Heteroatom Chemistry
Volume 3, Number 4, 1992

1,3-Azaphospholo[5,1-*b*]thiazolines and Benzothiazoles†

Raj K. Bansal,* Ruchi Mahnot, and Dinesh C. Sharma

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

Konstantin Karaghiosoff and Alfred Schmidpeter

Institut für Anorganische Chemie, Universität München, Meiserstr. 1, D-8000 München 2, Germany

Received 27 August 1991.

ABSTRACT

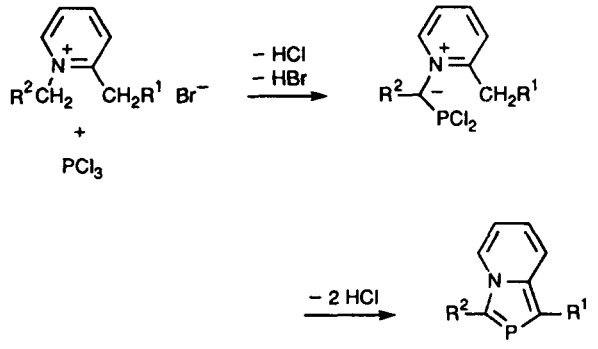
The title compounds **3** *and* **7** *are novel heterocyclic systems incorporating two-coordinate phosphorus. They are obtained in reasonable to good yields from the condensation of suitable 2-ethyl-3-alkylthiazolinium and -benzothiazolium bromides* **2** *and* **6** *with phosphorus trichloride in the presence of triethylamine in an aprotic solvent. Intermediate dichlorophosphino-substituted N-ylides can be observed or isolated in some cases. From a 2-methyl-3-alkylthiazolinium bromide* (**2a**)*, a 1-(dichlorophosphino) substituted 1,3-azaphospholo[5,1-b]thiazoline* (**4**) *was obtained.*

The chemical shift of the two-coordinate phosphorus in 1,3-azaphosphole derivatives clearly reflects the influence of the heterocyclic system annulated to its 1,5-bond and of the substituents in its 2- and 4- positions.

INTRODUCTION

Since the synthesis of the first phosphinines (phosphabenzenes) in 1966, many additional five- and six-membered heterocycles with carbon-bonded two-coordinate phosphorus have been prepared [1, 2]. They are aromatic systems, and they demonstrate that two-coordinate phorphorus can take part in a cyclic delocalization. Although the P=C "double bond" in these systems is less reactive than in acyclic compounds, it is still the most reactive site of the heterocycles in question and provides promising possibilities for their further synthetic use.

Facile methods for the synthesis of these heterocycles are needed, preferably using phosphorus trichloride as the direct source of the phosphorus ring member. Only two such syntheses have been described so far [3–5]. In a preceding article [3] we reported the synthesis of 2-phosphaindolizines by the condensation of 1,2-dialkylpyridinium bromides with PCl_3 in the presence of triethylamine (Reaction 1). An intermediate pyridinium *N*-(dichlorophosphinomethylide) could be isolated and identified. This indicates that the reaction is initiated by the formation of the pyridinium *N*-ylide,



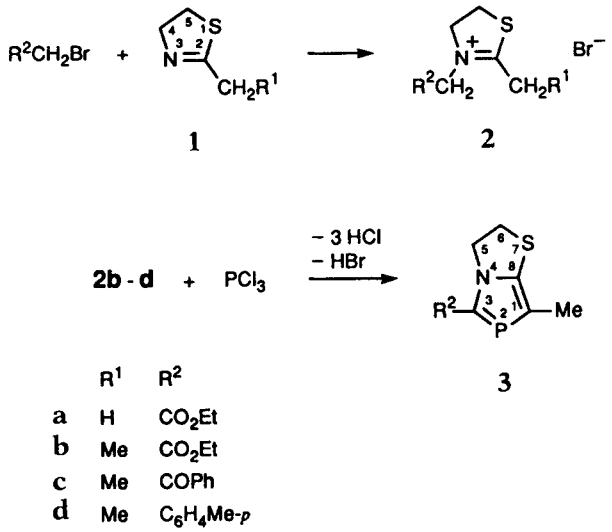
REACTION 1

* To whom correspondence should be addressed.
† In part reported at the 8th International IUPAC Conference on Organic Synthesis, Helsinki 1990.

