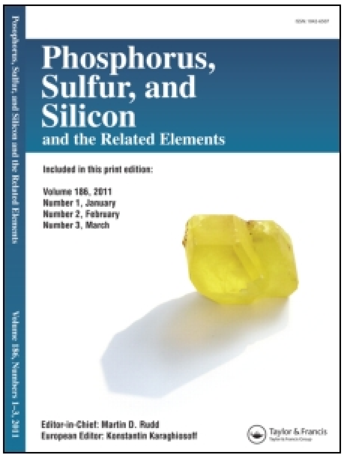


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF SUBSTITUTED 2,3-DIHYDRO-1,3,4,2-THIADIAZAPHOSPHOLES

Tian-Bao Huang[a]; Jing-Ling Zhang[a]
[a] Institute of Organic Synthesis, Central China Normal University Wuhan, Peoples Republic of China

To cite this Article Huang, Tian-Bao and Zhang, Jing-Ling(1995) 'SYNTHESIS OF SUBSTITUTED 2,3-DIHYDRO-1,3,4,2-THIADIAZAPHOSPHOLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 104: 1, 33 — 44
To link to this Article: DOI: 10.1080/10426509508042575
URL: http://dx.doi.org/10.1080/10426509508042575

Phosphorus, Sulfur, and Silicon, 1995, Vol. 104, pp. 33–44
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF SUBSTITUTED 2,3-DIHYDRO-1,3,4,2-THIADIAZAPHOSPHOLES

TIAN-BAO HUANG* and JING-LING ZHANG
Institute of Organic Synthesis, Central China Normal University,
Wuhan, 430070, Peoples Republic of China

(Received November 24, 1993; in final form January 26, 1995)

Reactions of phosphorus trichloride (PCl_3), thiophosphoryl trichloride ($PSCl_3$) and tris(dialkylamino)phosphine ($P(NR_2)_3$) with substituted thiohydrazides (1a–1) under a variety of conditions led to thirty one substituted 2,3-dihydro-1,3,4,2-thiadiazaphospholes (2a–1, 3a–c, 4a–1). The side-reactions leading to 4h and 5 also are discussed. The elimination of HCl from 2-chloro-5-methylthio-2,3-dihydro-1,3,4,2-thiadiazaphosphole (2b) by 1,8-diazabicyclo-[5,4,0]-undec-7-ene ("DBU") gave rise to 5-methylthio-1,3,4,2-thiadiazaphosphole dimer (6). The Staudinger reaction and sulfuration of 2-diethylamino-3-*N*-phenyl-5-methylthio-2,3-dihydro-1,3,4,2-thiadiazaphosphole (4a) with Me_3SiN_3 and S_8 result in the formation of 2-(trimethylsilyl)imino-(7) and 2-thiono-(8) substituted counterparts respectively. The structures of the above products were confirmed by elemental analysis, IR, MS, and ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR.

Key words: Thiohydrazide, 1,3,4,2-thiadiazaphosphole, 1,2,3-diazaphosphole, NMR spectra, tris(dialkylamino)phosphine, cyclocondensation, Staudinger reaction.

INTRODUCTION

Although heterocyclic compounds of phosphorus have received considerable attention over the past three decades, there remain a number of interesting problems to be solved. Thus, the nitrogen- and sulfur-containing heterophospholes, especially including a [N—P—S] unit, have been less studied,[1] primarily due to difficult synthesis and intrinsically due to the weakness of the P—S bond, and to sulfur as another large member in the ring in enhancing the ring strain.[2] However, it was found that some of them are useful not only in the syntheses of pesticides[3,4] and oligonucleotides[5] but also in preparing σ^3-phosphenium and σ^3-phosphonium cations (two- and three-coordinate phosphorus cations).[6–8] These findings encouraged us to synthesize five-membered heterocyclic compounds which include [N—P—S] units.

This paper describes the syntheses of 2,3,5-trisubstituted-2,3-2(H)-1,3,4,2-thiadiazaphospholes (2, 3, 4) by reactions of substituted thiohydrazides with PCl_3, $PSCl_3$ and $P(NR_2)_3$. Some characteristic properties of products also are reported.

RESULTS AND DISCUSSION

1. Synthesis

Tautomerism causes the substituted-thiohydrazides (1) to have an unsaturated four-membered chain terminated by mercapto and amino groups that can condense with

TABLE I

Data for compounds 2–8

Compound				Molecular		Yield[a]	Physical Properties			P(%)		
No.	R¹	R²	R³	Formula	M.W.	(%)	b.p.[b]	m.p.[b]	State	Calcd.	Found[c]	Eluent[e]
2a	MeS	Ph		$C_8H_8ClN_2PS_2$	262.71	96	194/0.02	39–41	white solid	11.79	11.61	
2b	Mes	H		$C_2H_4ClN_2PS_2$	186.61	69	decomp.[d]		white solid	16.60	16.43	4:1[f]
2c	MeS	Ac		$C_4H_6ClN_2OPS_2$	228.65	75	170/1	68–69	white solid	14.56	14.50	
2d	$PhCH_2$	Ph		$C_{14}H_2ClN_2PS$	306.75	69	192/0.1		colorless oil	10.10	9.91	1:0
2e	2-furyl	Ph		$C_{11}H_8ClN_2OPS$	282.69	54			colorless oil	10.96	11.15	1:0
2f	α-$C_{10}H_7$	Ph		$C_{17}H_{12}ClN_2PS$	342.78	64			colorless oil	9.03	9.27	1:0
2g	Ph	Ph		$C_{13}H_{10}ClN_2PS$	292.72	72	196/0.1		colorless oil	10.58	10.49	1:0
2h	pMeOC_6H_4	Ph		$C_{14}H_{12}ClN_2OPS$	322.75	56	116/0.01		yellow oil	9.60	9.39	1:0
2i	pBrC_6H_4	Ph		$C_{13}H_9BrClN_2PS$	371.62	17	165/0.01		red oil	8.33	8.50	1:0
2j	Ph	*i*-Pr		$C_{10}H_{12}ClN_2PS$	258.71	55			colorless oil	11.97		1:0
2k	$PhCH_2$	*i*-Pr		$C_{11}H_{14}ClN_2PS$	272.73	28			colorless oil	11.36		1:0
2l	Et	Ph		$C_9H_{10}ClN_2PS$	244.68	13	120/0.08		colorless oil	12.66	12.47	1:0
3a	MeS	Ph		$C_8H_8ClN_2PS_3$	294.77	81	195/0.02	60–61	white solid	10.51	10.35	8:1
3b	MeS	H		$C_2H_4ClN_2PS_3$	218.67	43			yellow oil	14.16	13.89	4:1
3c	MeS	Ac		$C_4H_6ClN_2OPS_3$	260.71	67		55–56	white solid	11.88	11.73	4:1
4a	MeS	Ph	Et	$C_{12}H_{18}N_3PS_2$	299.39	95			yellow oil	10.34	10.27	12:1
4b	MeS	Ph	*i*-Pr	$C_{14}H_{22}N_3PS_2$	327.33	27			yellow oil	9.46	9.48	7:1
4c	MeS	H	Et	$C_6H_{14}N_3PS_2$	223.36	53			colorless oil	13.86	13.69	2:1
4d	$PhCH_2$	Ph	Et	$C_{18}H_{22}N_3PS$	343.43	86			colorless oil	9.02	8.86	6:1

