b) In Chlorobenzene. When diphenylphosphine oxide (25 g, 124 mmol) was allowed to react with ammonium thiocyanate (11 g, 145 mmol) in 100 *ml* of chlorobenzene at 100°C for 1.5 hr under hydrogen chloride stream, only IVc was obtained in 25% yield. Mp 230—231°C (dec.). The IR and mass spectra were identical with those obtained by the reaction mentioned above.

Diphenylthiophosphinyl isothiocyanate (V), mp 48—49°C (lit[16] 48°C), and diphenylthiophosphinic anhydride (VI), mp 198—199°C (lit[17] 197—198°C), were often obtained in 3—10% yield in these reactions.

Reactions of Diphenylthiophosphinic Acid (IX) with Thiocyanic Acid and Diphenylthiophosphinyl Isothiocyanate (V). Diphenylthiophosphinic acid (IX) was prepared conveniently from diphenylphosphine oxide and sulfur in the presence of hydrogen chloride in refluxing benzene for 1.5 hr. The precipitated needles were washed once with carbon disulfide. Yield: 70%. Mp 142—144°C (lit[18] 143—144°C). IR(Nujol): 895 cm^{-1} ($\nu_{\mathrm{P-OH}}$). Two grams (8.6 mmol) of IX was allowed to react with 1.0 g (13.2 mmol) of ammonium thiocyanate and hydrogen chloride in chlorobenzene at 100—110°C for 1.5 hr. After the solvent was removed, the IR spectrum of the residue showed a strong band at 1960 cm^{-1} ($\nu_{\mathrm{N=C=S}}$), which is identical with that of V. Diphenylthiophosphinyl isothiocyanate (V) (1.0 g, 4.0 mmol) and IX (0.5 g, 2.14 mmol) were mixed without solvent and heated at 90—96°C for 3 hr and the IR spectrum of the reaction mixture was measured. There appeared[16] strong new peaks at 940(sh), 925, and 915 cm^{-1} ($\nu_{\mathrm{P-O-P}}$) which is identical with that of VI.

Reaction of Di-*p*-tolylphosphine Oxide with Ammonium Thiocyanate under Hydrogen Chloride. Di-*p*-tolylphosphine oxide (10 g, 43.5 mmol) was reacted with ammonium thiocyanate (3.3 g, 43.5 mmol) in 100 *ml* of chlorobenzene under hydrogen chloride stream at 100—105°C for 1.5 hr. Treatment similar to that for the reaction of diphenylphosphine oxide gave di-*p*-tolylphosphinyliminomethyl di-*p*-tolylthiophosphinyliminomethyl sulfide (IVd) (7—10%), colorless prisms, mp 226—227°C (dec.). IR (Nujol): 3460, 3260, 3150 (sh) (ν_{NH}), 1540($\nu_{\mathrm{C=N}}$), and 1175 cm^{-1} ($\nu_{\mathrm{P=O}}$). NMR(DMSO): δ 8.15 (NH, doublet, J_{PCNH}=10.5 Hz). Mass spectrum (significant peaks): m/e=560 (M^+, 2.5), 544 (M^+-16, 90), 528 (M^+-32, 10), 246 ($\mathrm{T_2PSH}^+$, 90), 245 ($\mathrm{T_2PS}^+$, 100), 230 ($\mathrm{T_2POH}^+$, 85), 229 ($\mathrm{T_2PO}^+$, 95), 213 ($\mathrm{T_2P}^+$, 85), 154 (TPS^+, 65), 138 (TPO^+, 50), 122 (TP^+, 80), 91 (T^+, 90), 63 (PS^+, 45), and 47 (PO^+, 25), where T represents *p*-$\mathrm{CH_3C_6H_4}$.

Found: C, 63.83; H, 5.64; N, 4.96; S, 11.16%. Calcd for $\mathrm{C_{30}H_{30}N_2OP_2S_2}$: C, 64.29; H, 5.36; N, 5.00; S, 11.43%.

IR spectrum, 1965 cm^{-1} ($\nu_{\mathrm{N=C=S}}$), of a benzene eluate by column chromatography on alumina showed formation of isothiocyanate, which might be the *p*-tolyl derivative of V, but was not isolated in pure state. When this reaction was carried out in benzene under reflux for 2 hr, IVd, mp 226—227°C (dec.), was also obtained in 7% yield.