1042-7163/92/$3.50 + .25

which then effects a nucleophilic displacement on PCl_3, followed by another deprotonation of the *N*-alkyl group to give the intermediate. Finally, the ring is closed by an intramolecular condensation of the latter.

The results obtained suggest extensions of this route to other 1,2-dialkylcycloimmonium salts capable of *N*-ylide formation [6]. Like *N*-alkylpyridinium salts, *N*-alkylbenzothiazolium salts, on reacting with a base, can also furnish ylides, which, however, exist in a prototropic equilibrium with 2-carbenes that can dimerize to olefines [7]. Besides this, the two classes of ylides show some other dissimilarities [8]. Methylene bases derived from 2-methylbenzothiazolium salts have a strong tendency to dimerize [9]. In view of these comparisons, it was worthwhile to investigate the reaction of 2,3-dialkylbenzothiazolium salts with PCl_3 and Et_3N. It was also of interest to determine whether 2,3-dialkylthiazolinium salts as examples of non-aromatic cycloimmonium salts, could be used for this synthesis. 1,4,2-Diazaphospholo[5,4-*b*] thiazolines and -benzothiazoles, that is, systems having one nitrogen ring member more than the ones described herein, have recently been reported [10].



REACTION 2

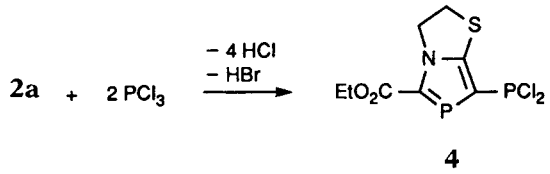
RESULTS AND DISCUSSION

1,3-Azaphospholo[5,1-b]thiazolines

As starting materials for the intended syntheses, the 2,3-dialkylthiazolinium salts must provide, in both positions at the ring, methylene groups that are sufficiently reactive. Suitable salts can readily be obtained by the alkylation of thiazolines according to a literature procedure [11]. 2-Methyl- and 2-ethylthiazoline **(1a, b)** were used. Compounds **2a–d**, to our knowledge, have not been described previously (Reaction 2). For the condensation, equimolar amounts of **2** and PCl_3 are treated with a four-fold molar amount of triethylamine in acetonitrile. Complete reaction requires heating to 60–70°C for 8–12 hours. The resulting azaphospholothiazolines are isolated by extraction with diethyl ether and are obtained in about 50% yield.

It should be noted that the condensation is successful even in the case of **2d**. Thus, the presence of R^2 = *p*-tolyl in the thiazolinium cation proves to be a sufficient structural influence to activate the *N*-methylene unit. In contrast, 1-benzyl-2-ethylpyridinium bromide, under comparable conditions [3], did not react with PCl_3 [12] and did not give the 2-phosphaindolizine.

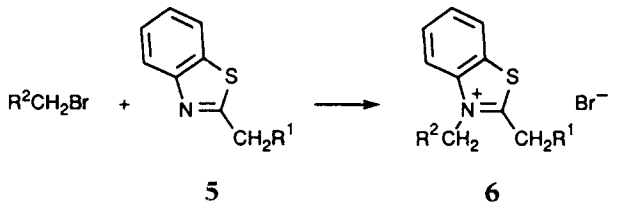
The condensation of **2a** with PCl_3 did not give the expected azaphospholothiazoline **3a** with R^1 = H. This is obviously because of the greater reactivity of a methyl group as against an ethyl group in **2** toward PCl_3. Substitution by PCl_3 has been experienced for the analogous position of other azaphospholes [3, 13–15]. With a ratio of two moles of phosphorus trichloride to one mole of **2a** the 1-(dichlorophosphino) derivative **4** is isolated in 40% yield (Reaction 3).