4e	2-furyl	Ph	Et	$C_{15}H_{18}N_3OPS$	319.36	12		69–71	white solid	9.70	9.30	1:0
4f	α-$C_{10}H_7$	Ph	Et	$C_{21}H_{22}N_3PS$	379.46	79			yellow solid	7.79	7.91	1:0
4g	Ph	Ph	Et	$C_{17}H_{20}N_3PS$	329.40	77			colorless oil	9.40	9.64	1:0[f]
4h	MeS	PN_2Et_4	Et	$C_{14}H_{33}N_5P_2S_2$	397.51	18			colorless oil	15.58	15.33	2:1[f]
4i	MeS	H	*i*-Pr	$C_8H_{18}N_3PS_2$	251.34	69			colorless oil	12.32	12.71	1:1
4j	MeS	Ac	Et	$C_8H_{16}N_3OPS_2$	265.33	51			colorless oil	11.66	11.54	4:1
4k	MeS	Ac	*i*-Pr	$C_{10}H_{20}N_3OPS_2$	293.38	70			colorless oil	10.55	10.58	4:1
4l	MeS	Ac	*n*-Pr	$C_{10}H_{20}N_3OPS_2$	293.38	80			colorless oil	10.56	10.38	4:1
5				$C_8H_{16}N_3OPS_2$	265.33	36			white solid	11.67	11.81	4:1
6	MeS			$C_4H_6N_4P_2S_4$	300.30	17			green solid	20.62	20.50	1:1[f]
7	MeS	Ph	Et	$C_{15}H_{27}N_4PS_2Si$	386.59	58			colorless oil	8.01	7.81	10:1
8	MeS	Ph	Et	$C_{12}H_{18}N_3PS_3$	331.45	80			colorless oil	9.34	9.55	9:1

[a] Yield of purified products.

[b] The b.p. in °C/mmHg is for the first drop; the m.p. in °C is uncorrected.

[c] The maximum analysis deviations of C and H are C ± 0.35, H ± 0.10; C, H analyses were obtained except for **2j** and **2k**.

[d] Decomposed above 120°C.

[e] Light petroleum ether: ether.

[f] In the presence of 10% (v/v) Et_3N.

