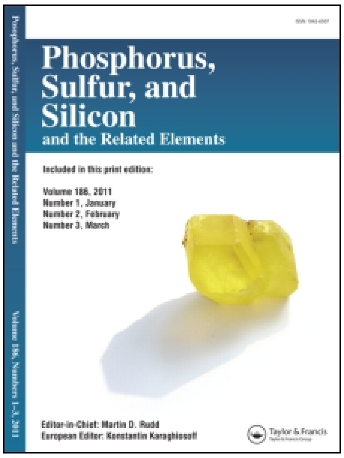

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NEW ACYCLIC AND FUSED TRICYCLIC PHOSPHORUS COMPOUNDS AFFORDED BY NOVEL CONDENSATION

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NEW ACYCLIC AND FUSED TRICYCLIC PHOSPHORUS COMPOUNDS AFFORDED BY NOVEL CONDENSATION

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The condensation of 1-(2-benzothiazolyl)-4-phenylsemicarbazide with $(R_2N)_2PX(X = R_2N, RO, Ph)$ proceeds with cleavage of the N—C(O) bond and formation of the title compounds which were also synthesized via similar treatment of 2-hydrazinobenzothiazole in good yields. Reactivities of $(R_2N)_2PX$, spectroscopic properties of the products and preliminary mechanism of these reactions were discussed.

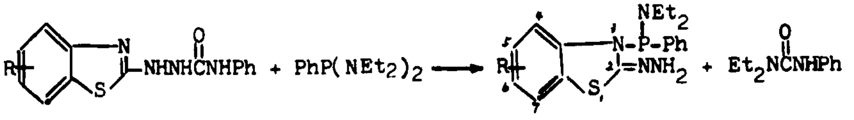
Key words: Fused tricyclic triazaphosphole; tricoordinate phosphorus reagents; delocalization; benzothiazole derivatives; cyclocondensation; semicarbazide derivatives.

INTRODUCTION

In previous papers[1–6] we have reported the synthesis of the first fused tricyclic triazaphospholes by the reaction of 2-(2-phenylhydrazino) (or hydrazino)-1,3-benzothiazole with tris(dialkylamino)phosphine and described their reactivities and spectral properties, but the attempts to remove the substituted group on the cyclic phosphorus atom of fused tricyclic triazaphosphole to form two-coordinate phosphorus compounds did not succeed. Our continuing interest in this topic led us to consider the reactions of the derivatives of 2-hydrazino-1,3-benzothiazole with tricoordinate phosphorus reagents which were of different reactivities suggesting some information on the mechanism of the reactions. Here we report the preparations of a new class of fused tricyclic triazaphosphole and acyclic phosphorus compounds by the condensation reaction of the derivatives of 2-hydrazino-1,3-benzothiazole with $(R_2N)_2PX(X = RO, R_2N, \text{or } Ph)$ to eliminate some small molecules such as dialkylamine, *N,N*-dialkyl-*N'*-phenylurea.

RESULTS AND DISCUSSION

The reaction of 1-(2-benzothiazolyl)-4-phenylsemicarbazide **1** with bis(diethylamino)phenylphosphine without solvent took place at 140–145°C under a nitrogen atmosphere. It was found that the N—C(O) bond was cleaved to give rise to an acyclic phosphorus compound, 2-hydrazono-3-(diethylaminophenylphosphino)-2,3-dihydro-1,3-benzothiazole **2**, in low yields together with *N*,*N*-diethyl-*N*′-phenylurea **3b**.

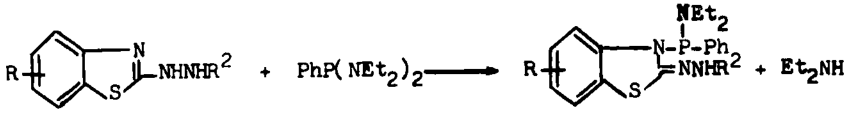


(1)

1 2 3b

2a–c: R = H, 6-Me, 4-Cl.

However, when 2-(2-phenylhydrazino)(or hydrazino)-1,3-benzothiazole **4** instead of **1** was treated with $PhP(NEt_2)_2$ at 110–115°C under a nitrogen atmosphere and reduced pressure of 5–10 torr, the acyclic phosphorus compounds **2** were obtained in good yields.