Reaction of Diphenylphosphine with Thiocyanic Acid. To ammonium thiocyanate (6.9 g, 91 mmol) in 7.0 g of water was added concd. sulfuric acid (4.5 g) in 9.0 g of water, and the aqueous solution was shaken twice with 50 *ml* of ether. According to Klason,[8] 95% of thiocyanic acid generated is extracted by ether. The ethereal solution of thiocyanic acid was added dropwise to 15.0 g (81 mmol) of diphenylphosphine in ether (20 *ml*) under nitrogen atmosphere and then the mixture was allowed to stand at room temperature for a week with stirring. The residue after concentration was chromatographed on silica gel (Davison No. 922). Unreacted diphenylphosphine was oxidized during chromatography and 5.0 g of diphenylphosphine oxide was eluted with benzene. Thiocarbamoyldiphenylphosphine (IIIa) was eluted with benzene-chloroform and recrystallized from isobutyl alcohol as colorless needles, mp 114—116°C. Yield: 7.8 g (31.8 mmol, 57%). Mass spectrum (significant peaks): m/e=245 (M^+, 90), 211 (M^+-34, 60), 186 ($\mathrm{Ph_2PH}^+$, 95), 185 ($\mathrm{Ph_2P}^+$, 35), 108 (PhP^+, 100), 77 (Ph^+, 30), and 60 ($\mathrm{CSNH_2}^+$, 40).

Found: C, 63.85; H, 5.08; N, 5.57; S, 13.18%. Calcd for $\mathrm{C_{13}H_{12}NPS}$: C, 63.67; H, 4.90; N, 5.72; S, 13.06%.

Bis(iminomethyl) sulfide (IVb) was also eluted with ethyl acetate and recrystallized from isobutyl alcohol. Yield: 1.35 g (5.6 mmol, 10.0%). Mp 228—229°C.

Preparation of Thiocarbamoyldiphenylphosphine Oxide (IIIb). Thiocarbamoyldiphenylphosphine (IIIa) (489 mg, 2.00 mmol) was dissolved in 50 *ml* of ethyl alcohol, and 3.0 g of alumina was suspended and oxygen was passed through the mixture under reflux for 2 hr. After removal of alumina and the solvent, the residue was recrystallized from isobutyl alcohol to give 325 mg (1.25 mmol, 62.3%) of pure IIIb, mp 205°C (dec.). Mass spectrum (significant peaks): m/e=261 (M^+, 11), 227 (M^+-34, 28), 202 ($\mathrm{Ph_2POH}^+$, 100), 201 ($\mathrm{Ph_2PO}^+$, 56), 185 ($\mathrm{Ph_2P}^+$, 22), 124 (PhPO^+, 17), 108 (PhP^+, 17), 77 (Ph^+, 95), 60 ($\mathrm{CSNH_2}^+$, 39), and 47 (PO^+, 95).

Found: C, 60.00; H, 4.68; N, 5.59; S, 12.74%. Calcd for $\mathrm{C_{13}H_{12}NOPS}$: C, 59.77; H, 4.60; N, 5.37; S, 12.26%.

Preparation of Thiocarbamoyldiphenylphosphine Sulfide (IIIc). Sulfur (73 mg, 2.28 g atom) and IIIa (503 mg, 2.05 mmol) were dissolved in 50 *ml* of benzene, and the mixture was heated under reflux for 2 hr. After the solvent was removed, the residue was recrystallized from isobutyl alcohol. Yellow prisms thus obtained were washed once with 5 *ml* of carbon disulfide to afford 397 mg (1.43 mmol, 70%) of pure IIIc, mp 132—135°C. Mass spectrum (significant peaks): m/e=277 (M^+, 23), 243 (M^+-34, 10), 218 ($\mathrm{Ph_2PSH}^+$, 100), 217 ($\mathrm{Ph_2PS}^+$, 30), 185 ($\mathrm{Ph_2P}^+$, 53), 140 (PhPS^+, 53), 108 (PhP^+, 47), 77 (Ph^+, 63), and 63 (PS^+, 77).

Found: C, 56.48; H, 4.09; N, 5.05; S, 22.98%. Calcd for $\mathrm{C_{13}H_{12}NPS_2}$: C, 56.32; H, 4.33; N, 5.05; S, 23.10%.

Reaction of Thiocarbamoyldiphenylphosphine

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(IIIa) with Dicyclohexylcarbodiimide. Dicyclohexylcarbodiimide (813 mg, 3.95 mmol) and IIIa (1.003 g, 4.09 mmol) were heated in 20 m*l* of benzene under reflux for 6 hr. Then the reaction mixture was cooled and 754 mg (3.14 mmol, 80%) of *N*,*N'*-dicyclohexylthiourea thus obtained, mp 179—181°C (lit[19] 180—181°C), was filtered off. The filtrate was chromatographed on silica gel (Davison No. 922). Diphenylcyanophosphine (X)[20] (596 mg, 2.82 mmol) was eluted with benzene as colorless oil in 71% yield. (Found: C, 73.24; H, 5.12; N, 6.39%). IR: 2180 cm^{-1} ($\nu_{C\equiv N}$, weak).

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