TABLE II

^{1}H-, ^{13}C- and ^{31}P-NMR spectra of $\underline{2}$–$\underline{8}$

No.	δ ^{31}P (ppm)	δ ^{1}H and J (ppm) (Hz)	δ ^{13}C and J (ppm) (Hz)
2a	149.9	2.62 (s, 3H, SCH_3), 6.9–7.6 (5H, C_6H_5)	17.58 (SCH_3), 113.2, 119.67, 124.9, 129.44, 142.38 (C═N)
2b[a]	151.8	2.69 (s, 3H, SCH_3), 8.96 (br, NH)	
2c	147.8	2.34 (s, 3H, $COCH_3$), 2.65(s, 3H, SCH_3)	
2d	151.4	4.03 (d, 1H, $^2J_{Ha—Hb}$ = 12.8, $\underline{Ha}$—C—Hb), 4.13 (d, 1H, $^2J_{Ha—Hb}$ = 12.8, Ha—C—$\underline{Hb}$) 6.8–7.6 (m, 10H, 2 × C_6H_5)	37.95 (CH_2), 115.28, 120.77, 121.03, 125.90, 128.19, 129.59, 130.19, 136.39 (d, $^2J_{PNC}$ = 16), 151.29 (d, $^2J_{PSC}$ = 15.3)
2e	144.2	6.56 (t, 1H, $^3J_{H—H}$ = 2.6, C(4′)—H), 6.99(d, 1H, $^3J_{H—H}$ = 3.3, C(5′)—H), 7.72–7.66 (m, 6H, Ar—H)	113.04, 121.06, 121.73, 126.26, 130.26, 145.43, 146.07, 156.76, 159.43
2f	145.2	7.20–7.96 (m, 11H, Ar—H), 8.78 (d, 1H, $^3J_{H—H}$ = 7.5, C(8′)—H)	116.34, 120.86, 121.13, 124.01, 125.68, 126.14, 127.33, 128.00, 129.05, 129.29, 130.01, 130.31, 134.60, 138.45, 145.64
2g	148.5	6.8–7.8 (m, Ar—H)	116.0, 120.68, 120.95, 125.95, 127.84, 128.45, 129.25, 130.10, 131.26, 132.26, 139.13, 143.25, 145.80
2h	148.3	3.81 (s, 3H, OCH_3), 6.93–7.65 (m, Ar—H)	56.12 (OCH_3), 114.90, 115.33, 118.43, 118.66, 120.93, 124.14, 124.86, 125.34, 125.79, 130.19, 130.63, 134.56, 152.3
2i	148.7	6.97–7.71 (m, Ar—H)	
2j	154.38	1.24 (d, 6H, $^3J_{H—H}$ = 7.32, $CH(\underline{CH_3})_2$), 3.8 (m, 1H, N $\underline{CH}$ Me_2), 7.40–7.80 (m, 5H, Ph)	
2k	154.7	1.6 (d, 6H, $^3J_{H—H}$ = 6.26, CH $(\underline{CH_3})_2$), 3.90 (m, 1H, N $\underline{CH}$), 4.50 and 4.58 (d × d, 2H, $^2J_{Ha—Hb}$ = 8.15, $\underline{Ha—C—Hb}$),7.38–8.10 (m, 5H, C_6H_5)	18.82, 46.14, 65.0, 128.65, 129.03, 129.70, 131.03, 133.02, 134.14, 140.00
2l	149.9	1.08 (t, 3H, $^3J_{H—H}$ = 7.0, CH_3), 2.15 (q, 2H, $^3J_{H—H}$ = 7.0, CH_2), 6.8–7.6 (m, Ph)	13.52, 26.28, 118.39, 124.91, 129.78, 142.96, 143.50
3a	81.2	2.60 (s, 3H, SCH_3), 7.0–7.6 (m, 5H, Ph)	
3b[b]	71(40)	2.66 (S, 3H, SCH_3), 9.6 (br, NH)	
3c	72.1	2.38 (s, 3H, $COOH_3$), 2.55 (s, 3H, SCH_3)	
4a	102.7	0.93 (t, 6H, $^3J_{H—H}$ = 7.15, CH_2 $\underline{CH_3}$), 2.64, (s, 3H, SCH_3), 2.85 (m, 4H, $\underline{CH_2}CH_3$), 6.95–7.48 (m, 5H, Ph)	13.18, 41.37 (CH_2CH_3), 16.44 (SCH_3), 116.85, 121.2, 128.6, 141.63 (Ph), 144.73 (C═N)
4b	101.2	1.05 (d, 6H, $^3J_{H—H}$ = 7.1, $CH(\underline{CH_3})_2$), 1.15 (d, 6H, $^3J_{H—H}$ = 7.1, $CH(\underline{CH_3})_2$), 2, 62 (s, 3H, SCH_3), 3.2 (m, 2H, N $(\underline{CH}Me_2)_2$), 7.0–7.6 (m, 5H, Ph)	14.2, 39.05 (CH_2CH_3), 16.6 (SCH_3), 124.5, 126.9, 129.1, 131.8 (Ph), 142.0 (C═N)

4c	106.8	1.10 (m, 6H, 2 × CH_3), 2.56 (s, 3H, SCH_3), 2.86 (m, 4H, $N(CH_2—)_2$), 8.90 (br, N—H)	8.75, 45.76 (CH_2CH_3), 17.2 (SCH_3), 145.0 (C═N)
4d	100.4	0.78 (t, 6H, $^3J_{H—H}$ = 7.0, 2 × CH_3), 2.71 (m, 4H, $N(CH_2)_2$), 3.99 and 4.16 (d × d, 2H, $^2J_{H—H}$ = 14.65, $\underline{\text{Ha—C—Hb}}$), 7.0–7.6 (m, 5H, Ph)	14.81, 42.26 (CH_2CH_3), 39.91 ($PhCH_2$), 118.45, 122.37, 127.54, 129.15, 129.66, 130.24, 137.97 (2 × Ph), 145.75 (C═N)
4e	98.0	0.88 (t, 6H, $^3J_{H—H}$ = 7.0, 2 × $CH_2\underline{CH_3}$), 2.83 (q, 4H, $^3J_{H—H}$ = 7.0, 2 × $\underline{CH_2}CH_3$), 6.45, 6.67, 6.98 (furyl—H), 7.2–7.5 (m, 5H, Ph)	
4f	94.8	0.94 (t, 6H, $^3J_{H—H}$ = 7.15, 2 × $CH_2\underline{CH_3}$), 2.94 (m, 4H, 2 × $\underline{CH_2}CH_3$), 7.0–7.8 (m, 11H, Ar—H), 8.82 (d, 1H, $^3J_{H—H}$ = 8 Hz, C(8′)—H)	14.58, 42.35 (CH_2CH_3), 118–113 (m, Ar—C), 146 (C═N)
4g	100.2	0.91 (t, 6H, $^3J_{H—H}$ = 7.17, 2 × CH_3), 2.85 (quin., $^3J_{H—H}$ = 7.16, 2 × CH_2), 7.0–8.0 (m, 10H, 2 × Ph)	14.51, 42.31, (CH_2CH_3), 114.27, 118.55, 122.68, 127.46, 129.19, 129.68, 135.0 (2 × Ph)
4h[c]	97.2 106.4	0.9 (m, 12H, 2 × $N(CH_2\underline{CH_3})_2$), 1.26 (t, 6H, $N(CH_2\underline{CH_3})_2$), 2.48 (s, 3H, SCH_3), 2.80 (m, 12H, 3 × $N(\underline{CH_2}CH_3)_2$)	11.1, 13.7, 40.8, 41.9 (2 × CH_2CH_3), 16.0 (SCH_3), 148.5 (C═N)
4i	107.9	1.10 (m, 12H, N $(CH(\underline{CH_3}))_2$), 2.67 (s, 3H, SCH_3), 3.2 (m, 2H, $N(\underline{CH}CH_3)_2$), 8.92 (br, N—H)	
4j	103.3	1.0 (t, 6H, $^3J_{H—H}$ = 6.20, 2 × CH_3), 2.44 (s, 3H, $COCH_3$), 2.55 (s, 3H, SCH_3), 2.88 (m, 4H, 2 × CH_2)	13.62, 41.56 (CH_2CH_3), 15.7 (SCH_3), 22.90 ($COCH_3$), 149.7 (C═N), 173.1 (C═O)
4k	103.1	1.23 (d, 12H, $^3J_{H—H}$ = 6.2, $N(CH(\underline{CH_3})_2)_2$), 2.44 (s, 3H, $COCH_3$), 2.60 (s, 3H, SCH_3), 3.10 (m, 2H, $N(CH—)_2$)	
4l	100.5	1.0 (m, 10H, 2 × $CH_2\underline{CH_2}CH_3$), 2.34 (s, 3H, $COCH_3$), 2.60 (s, 3H, SCH_3), 3.05 (q, 4H, $^3J_{H—H}$ = 7.7, $N(\underline{CH_2}CH_2CH_3)_2$)	
5[d]	77.7	1.1 (t, 6H, $^3J_{H—H}$ = 7.0, $N((CH_2\underline{CH_3})_2)$, 2.48 (d × d, 1H, $^2J_{Ha—Hb}$ = 12.6, ^2J_PCH = 10.1, $\underline{\text{Ha}}$—C—Hb), 2.63 (s, 3H, SCH_3), 2.73 (d × d, 1H, $^2J_{Ha—Hb}$ = 12.64, ^2J_PCH = 27, Ha—C—$\underline{\text{Hb}}$), 3.08 (m, 4H, $N(CH_2—)_2$), 9.56 (br, 1H, NH)	13.09, 39.2 (CH_2CH_3), 20.3 (SCH_3), 29.1 (d, $^1J_{P—C}$ = 150, PCH_2), 167(C═S), 179 (C═O)
6	110.9	2.62 (s, 3H, SCH_3), 2.66 (s, 3H, SCH_3)	16.6, 17.1 (2 × CH_3), 143, 145 (2 × C═N)
7	24.6	0.1 (s, 9H, $Si(CH_3)_3$), 1.25 (t, 6H, $^3J_{H—H}$ = 7.2, 2 × CH_3), 2.60 (s, 3H, SCH_3), 3.1 (quint., 4H, $J \approx 7.2$, $PN(\underline{CH_2}CH_3)$), 7.0–7.8 (m, 5H, Ph)	
8	88.0	1.05 (t, 6H, $^3J_{H—H}$ = 7.3, 2 × $CH_2\underline{CH_3}$), 2.59 (s, 3H, SCH_3), 3.30 (quin., 4H, $J \approx 7.2$, $PN(\underline{CH_2}CH_3)$), 7.1–7.6 (m, 5H, C_6H_5)	