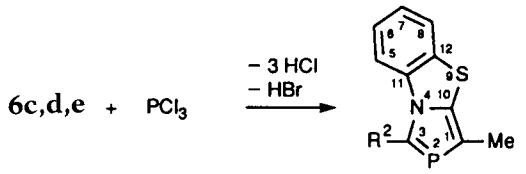
REACTION 3

1,3-Azaphospholo[5,1-b]benzothiazoles

The necessary 2,3-dialkylbenzothiazolium salts **6** are readily obtained from 2-methyl- or 2-ethylbenzothiazole (**5a,b**) and ethyl bromoacetate, phenacyl bromide, bromoacetonitrile, or 4-nitrobenzyl bromide; **6a–d** have been reported before [16]. For condensation, these salts are reacted as before with one equivalent of PCl_3 and four equivalents of triethylamine in acetonitrile. No 1-unsubstituted 1,3-azaphospholo[5,1-*b*]benzothiazoles could be obtained from **6a,b**. This negative result is contrary to that found for the reaction of 2-methylpyridinium salts where 1-unsubstituted 2-phosphaindolizines are obtained [3]. It may be because of a ready dimerization of the methylene bases from **6a,b** [9]. The 2-ethylbenzothiazolium salts **6c, d, e,** however, give the expected 1-methyl derivatives **7c, d, e.** The reaction is complete after 12 hours at room temperature or 5 hours at 60°C (Reaction 4).



5 **6**



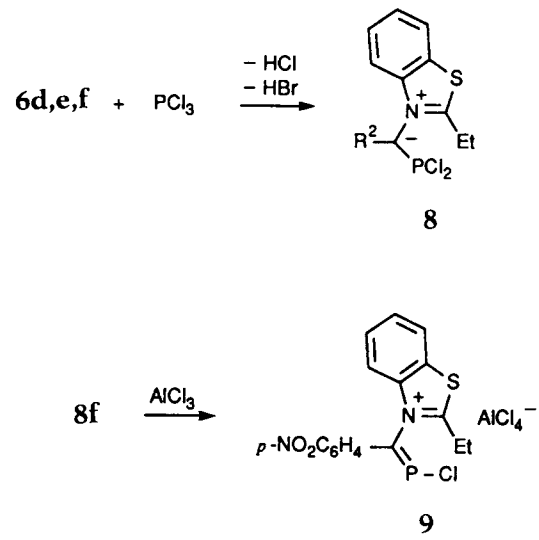
	R^1	R^2
a	H	CO_2Et
b	H	COPh
c	Me	CO_2Et
d	Me	COPh
e	Me	CN
f	Me	$C_6H_4NO_2$-*p*

7

REACTION 4

In the case of the reaction of **6e** with PCl_3, some dichlorophosphino *N*-ylide **8e** was isolated together with the cyclized product **7e**. Dichlorophosphino ylides, **8**, are most probably intermediates in all of the cyclocondensation reactions leading to **7**. The corresponding ^{31}P-NMR signal (Table 1) is also observed in the reaction of **6d**, but no such signal is detected in the reaction of **6c**. As has been mentioned in the introduction, analogous intermediates are found in the synthesis of the 2-phosphaindolizines. From the PCl_3 condensation of **6f**, only the ylide **8f** could be isolated, and it could not be cyclized even on heating for 5 h in the presence of excess triethylamine (Reaction 5). The ylidic nature of **8f** is emphasized by its behavior toward aluminum chloride. The observed low field chemical shift $\delta^{31}P = 268$ can be attributed to a chloride abstraction and the formation of the *C*-benzothiazolio *P*-chlorophosphaalkene tetrachloroaluminate **9** [17, 18].

From the deprotonation and condensation of *C,N*-dialkylcycloimmonium ions with phosphorus trichloride PCl_2 derivatives of the enamine or of



8 **9**

REACTION 5

the immonium ylide type may result: A 2-dichlorophosphinomethylene indoline of the former type has been obtained from the reaction of the Fisher base [19], while compounds **8** are examples of the latter type.

TABLE 1 ^{31}P NMR Chemical Shifts of the Dichlorophosphino Ylides **8**

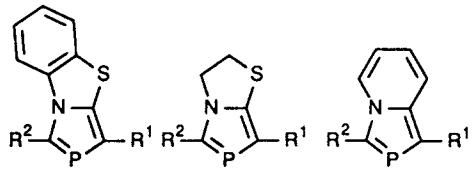
	R^2	$\delta^{31}P$
8d	COPh	178.0
8e	CN	185.9
8f	$C_6H_4NO_2$-*p*	176.9

NMR Spectra

The cyclization products **3**, **4** and **7** are unambiguously characterized by their NMR spectra (Tables 2, 3, and Experimental).