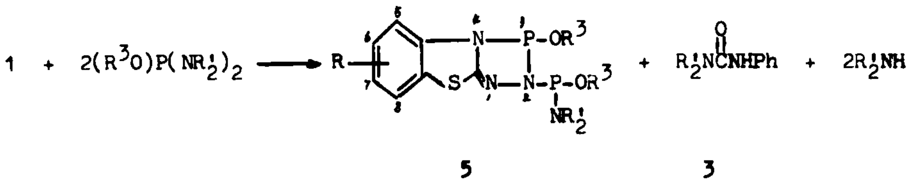


(2)

4 2

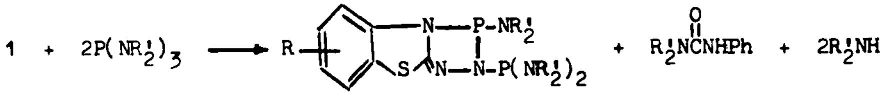
2a–c: R = H, 6-Me, 4-Cl, R^2 = H;
2d: R = H, R^2 = Ph.

Attempts to cyclocondense further in reactions (1) and (2) were also unsuccessful. However, when we used other tricoordinate phosphorus reagents such as tris(dialkylamino)phosphine and bis(dialkylamino)phosphite to treat **1**, new derivatives of fused tricyclic triazaphosphole, namely, 3-alkoxyl-2-(alkoxyldialkylaminophosphino)-2,3-dihydro[1,3]benzothiazolo[3,2-d][1,2,4,3]triazaphosphole **5** and 3-dialkylamino-2-[bis(dialkylamino)phosphino]-2,3-dihydro[1,3]benzothiazolo[3,2-d][1,2,4,3]triazaphosphole **6** were formed, and the N—C(O) bonds were also cleaved to give *N*,*N*-dialkyl-*N*′-phenylurea in both of the reactions.



(3)

5 3



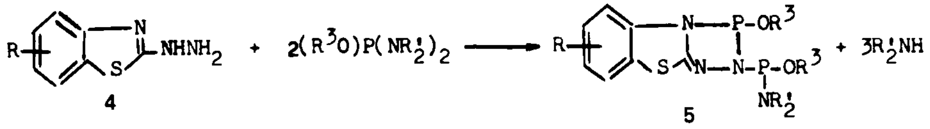
(4)

6 3

5a–b: R = H, R′ = R^3 = Me, Et;
5c: R = H, R′ = Et, R^3 = Me;
5d–e: R = 7-Me, R′ = R^3 = Me, Et;
5f–g: R = 5-Cl, R′ = R^3 = Me, Et.

6a–c: R = H, R′ = Me, Et, *n*-Pr;
6d–f: R = 7-Me, R′ = Me, Et, *n*-Pr;
6g–i: R = 5-Cl, R′ = Me, Et, *n*-Pr.
3a–c: R′ = Me, Et, *n*-Pr.

As compared with the above reactions, we investigated the reaction of 2-hydrazino-1,3-benzothiazole **4** ($R^2 = H$) with bis(dialkylamino)phosphite, which occurred at 100–105°C under a nitrogen atmosphere of 60–65 torr to give **5** in 75–76% yields.



(5)

5a–b: $R = H$, $R' = R^3 = Me, Et$; 5d–e: $R = 7\text{-}Me$, $R' = R^3 = Me, Et$;
5c: $R = H$, $R' = Et$, $R^3 = Me$; 5f–g: $R = 5\text{-}Cl$, $R' = R^3 = Me, Et$.

In addition, when 2-(2-tosylhydrazino)benzothiazole was heated with $PhP(NEt_2)_2$ under reduced pressure, there was no reaction occurred.