---

[a] $^2J_{P—N—H}$ = 40.5 Hz
[b] $^2J_{P—N—H}$ = 40 Hz
[c] $^2J_{P—N—P}$ = 18.3 Hz
[d] $^2J_{P—C—Ha}$ = 10 Hz, $^2J_{P—C—Hb}$ = 27 Hz

TABLE III

MS and IR spectra of 2–8

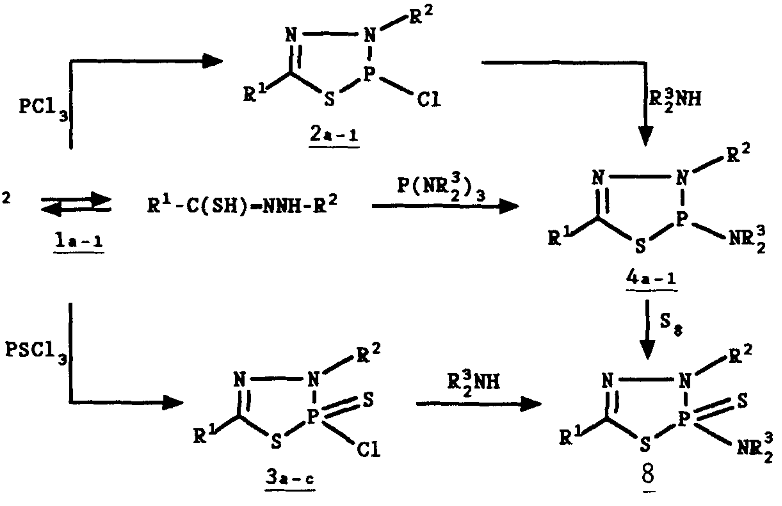
No.	MS(int.)	IR
2a	262 1.3, M), 227 (100, M—Cl), 150 (46.3, M—Cl—Ph), 91 (78, PhN), 77 (56, Ph)	1595, 1490 (C=C), 1520 (C=N), 750, 690 (Ar—H), 670 (S—Me)
2b	151 (100, M—Cl), 103 (14, CN$_2$PS)	3350 (N—H), 1530 (C=N), 666 (S—Me)
2c	228 (5.4, M), 193 (8.8, M—Cl), 103 (100, CN$_2$PS)	1690 (C=O), 1540 (C=N), 660 (S—Me)
2d		1600, 1490 (C=C), 1535 (C=N), 750, 710, 690 (Ar—H)
2l	246 (5.1, M + 2), 244 (14, M), 209 (46.5, M—Cl), 164, 154 (31, PhNPS), 150 (EtCSPh), 108, 91(PhN), 77 (Ph), 65 (C$_5$H$_5$)	
3a	296 (22, M + 2), 294 (52, M), 259 (5., M—Cl), 227 (31, M:b1Cl—S), 164 (19, M—PS$_2$Cl), 122 (10, M—Cl—PhNN)	1600, 1495 (C=C), 1520 (C=N), 930 (P—N), 773 (P=S), 760, 705 (Ar—H), 695 (S—Me)
4a	301 (5.45, M + 2), 299 (55.6, M), 227 (100, M—NEt$_2$), 150 (62, MeS + CN$_2$PS), 91 (86, PhN), 77 (23, Ph)	1595, 1492 (C=C), 1530 (C=N)
4b	329 (2.8, M + 2), 327 (26, M), 227 (100, M—NPr$^i_2$, 91 (39, PhN), 77 (19, Ph)	1595, 1490 (C=C), 1525 (C=N), 1390, 1380 (i—Pr) 930 (P—N), 750, 690 (Ar—H), 665 (S—Me)
4d		3050 (Ar—H), 1600, 1490 (C=C), 1520 (C=N), 930 (P—N), 790, 750, 720, 690 (Ar—H)
4e		1600, 1490 (C=C), 890, 765, 690 (Ar—H)
4f		1600, 1490 (C=C), 1530 (C=N), 920 (P—N), 775, 755, 690 (Ar—H)
4g		3070 (Ar—H), 1600, 1490 (C=C), 1545 (C=N), 940 (P—N), 790, 750, 720, 690 (Ar—H)
4j	265 (14, M), 193 (19, M—NEt$_2$), 151 (100, M—Ac—NEt$_2$), 146 (43, M—MeS—NEt$_2$) 103 (4.3, CN$_2$PS), 72 (40, NEt$_2$)	1670 (C=O), 1540 (C=N), 960 (P—N), 660 (S—Me)
4k	293 (5, M), 193 (21, M—i—Pr2N), 151 (100, MeS + CN$_2$PS) 103 (4, CN$_2$PS), 100 (36, *i*—Pr^{2}N)	1678 (C=O), 1520 (C=N), 1380, 1368 (*i*—Pr) 970 (P—N), 660 (S—Me)
5	263 (5.7, M—2), 164 (15, Et$_2$NCS$_2$Me + H), 146 (6.9, M—Et$_2$N—MeS), 129 (11, PNC + NEt$_2$), 117 (NPNEt$_2$), 91 (45, CS$_2$Me), 86 (100, NPCHCO)	3100—3300 (N—H), 1700—1665 (—NH—C=O)
6	151 (100, 1/2M, or M+ +)	1520, 1510 (C=N), 950 (P—N), 650 (S—Me)
8	331 (4, M), 259 (100, M—NEt$_2$), 182 (50, M—NEt$_2$—Ph), 91(54, PhN), 77 (41, Ph)	1595, 1490 (C=C), 1520 (C=N), 925 (P—N), 790 (P=S), 750, 695 (Ar—H), 670 (S—Me)