From the reactions described above, we can get some valuable information on the reactivities of the substrates. 2-(2-Phenylhydrazino)(or hydrazino)-1,3-benzothiazole **4** could react with $P(NR_2)_3$ at 80–90°C under a nitrogen atmosphere of 130 torr,[3] which was a much milder condition compared with that for the reaction of **4** with $(RO)P(NR_2)_2$ (Reaction 5). As shown in Table I, the highest temperature and vacuum were needed for the reaction of **4** with $PhP(NR_2)_2$ (Reaction 2) among the reactions (2), (5) and the reaction of **4** with $P(NR_2)_3$, which means that the cleavage of P—N bond in the molecule of $PhP(NEt_2)$ was more difficult than that for $P(NR_2)_3$ or $(RO)P(NR_2)_2$, since a low pressure favors the removal of dialkylamine. Similar comparison can be made for the reactions of 1-(2-benzothiazolyl)-4-phenylsemicarbazide **1** with $PhP(NEt_2)_2$ (Reaction 1), $(RO)P(NR_2)_2$ (Reaction 3) and $P(NR_2)_3$ (Reaction 4). Accordingly, the order of the reactivities of tricoordinate phosphorus reagents should be as following:

$$P(NR_2)_3 > (RO)P(NR_2)_2 > PhP(NR_2)_2$$

Furthermore, as compared with the reactions (2) and (5), a higher temperature and longer time were necessary for the reactions (1), (3) and (4) which involved the cleavage of N—C(O) bond, and the yields for the fused tricyclic triazaphospholes were very low in the reactions (1), (3) and (4), which may be resulted from the strong electron-withdrawing effect of the anilinocarbonyl group PhNHC(O)—. No reactions even took place when the anilinocarbonyl group was

TABLE I
Condensation reactions of **1** or **4** with P(III)[a]

Reaction	Molar Ratio 1 or 4: P(III)		N_2 Pressure torr	Temp. °C	Time h
1	1	1.8	5–10	140–150	1.5
2	1	1.8	5–10	110–115	1
3	1	2.6	60–65	130–135	1.5
4	1	2.5	130	125–130	1.5
5	1	2.6	60–65	100–105	1

[a] P(III) represents $(R_2N)_2PX$ ($X = RO$, R_2N or Ph).

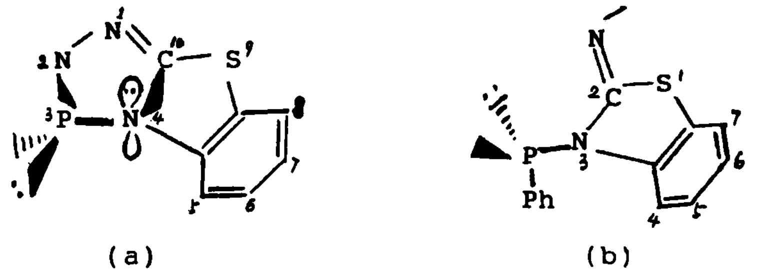
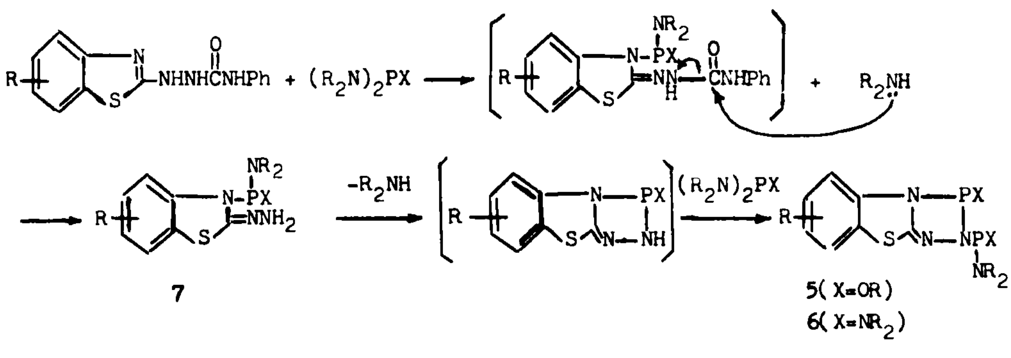


FIGURE 1 Structures of compounds **5**, **6(a)** and **2(b)**.

replaced by the tosyl group. It is, therefore, obvious that the reaction (1) proceeds most difficultly due to the involvement of the cleavages of N—C(O) bond in **1** and P—N bond in PhP(NEt$_2$)$_2$.