PCl_3, $PSCl_3$ and $P(NR_2)_3$. The routes for the preparation of 2, 3, and 4 are outlined in Scheme I, Experimental data for products 2, 3, and 4 are listed in Tables I, II and III.

Compounds 1a–l were treated with PCl_3 in benzene at 20°C–80°C with the elimination of HCl to afford 2-chloro-5-R^1-3-R^2-2,3-2(H)-1,3,4,2-thiadiazaphospholes (2a–l) in satisfactory yields. These cyclic chlorophosphines (2) could be purified either by molecular distillation or by centrifugal silica gel TLC under dry N_2; products 2b decomposed above 120°C. The compounds 2 are reported for the first time except for 2a and 2c.[9,10] All of the compounds 2 are oils or low-melting solids; they are stable at room temperature under N_2, but are sensitive to moisture, where they easily change back into 1. Compounds 2j and 2k are so hygroscopic that no accurate C, H, N and P elemental analyses or satisfactory IR spectra could be obtained, and their structure had to be confirmed by NMR, MS.

Applying the same procedure to $PSCL_3$, 2-chloro-5-R^1-3-*N*-R^2-2,3-2(H)-1,3,4,2-thiadiazaphospholes-2-thiono (3a–c) were prepared in high yields. Compounds 3 could be purified on flash silica gel by chromatography, and were stable in the air at room temperature. $P(NR_2)_3$ is a kind of versatile phosphorus-containing reagents, which are useful in the synthesis of cyclic compounds in which the phosphorus atoms are in either two- or three- or four-coordinated state.[1,12] Compounds 2-*dialkylamino-3-N-R^2-5-R^1-2,3-2(H)-1,3,4,2-thiadiazaphospholes* (4a–l) were produced when 1a–l and $P(NR_2)_3$ were refluxed in benzene for 3–4 hrs; they were easily purified by preparation TLC on silica gel. Most of the products 4a–4l are oily with unpleasant odor, and are sensitive to air, where they could be oxidized. These cyclic aminophosphines also can be prepared by the amination of 2, as outlined in Scheme I.

Depending on the different substituents (3-R^2-), there are two complicated cases, the first case is for 1b (R^2 = H), the refluxed mixture of methyl ester of dithio-



R^1, R^2, R^3 = MeS, Ac, Et, $PhCH_2$, Aryl (see Table 1)

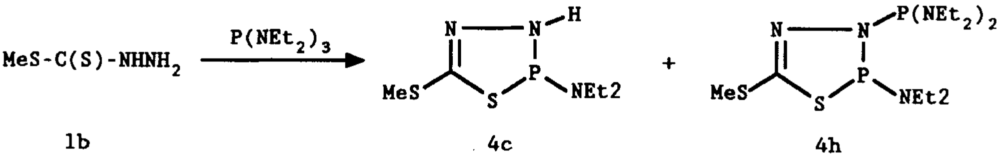
SCHEME I

carbazic acid (1b) with $P(NEt_2)_3$ gave 2-diethylamino-5-methylthio-2,3-2(H)-1,3,4,2-thiadiazaphosphole (4c, 52% yield), and diphosphorus compound (4h, 18% yield), as shown in Scheme II.

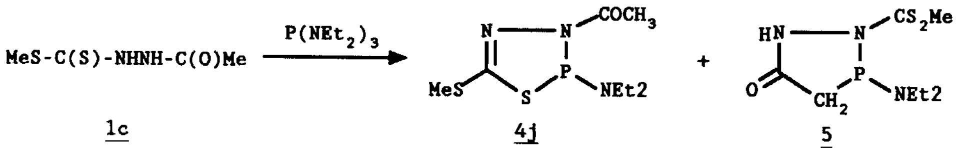
The second case was with 1c (R^2 = CH_3CO), the refluxed mixture of methyl ester of N^2-acetyl-dithiocarbazic acid (1c) with $P(NEt_2)_3$ produced 2-diethylamino-3-*N*-acetyl-5-methylthio-2,3-2(H)-1,3,4,2-thiadiazaphosphole (4j, 51% yield), and 2-diethylamino-3-*N*-[methyl ester of dithiocarboxy]-5-oxo-1,2,3,4-4(H)-1,2,3-diazaphosphole (5, 35% yield). Compound 5 also was chromatographically separated by centrifugal TLC using petroleum ether (30°C–60°C)/ether (4:1) as the eluent; the result is shown in Scheme III. The strange structure of 5 was well characterized, as discussed in the next part.