It is interesting to note that in the ^{13}C NMR spectra for compounds **5** and **6**, the chemical shift (137–154 ppm, $^2J_{PC} = 7.2$–8.5 Hz) attributed to C-10 is at the rather high field, in contrast to 170–172 ppm with the coupling constant of 35–37 Hz for the corresponding carbor (C-2) in compounds **2**. This phenomenon reflects the different environments for the two types of carbons and implies that the delocalization of electrons to a certain extent in the fused tricyclic triazaphosphole leads to the weaker deshielding. On the other hand, in compounds **5** and **6**, the lone pair of N-4 locates in the *p* orbital being vertical with ring plane. The orthogonality of the lone pair of P-3 with that of N-4^7 leads to the anticoplane of the lone pair of P-3 with N(4)–C(10) bond. However, the lone pair of phosphorus is *cis* to C(2)–N(3) bond in compounds **2** due to the strong interaction of the substituents on the phosphorus atom with hydrazino group. Therefore, the effect of lone pair of P-3 on C-10 is weaker than that of lone pair of phosphorus on C-2 in compounds **2** (Figure 1).

It seems reasonable to assume that reactions (1)–(5) proceed via similar mechanism and compounds **2** could be considered as the intermediates. As exemplified by reactions (1), (3) and (4), the reactions might occur as follows. **1** condensed with (R$_2$N)$_2$PX followed by the nucleophilic attack of the dialkylamine formed in the reaction on the carbonyl to give the intermediate **7** (when X = Ph, **7** is compound **2**) together with *N,N*-dialkyl-*N′*-phenylurea. The intermediate **7**



might condense further to lose another molecule of dialkylamine and react with a second molecule of $(R_2N)_2PX$ to give rise to the last products when X was alkoxyl or dialkylamino group, but the cyclocondensation would not proceed further when X was phenyl. The mechanism of these reactions will be studied in more detail in our laboratory.

EXPERIMENTAL

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not corrected. Spectral measurements were taken by members of the center of Analyses and Experiment of Huazhong Normal University, Wuhan, China using the following instruments: ^{1}H and ^{13}C NMR were recorded on Varian XL-300 and are reported in ppm downfield from intenal Me_4Si. Infrared spectra were measured as KBr plates or films in a NaCl cell on a Perkin-Elmer 983 spectrometer. Electron-impact mass spectra (MS) were determined with a JMS M-80A, GC-MS mass spectrometer (JEOL Ltd. Tokyo, Japan). Elemental analyses were performed by our Institute and Institute of Hydrobiology, Academia Sinica, Wuhan, China. The rotary T.L.C. apparatus used to purify the products was a LBG-1 Model from Qingying Instrument Factory, China.

Reaction of 1-(2-Benzothiazolyl)-4-phenylsemicarbazide **1** *with Bis(diethylamino)phenylphosphine.* General procedure. To a 50 ml round-bottom flask with 1.60 g (6.34 mmol) of bis(diethylamino)phenylphosphine, 1.00 g (3.52 mmol) of **1** was added under a gentle stream of nitrogen. The mixture was heated at 140–145°C with stirring for 1.5 h under a nitrogen atmosphere. The obtained yellow sticky mixture was dissolved in 5.0 mL of dichloromethane and purified by rotary T.L.C. apparatus on silica gel using diethyl ether/petroleum ether (1:2) as eluent firstly to afford **2a** (0.17 g, 14.0%) as a white crystal, and then using diethyl ether/petroleum ether (7:4) as eluent to afford **3b** (0.47 g, 69.5%). **3b**, m.p. 85–86.5°C (lit. 86–87°C).[8] For **2a**, m.p. 56–57°C. ^{1}H NMR: δ 1.1–1.5 (m, 6H, $2CH_3$), 10.5 (s, 2H, NH_2), 2.8–3.5 (m, 4H, $^{3}J_{HP}=8.1$ Hz, $2CH_2$), 7.0–8.0 (m, 9H, $^{3}J_{HP}=11.0$ Hz). Anal. Calcd for $C_{17}H_{21}N_4PS$: C, 59.30; H, 6.10; P, 9.01. Found: C, 59.23; H, 6.07; P,

TABLE II

IR, ^{31}P NMR data and yields of compounds **2**, **5** and **6**

Compd	Yield[a] %	IR ν cm^{-1}			^{31}P NMR[b] (ppm)		
		C—N	P—N	P—O	P_{cycl}	P_{acycl}	J_{PNP}(Hz)
2a	92.3(14.0)	1249	1169			99.3	
2b	89.7(16.0)	1260	1170			99.2	
2c	88.5(14.5)	1258	1169			100.2	
2d	87.8	1254	1166			99.3	
5a	77(21)	1275	1173	1022	75.6	126.3	107
5b	80(24)	1275	1183	1023	75.3	127.6	107
5c	76(26)	1275	1184	1020	75.4	128.5	105
5d	79(23)	1283	1174	1020	77.8	124.6	110
5e	78(25)	1275	1181	1017	76.6	125.7	102
5f	76(24)	1277	1185	1022	75.5	126.7	105
5g	75(24)	1275	1199	1024	31.6	83.4	102
6d	10.5	1242	1175		38.5	76.5	175
6e	10.0	1245	1194		77.6	112.8	189
6f	11.0	1243	1187		77.4	111.5	188
6g	12.2	1246	1186		78.1	109.8	151
6h	12.4	1247	1185		77.5	115.6	153
6i	11.5	1246	1195		77.1	117.3	154

[a] Isolated yields. Yields for reactions (1) and (3) are given in parentheses.

[b] ^{31}P NMR spectra were measured on Varian XL-300 in $CDCl_3$ using 85% H_3PO_4 as external reference.

8.99. MS: *m/e* (rel. intensity) 345 ($M^+ + 1$, 5), 271 ($C_{13}H_{10}N_3PS^+$, 2.9), 218 ($C_9H_5N_3PS^+$, 57), 165 ($C_7H_7N_3S^+$, base peak). Compounds **2a–c** were obtained similarly. For **2b**, m.p. 75–76.5°C. ^{1}H NMR: δ 0.9–1.1 (*t*, 6H, $2CH_3$), 10.3 (s, 2H, NH_2), 3.0–3.3 (m, 4H, $^3J_{HP} = 8.9$ Hz, $2CH_2$), 6.9–7.5 (m, $^3J_{HP} = 11.8$ Hz). MS: *m/e* (rel. intensity) 359 ($M^+ + 1$, 5), 285 ($C_{14}H_{12}N_3PS^+$, 11), 179 ($C_8H_9N_3S^+$, base peak). Anal. Calcd for $C_{18}H_{23}N_4PS$: C, 60.34; H, 6.42; P, 8.66. Found: C, 60.36; H, 6.34; P, 8.69. For **2c**, m.p. 93–95°C. ^{1}H NMR: δ 0.9 (t, 6H, $2CH_3$), 9.8 (s, 2H, NH_2), 2.9–3.2 (m, 4H, $^3J_{HP} = 8.2$ Hz, $2CH_2$), 6.8–7.7 (m, 8H, $^3J_{HP} = 11.0$ Hz). Anal. Calcd for $C_{17}H_{20}ClN_4PS$: P, 8.19; Found: P, 8.23.

Reaction of 2-Hydrazino-1,3-benzothiazole **4** *with Bis(diethylamino)phenylphosphine.* General procedure. To a 50 mL round-bottom flask with 2.75 g (10.9 mmol) of bis(diethylamino)phenylphosphine, 1.0 g (6.1 mmol) of **4** was added under a gentle stream of nitrogen. After removing the air in the flask, the stream of nitrogen was closed and the mixture was heated at 110–115°C with stirring

TABLE III

^{13}C NMR spectral data for compounds **2**, **5** and **6d-i**[a]