With Cl_2PNEt_2 instead of PCl_3 as a cyclocondensative reagent with thiobenzhydrazide (1), the 2-chloro-substituted product (2) was formed in nearly 100% yield, as indicated by ^{31}P NMR of the mixture. A typical example is given in Scheme IV. It is noted that the formation of P—Cl bond in this example differ somewhat from the formation of the P—N bond in the reaction between the derivatives of 2-hydrazinothiazole and Cl_2PNEt_2.[11]

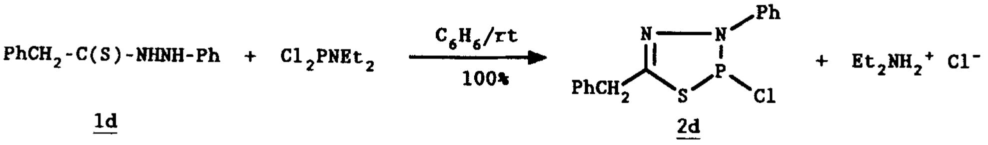
A dicoordinated-phosphole resulted from 2b by the elimination of HCl; thus when 2b was treated with 1,8-diazabicyclo-[5,4,0]-undec-7-ene ("DBU"; which is a strongbase with low nucleophilicity) at −70°C in CH_2Cl_2 under N_2, an immediate ^{31}P-NMR study on the mixture showed that a single signal at 110.9 ppm arose, with the disappearance of the signal of 151.8 ppm; above 200 ppm the absence of a ^{31}P NMR signal was indicative of no stable σ^2-species [—S—P=N—] persistence. After purification on centrifugal silica gel TLC using petroleum ether/ether/Et_3N (8:2:1) as eluent, the dimer of 2b (6) was obtained (Scheme V).



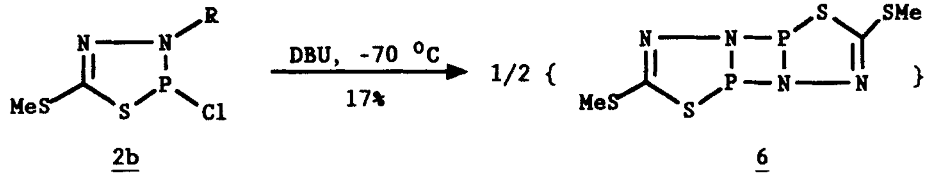
SCHEME II



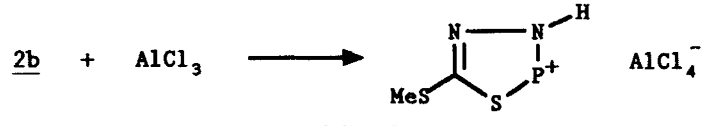
SCHEME III



SCHEME IV



SCHEME V

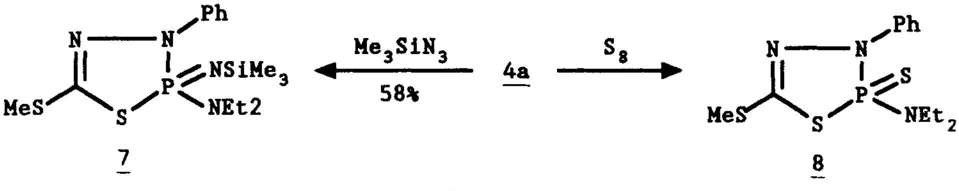


SCHEME VI

It is reasonable that 5-methylthio-1,3,4,2-thiadiazaphosphole is an intermediate in the formation of 6 from 2b by dimerization. There are three reasons possible for the absence of stable σ^2-species: the first is low resonance energy of this kind of ring, resulting from weakness of P—S bond; the second is the large ring strain caused by the large size of S and P atoms[2]; the third is the lone pairs of donating electrons from the MeS group. Whether strong electron-withdrawing groups such as 5-CF_3- or 5-NC- at carbon may stabilize this monomeric phosphole in a two-coordinated state or not will be considered further elsewhere.

C. Malavand and coworkers[13] found that 2-chloro-2,3-dihydro-benzo[1,3,2]-oxazaphosphole could be converted into a neutral σ^2-species by use of a Lewis acid. When we applied their method to 2b, surprisingly, a σ^2-cationic product (δ^{31} P = 269.7 ppm) was formed, as outlined in Scheme VI; the details will be reported elsewhere.[14]

The Staudinger reaction of 4a with Me_3SiN_3 gave rise to 7. Sulfuration of 4a with S_8 afforded 8. The structures of 7 and 8 were proved by spectroscopic methods. The equation is outlined in Scheme VII:



SCHEME VII

2. *Spectra and Structure*

The structures of 2–8 were confirmed by MS, IR, ^{1}H-, ^{13}C-, ^{31}P-NMR and/or elemental analyses, as summarized in Tables I, II and III. The ^{31}P chemical shifts of 2, 3, and 4 were about 150 ppm, 75 ppm and 100 ppm respectively. The facts that the values of the ^{31}P chemical shifts of compounds 2 and 4 with a 5-MeS group are close to those with $PhCH_2$, Ph, 2-furyl, α-naphthyl and p-Br-C_6H_5 in the 5-position demonstrate that 5-substituted groups have only weak effect on the ^{31}P chemical shifts of these heterocycles.

Two phosphorus nuclei of 4h give rise to two signals at 97.2 ppm and 106.4 ppm with $^2J_{PNP}$ = 18.3 Hz in the ^{31}P NMR spectra. From Table II, it is easy to recognize that the signal of 4h in low field (106.4 ppm) can be attributed to the cyclic phosphorus nucleus and that the signal of exo-cyclic phosphorus appears in a relative high field (97.2 ppm). This can be supported by the ^{31}P NMR of 4c. The ^{13}C NMR spectrum which exhibits six signals is consistent with the proposed structure for 4h in Scheme II.