Compd	C-2 or C-10	α-C(NR')	α-C(OR)
2a	170.5(35.0)	42.5(14.8)	
2b	171.8(35.4)	43.5(15.7)	
2c	172.5(36.6)	43.5(14.1)	
2d	171.0(37.0)	43.0(15.5)	
5a	152.5(7.5)	37.6(17.6)	[50.5(14.4)] 52.6(14.6)
5b	154.0(7.2)	42.4(18.2)	[60.5(15.0)] 61.5(14.6)
5c	149.4(7.8)	38.2(19.5)	[50.4(14.2)] 51.9(21.1)
5d	154.0(7.2)	38.2(18.5)	[50.8(14.6)] 51.6(20.6)
5e	154.5(7.5)	46.5(18.5)	[60.4(14.2)] 61.3(13.9)
5f	154.3(8.5)	38.4(16.4)	[51.3(14.5)] 51.8(21.5)
5g	152.5(7.9)	46.8(17.8)	[59.7(13.5)] 60.9(15.0)
6d	138.2(7.6)	[36.2(18.0)] 37.3(19.0) 37.8(18.5)	
6e	142.7(7.7)	[39.6(16.6)] 40.2(17.0) 41.2(17.3)	
6f	140.6(7.5)	[46.8(16.0)] 46.8(18.0) 49.2(18.0)	
6g	139.6(7.6)	[37.5(16.0)] 38.2(15.5) 39.0(16.2)	
6h	137.4(7.5)	[42.6(17.5)] 43.5(17.8) 43.9(18.2)	
6i	140.5(7.8)	[47.5(15.0)] 49.6(16.0) 49.8(16.2)	

[a] The data are only given for α-C of alkoxyl or dialkylamino group connecting with cyclic (see the data in square brackets) and acyclic (see the others) phosphorus atom and C-2 or C-10 of the benzothiazolyl ring. The coupling constant of the carbon as split by the phosphorus atom is given in hertz in parentheses.

under a nitrogen atmosphere of 5–10 torr for 1 h. The heater was removed. After the mixture was cooled to the ambient temperature, the reaction system was opened to the air carefully. 5.0 mL of dichoromethane was added to dissolve the obtained yellow sticky mixture. Preparative T.L.C. on silica gel using diethyl ether/petroleum ether (1:2) as eluent afforded compound **2a** (1.92 g, 92%) as a white crystal. **2a–c** were characterized by spectroscopic and elemental analyses. For the data, see the statement above. For **2d**, m.p. 48–49.5°C. ^{1}H NMR: δ 0.9–1.6 (m, 6H, 2CH_3), 2.9–3.2 (m, 4H, $^3J_{HP}$ = 8.9 Hz, 2CH_2), 6.9–7.9 (m, 14H, $^3J_{HP}$ = 10.8 Hz). 9.6 (s, 1H, NH). MS: *m/e* (rel. intensity) 420 (M^+, 31), 347 ($C_{19}H_{14}N_3PS^+$, 54), 241 ($C_{13}H_{11}N_3S^+$, base peak). Anal. Calcd for $C_{23}H_{25}N_4PS$: C, 65.71; H, 5.95; P, 7.38. Found: C, 65.70; H, 5.90; P, 7.43.