Compound 5 is a minor product in Scheme III. The formation of 5 is very unexpected, and the structure is uncommon. A comprehensive survey of IR, MS, and NMR data rules out the possibility of the 1,3,4,2-oxadiazaphosphole species expected. The ^{31}P NMR spectrum of 5 in $CDCl_3$ shows a single signal at 77.7 ppm, which is far below that of the main product 4j; in the 5 the coupling constants for the P—C(—H$_a$)—H$_b$ unit, of which AMX-system is consisted, are $^2J_{PCH_a}$ = 10.1 Hz, $^3J_{PCH_b}$ = 27 Hz, and $^3J_{H_aCH_b}$ = 12.64 Hz. Elemental analysis is consistent with $C_8H_{16}N_3OPS_2$. A strong broad band from 1650 to 1700 cm^{-1} in the IR spectrum is indicative of the presence of carbonyl (C═O) group. The ^{1}H NMR spectrum gives six kinds of signal: 1.1, 2.48, 2.63, 2.73, 3.1 and 9.56 ppm, with integrals 6:1:3:1:4:1; these imply that there is an anisotropoic methylene, besides MeS, NEt$_2$, NH (or OH) groups. In consideration also of the MS data (prominent peak m/z 91 is from CS$_2$Me, base peak m/z 86 is from NPCHCO), the structure of 5 is concluded to be 2-diethylamino-3-*N*-[methyl ester of dithiocarboxy]-5-oxo-1,2,3,4-4(H)-1,2,3-diazaphosphole. The ^{13}C NMR spectrum also supports this conclusion.

Another interesting phenomenon revealed by ^{1}H-NMR is that the methylene groups of PhCH$_2$ in 2d, 2k and 4d are to AB-system; this demonstrates that the rotation around the CH$_2$—C(N)S bond is restricted at room temperature.

A comprehensive view of all of the IR data show that the $v_{C=N}$ spreads between 1520 ~ 1570 cm $^{-1}$ as a strong band. v_{S-Me}, $v_{P=S}$ and v_{P-N} fall in the ranges of 660 ~ 670, 770 ~ 790 and 930 ~ 970 cm^{-1} respectively. As to ^{13}C NMR, the δ_{13C} of C═N and CH_3S are about 145 ppm and 17 ppm; $^2J_{PSC}$ is about 15 ~ 25 Hz. Most of the MS spectra give peaks at 103 (ring species CN$_2$PS) and 150 (MeS + CH$_2$PS) as base or prominent signals, implying that cations of thiadiazaphosphole have considerable stability in the gas phase.

EXPERIMENTAL

Instruments: Elemental analyses were obtained with a PE-2400 elementary analyzer. Mass spectra were recorded with a HEWLETT-PACKARD HP5988A spectrometer at 70ev ionization energy. ^{1}H-, ^{13}C- and ^{31}P-NMR were recorded with Varian XL-200 spectrometer. The chemical shifts are reported in ppm relative to the internal standard TMS for ^{1}H- and ^{13}C-NMR, and the external standard 85%H_3PO_4 for ^{31}PNMR. IR were recorded on PE-983G spectrometer.

Solvents: Ether was distilled from benzophenone ketyl; *n*-hexane, benzene and xylene were dried with sodium and calcium hydride; CH_2Cl_2 was dried over P_2O_5 and stored over CaH_2.

Reagents: Substituted thiohydrazides (1a–l),[15,16] Et_2NPCl_2 and $P(NEt_2)_3$[17] were respectively prepared according to the reported procedures. PCl_3, $PSCl_3$, R_2NH and Et_3N were obtained commercially and distilled before use. 1,8-diazabicyclo-[5,4,0]-undec-7-ene ("DBU") and S_8 were purchased from ALDRICH.

All manipulations were carried out under an atmosphere of dry nitrogen.

2-chloro-3-N-R²-5-R¹-2,3-2(H)-1,3,4,2-thiadiazaphospholes (2a–l): To a stirred solution of an appropriate thiocarohydrazide (1, 10 mmol) in 45 ml of anhydrous benzene, below 0°C during 30 min, was syringed PCl_3 (1.6 g, 12 mmol) in 5 ml of benzene. The mixture was stirred for 2 hrs at 20–30°C and then refluxed until the disappearance of HCl. Most of the solvent was removed under reduced pressure, 20 ml of *n*-hexane was added to the concentrated solution, the mixture was stirred for 30 min and kept overnight at room temperature, a clear filtrate was obtained by filtration. Removing the solvent from the above filtrate left an oily residue, which was either distilled under vacuum or chromatographed on silica gel by centrifugal TLC using an appropriate eluent. All experimental data are listed in Tables 1, II and III.

2-chloro-3-N-R²-5-R¹-2-thiono-2,3,-2(H)-1,3,4,2-thiadiazaphospholes (3): The mixture of the appropriate thiohydrazine (1, 10 mmol) in 45 ml of benzene and $PSCl_3$ (1.86 g, 11 mmol) were refluxed for 3 hrs. Completion was indicated by the disappearance of 1 on silica gel TLC. The clear filtrate which was obtained by filtration was concentrated at reduced pressure. The residue was purified on a flash silica gel column or by molecular distillation. All data of 3 are listed in Tables I, II and III.

2-dialkylamino-3-N-R²-5-R¹-2,3-dihydro-1,3,4,2-thiadiazaphosphole (4): The appropriate thiohydrazide (1,, 2.5 mmol), tris(dialkylamino)phosphine (5 mmol) and benzene (10 ml) were placed in a 50-ml two-neck round-bottom flask. The mixture was refluxed for 3–4 hrs. Silica gel TLC indicated the completion of the reaction. The solvent was evaporated under reduced pressure, the residue was chromatographed on three 20 cm × 20 cm silica gel plates, or on a centrifugal silica gel plate, so the pure Products 4 could be obtained.

The details for 4j *and* 5 *from* 1c: under nitrogen atmosphere, 10 ml of dry benzene, 0.85 g of N^2-aceto-hydrodrazniodithiocarbazic methyl ester (1c, 5.2 mmol) and 3 ml of $P(NEt_2)_3$(11 mmol) were placed in a round-bottom flask. The mixture was heated at 80°C for 4 hrs. Then the solvent was evaporated in vacuo and residual crude product was purified on silicon gel TLC using petroleum ether/ether (4:1) as eluent. Pure 5 (0.48 g) and pure 4j (0.70 g) were obtained in the yield of 35% and 51% respectively. The products 4 could be also prepared through the amination of 2 with the corresponding R_2NH in the presence of Et_3N. The related data are listed in Tables I, II and III.

The dimer of 5-methylthio-1,3,4,2-thiadiazaphosphole (6): To a solution of purified 2-chloro-2,3-2(H)-1,3,4,2-thiadiazaphosphole (2b; 0.372 g, 2 mmol) in 10 ml of CH_2Cl_2 was dropped a solution of 1,8-diazabicyclo-[5,4,0]-undec-7-ene ("DBU"; 0.466 g, 3 mmol) in 5 ml of CH_2Cl_2 below −70°C over 5 min with stirring. An immediate and successive ^{31}P NMR study on the mixture indicated that the signal at 110.9 ppm was growing with that at 151.8 ppm was lowering. The precipitate was filtered and discarded. CH_2Cl_2 in the filtrate was stripped off by dry N_2, and the residue was purified by preparative TLC using ether/petroleum ether/triethylamine (5:5:1) as the eluent. The yield of 6 was 17% (63.4 mg, m.p. 99–100°C). The data are listed in Tables I, II and III.

2-diethylamino-3-N-phenyl-5-methylthio-2,3,-dihydro-1,3,4,2-thiadiazaphosphole-2-(trimethylsilyl) imino- (7) *and -2-thino* (8): The mixture of 4a (190 mg, 0.64 mmol), Me_3SiN_3(95 mg, 0.82 mmol), and 2 ml of benzene was refluxed for 2 hrs, then cooled. Most of the solvent was removed under reduced pressure. The residue was purified on silica gel preparative TLC using ether/petroleum ether (1:10) as the eluent. Compound 2-(trimethylsilyl)imino-2-diethylamino-3-*N*-phenyl-5-methylthio-1,3,4,2-2,3-2(H)-thiadiazaphosphole (7, 140 mg) was obtained in 58% yield.

The mixture of 4a (172 mg, 0.58 mmol), S_8 (100 mg, 3 mmol) and 5 ml of benzene was refluxed for 4 hrs, then cooled. The excess sulfur was filtered off, and most of the solvent was removed under reduced pressure. The residue was purified on silica gel preparative TLC using the ether/petroleum ether (1:9) as the eluent. A colorless oil 8 (152 mg) was obtained in the yield of 80%.

After the mixture of 3a (2.94 g, 10 mmol) and Et_2NH (2 ml, 20 mmol) were stirred at room temperature for 2 hrs., a flash column chromatography on silica gel using light petroleum as the eluent could afford 8 (3.2 g, 97%).

The related data are listed in Tables I, II and III.

ACKNOWLEDGEMENTS

This work has been supported by the National Natural Science Foundation of China. We thank Dr. J. Q. Lu, Prof. W. F. Huang, and Prof. X. L. Xu for helpful discussion. We are also pleased to acknowledge the Centre of Analysis and Testing in Central China Normal University for NMR, IR and MS spectra, and the Department of Chemistry in WuHan University for elemental analyses.

REFERENCES AND NOTES

1. A. Schmidpeter and K. Karaghiosoff in "Multiple Bonds and Low Coordination in Phosphorus Chemistry," M. Regitz and O. J. Scherer Eds., Georg Thieme Verlag, Stuttgart, 1990, p. 258.
2. A. Schmidpeter, *Phos. Sulf.*, **28,** 71 (1986).
3. S. Y. Wu and A. Hirashima, *Agric. Biol. Chem.*, **52,** 2911 (1988).
4. H. Ota, T. Tanaka, S. Tono and T. Fukuchi, *Jpn. KoKai Tokkyo Kono JP*, 62, 234,090 (1986); C. A. 109:229.69.
5. W. Richter, R. Kar and Z. Ugi, *Tetrahedron*, **46,** 3167 (1990).
6. N. Burford, A. I. Dipchand, B. W. Royan and P. S. White, *Inorg. Chem.*, **29,** 4938 (1990).
7. T. B. Huang, J. L. Zhang, C. G. Zhan and Y. J. Zhang, *Science in China (B)*, **36,** 641 (1993).
8. T. B. Huang, J. L. Zhang *et al.*, to be published.
9. N. I. Shvetsov-shivskii, D. P. Nesterenko and A. A. Stepanova, *Zh. Obshch. Khim.*, **49,** 1896 (1979); C. A. 92:41846.
10. A. Schmidpeter, J. Gross and E. Schrenk, *Phos. Sulf.*, **14,** 49 (1982).
11. J. L. Zhang and W. Xu, *Phos. Sulf. Silic.*, **47,** 173 (1990).
12. A. Schmidpeter and K. Karaghiosoff, *Z. Naturforsch*, **36B,** 1273 (1981).
13. C. Malavand, L. Lopez, Th. N'gando M'Pondo, M. T. Boisdon, Y. Charbonel and J. Barrans, *ACS., Symp.*, **171,** 413 (1981).
14. T. B. Huang and J. L. Zhang, *Zh. Obshch. Khim*, in press, 1995.
15. K. A. Jensen, H. R. Baccaro, O. Buchardt, G. E. Olsen, C. Pedersen and J. Toft, *Acta Chem. Scand.*, **15,** 1109 (1961).
16. J. Beger, T. T. Luong, C. Thielemann and P. D. Thong, *J. prakt. Chem.*, **321,** 959 (1979).
17. C. Stuebe and H. P. Lankelma, *J. Am. Chem. Soc.*, **78,** 976 (1956).