Reaction of 1-(2-Benzothiazolyl)-4-phenylsemicarbazide **1** *with Bis(dialkylamino)phosphite.* General procedure. In a 50 mL round-bottom flask containing ethyl bis(diethylamino)phosphite (2.01 g, 9.15 mmol) was added 1.0 g (3.52 mmol) of **1**. The mixture was heated at 130–135°C with stirring under a nitrogen atmosphere of 60–65 torr for 1.5 h, and then cooled to room temperature and recovered to normal pressure. The obtained purple sticky mixture was dissolved in 5.0 mL of dichloromethane and purified by rotary T.L.C. apparatus on silica gel employing diethyl ether/petroleum ether (3:8) as eluent firstly to give **5b** (0.33 g, 24.3%) as a yellow sticky liquid with a strong odor, and then employing diethyl ether/petroleum ether (7:4) to give **3b** (0.4 g, 71.0%). For **5b**, ^{1}H NMR: δ 1.1 (t, 6H, 2CH_3), 1.4 (t, 6H, 2CH_3), 2.8–3.4 (m, 4H, $^2J_{HP}$ = 7.8 Hz, 2CH_2), 3.4–4.3 (m, 4H, $^3J_{HP}$ = 7.5 Hz, 2CH_2), 6.9–7.5 (m, 4H). MS: *m/e* (rel. intensity) 386 (M^+, 45), 314 ($C_{11}H_{14}N_3O_2P_2S^+$, 35.5), 148 ($C_7H_4N_2S^+$, base peak). Anal. Calcd for $C_{15}H_{24}N_4O_2P_2S$: C, 46.63; H, 6.22; P, 16.06. Found: C, 46.62; H, 6.20; P, 16.09. Compounds **5a**, **5c–g** were obtained similarly. **5a**, **5c–g** were all yellow sticky liquid with a strong odor. For **5a**, ^{1}H NMR: δ 0.9–1.2 (m, 6H, $^3J_{HP}$ = 8.0 Hz, 2CH_3), 3.7–4.0 (m, 6H, $^3J_{HP}$ = 14.0 Hz, 2CH_3), 7.1–7.3 (m, 4H). MS: *m/e* (rel. intensity) 330 (M^+, 56). For **5c**, ^{1}H NMR: δ 0.8–1.3 (m, 6H, 2CH_3), 2.8–3.3 (m, 4H, $^3J_{HP}$ = 7.6 Hz, 2CH_2), 3.5–3.7 (m, 6H, $^3J_{HP}$ = 15.5 Hz, 2CH_3), 7.1–7.4 (m, 4H). MS: *m/e* (rel. intensity) 358 (M^+, 47). Anal. Calcd for $C_{13}H_{20}N_4O_2P_2S$: C, 43.58; H, 5.59; P, 17.32. Found: C, 43.56; H, 5.58; P, 17.38. For **5d**, ^{1}H NMR: δ 0.9–1.1 (m, 6H, $^3J_{HP}$ = 8.3 Hz, 2CH_3), 2.2 (s, 3H, CH_3), 7.1–7.8 (m, 3H), 3.8–4.1 (m, 6H, $^3J_{HP}$ = 15.0 Hz, 2CH_3). Anal. Calcd for $C_{12}N_{18}N_4O_2P_2S$: C, 41.86; H, 5.23; P, 18.02. Found: C, 41.88; H, 5.25; P, 17.99. For **5e**, ^{1}H NMR: δ 0.7–1.3 (m, 12H, 4CH_3), 2.15 (s, 3H, CH_3), 2.5–3.1 (m, 4H, $^3J_{HP}$ = 7.1 Hz, 2CH_2), 3.3–4.0 (m, 4H, $^3J_{HP}$ = 8.3 Hz, 2CH_2). Anal. Calcd for $C_{16}H_{26}N_4O_2P_2S$: C, 48.00; H, 6.50; P, 15.50. Found: C, 47.98; H, 6.48; P, 15.48. For **5f**, ^{1}H NMR: δ 1.0–1.2 (m, 6H, $^3J_{HP}$ = 8.1 Hz, 2CH_3), 3.9–4.2 (m, 6H, $^3J_{HP}$ = 14.5 Hz, 2CH_3), 7.1–7.9 (m, 3H). Anal. Calcd for $C_{11}H_{15}ClN_4O_2P_2S$: C, 36.21; H, 4.12; P, 17.01. Found: C, 36.25; H, 4.14; P, 17.04. For **5g**, ^{1}H NMR: δ 0.9–1.6 (m, 12H, 4CH_3), 7.0–7.4 (m, 3H), 2.9–3.4 (m, 4H, $^3J_{HP}$ = 8.0 Hz, 2CH_2), 3.6–4.1 (m, 4H, $^3J_{HP}$ = 8.9 Hz, 2CH_2). Anal. Calcd for $C_{15}H_{23}ClN_4O_2P_2S$: C, 42.81; H, 5.47; P, 14.74. Found: C, 42.84; H, 5.49; P, 14.7.

Reaction of 1-(6-Methyl-2-benzothiazolyl)-4-phenylsemicarbazide with Tris(dialkylamino)phosphine. General procedure. To a 50 mL round-bottom flask with tris(dimethylamino)phosphine (1.37 g, 8.39 mmol), 1-(6-methyl-2-benzothiazolyl)-4-phenylsemicarbazide (1.00 g, 3.36 mmol) was added. The mixture was heated at 125°C under a nitrogen atmosphere of 130 torr for 1.5 h, and then cooled to the ambient temperature and recovered to the normal pressure. The residual crude product was purified by rotary T.L.C. apparatus on silica gel using diethyl ether/petroleum ether (1:4) as eluent firstly to afford **6d** as a yellow sticky liquid (0.15 g, 10.0%), and then using diethyl ether/petroleum ether (7:3) as eluent to afford **3a** (0.48 g, 75%). For **3a**, m.p. 134–135°C (lit. 135°C).[8] For **6d**, ^{1}H NMR: δ 1.9 (d, 6H, $^3J_{HP}$ = 8.5 Hz, 2CH_3), 2.2 (s, 3H, CH_3), 2.1 (d, 6H, $^3J_{HP}$ = 9.8 Hz, 2CH_3), 6.8–7.3 (m, 3H), 2.3 (d, 6H, $^3J_{HP}$ = 10.1 Hz, 2CH_3). MS: *m/e* (rel. intensity) 370 (M^+, 34), 251 ($C_{10}H_{12}N_4PS^+$, 22), 326 ($C_{12}H_{18}N_5P_2S^+$, 17). Anal. Calcd for $C_{14}H_{24}N_6P_2S$: C, 45.41; H, 6.49; P, 16.76. Found: C, 45.38; H, 6.46; P, 16.70. Compounds **6a–c**, **6e–i** and **3b–c** could be obtained similarly. **3c**, m.p. 71–72°C (lit. 70–72°C).[8] **6a–c** are known.[3] **6e–i** are also yellow sticky liquid with strong odors. For **6e**, ^{1}H NMR: δ 0.9 (t, 6H, 2CH_3), 1.1 (t, 6H, 2CH_3), 1.2 (t, 6H, 2CH_3), 2.2 (s, 3H, CH_3), 2.9–3.4 (m, 12H, $^3J_{HP}$ = 7.7 Hz, 6CH_2), 6.8–7.2 (m, 3H). Anal. Calcd for $C_{15}H_{26}N_6P_2S$: C, 46.88; H, 6.77; P, 16.15. Found: C, 46.91; H, 6.82; P, 16.20. For **6f**, ^{1}H NMR: δ 0.8–1.2 (m, 18H, 6CH_3), 1.2–2.8 (m, 12H, 6CH_2), 2.8–3.1 (m, 12H, $^3J_{HP}$ = 7.8 Hz, 6CH_2), 2.2 (s, 3H, CH_3), 6.8–7.3 (m, 3H). Anal. Calcd for $C_{16}H_{28}N_6P_2S$: C, 48.24; H, 7.04; P, 15.58. Found: C, 48.20; H, 6.98; P, 15.53. For **6g**, ^{1}H NMR: δ 1.9 (d, 6H, $^3J_{HP}$ = 8.6 Hz, 2CH_3), 2.1 (d, 6H, $^3J_{HP}$ = 10.1 Hz, 2CH_3), 2.3 (d, 6H, $^3J_{HP}$ = 10.2 Hz, 2CH_3), 7.0–7.5 (m, 3H). Anal. Calcd for $C_{13}H_{21}ClN_6P_2S$: C, 39.95; H, 5.38; P, 15.58. Found: C, 39.91; H, 5.35; P, 15.85. For **6h**, ^{1}H NMR: δ 0.9–1.2 (m, 18H, 6CH_3), 2.9–3.3 (m, 12H, $^3J_{HP}$ = 7.8 Hz, 6CH_2), 7.1–7.5 (m, 3H). Anal. Calcd for $C_{14}H_{23}ClN_6P_2S$: P, 15.33. Found: P, 15.31. For **6i**, ^{1}H NMR: δ 0.7–1.1 (m, 18H, 6CH_3), 1.1–2.8 (m, 3H), 2.8–3.1 (m, 12H, $^3J_{HP}$ = 7.7 Hz, 6CH_2), 7.1–7.5 (m, 3H). Anal. Calcd for $C_{15}H_{25}ClN_6P_2S$: P, 14.81. Found: P, 14.78.

Reaction of 2-Hydrazino-1,3-benzothiazole **4** *with Bis(dialkylamino)phosphite.* The general procedure was similar to reaction (3) except that the temperature was changed to 100–105°C. Compounds **5** (75–79%) were obtained by similar isolating method as described above using diethyl ether/petroleum ether (3:8) as eluent. The products were identified by IR, NMR, MS and elemental analyses to be the same as the corresponding products in the reaction (3).

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