The ^{31}P-NMR signals of heterophospholes are generally found at low field, their shift depending

TABLE 2 ^{31}P NMR Chemical Shifts of the Two-Coordinate Phosphorus in 4-Methyl and 4-Dichlorophosphino 1,3-Azaphospholes with a Benzothiazole, Thiazoline, or Pyridine Ring Annulated to their 1,5 Bond



R^2	R^1=Me					
COPh	**7d**:	202.6	**3c**:	193.8	183.6	[3]
CN	**7e**:	191.6			165.2	[3]
CO_2Et	**7c**:	184.8	**3b**:	173.7	163.3	[3]
$C_6H_4NO_2$-*p*					136.0	[3]
C_6H_4Me-*p*			**3d**:	130.0		
	$R^1 = PCl_2$					
COPh					197.1	[20]
CO_2Et			**4**:	187.0	180.4	[20]
$C_6H_4NO_2$-*p*					164.3	[20]

TABLE 3 ^1H and ^{13}C NMR Data of the 1,3-Azaphospholo[5,1-*b*]benzothiazoles **7** (in $CdCl_3$)

δ J[Hz]	**7c**[a]	**7d**[b]	**7e**
5-H	8.92	8.48	8.50
^3J(5-H, 6-H)	8.1	8.3	8.3
^4J(5-H, 7-H)	1.2	1.2	1.2
6-H	7.38	7.40	7.46
^3J(6-H, 7-H)	7.3	7.3	7.3
^4J(6-H, 8-H)	1.5	1.5	1.2
7-H	7.29	7.34	7.38
^3J(7-H, 8-H)	7.8	7.8	7.8
8-H	7.59	7.67	7.68[c]
1-CH_3	2.36	2.40	2.39
^3J(P, H)	10.5	10.7	11.2
C-1	130.9	132.2	131.5
^1J(P, C)	45.1	47.2	51.3
^2J(C, H)	6.4	6.2	
C-3	143.2	151.3	117.5
^1J(P, C)	53.5	57.6	47.1
C-5	118.5[d]	118.7	114.4
^4J(P, C)	2.1	1.9	1.6
^1J(C, H)	169.1	168.7	
^3J(C, H)	7.9	8.1	
C-6	125.1[e]	125.5	126.0
^5J(P, C)	2.1	1.9	1.9
^1J(C, H)	163.0	162.5	
^3J(C, H)	7.9	8.3	
C-7	125.6	125.8	126.5[f]
^1J(C, H)	162.8	163.0	
^3J(C, H)	7.8	7.6	
C-8	123.5	123.7	124.3
^5J(P, C)	2.0	1.9	1.6
^1J(C, H)	166.9	164.4	
^3J(C, H)	8.9	8.8	
C-10	143.9	146.7	141.5
^2J(P, C)	11.5	11.5	13.8
^3J(C, H)	6.3	5.9	
C-11	136.7	136.6	135.7
^3J(P, C)	4.2	4.2	3.9
^2J(C, H)	2.1	2.6	
^3J(C, H)	7.6	9.7	
C-12	131.6[g]	131.7	131.8
^3J(C, H)	7.8, 9.5	7.1, 8.5	
1-CH_3	13.8	13.7	13.7
^2J(P, C)	23.0	22.0	23.7
^1J(C, H)	128.5	128.4	
CO, CN	162.6	184.9	116.0
^2J(P, C)	19.9	25.2	24.1
^3J(C, H)	3.4	3.8	

[a] Et: δ^1H = 4.39 (q, ^3J(H, H) = 7.1 Hz, 2H, CH_2), 1.42 (t, ^3J(H, H) = 7.1 Hz, 3H, CH_3); $\delta^{13}C$ = 60.8 (tqd, ^1J(C, H) = 147.4 Hz, ^2J(C, H) = 4.6 Hz, ^4J(P, C) = 0.6 Hz, CH_2), 14.3 (qt, ^1J(C, H) = 127.0 Hz, ^2J(C, H) = 2.5 Hz, CH_3).

[b] Ph: δ^1H = 8.06 (m, 2H, *o*-H), 7.47 (m, 2H, *m*-H), 7.59 (m, 1H, *p*-H); $\delta^{13}C$ = 139.9 (s, C-*i*), 130.3 (d, ^4J(P, C) = 6.3 Hz, C-o), 127.9 (s, C-*m*), 132.3 (s, C-*p*).

[c] ^6J(P, 8-H) = 0.5 Hz.

[d] ^2J(C, H) = 0.9 Hz.

[e] ^2J(C, H) = 1.2 Hz.

[f] ^6J(P, C) = 1.0 Hz.

[g] ^2J(C, H) = 0.9 Hz.

mainly on the ring members adjacent to the two-coordinate phosphorus. For the *C,C*-bonded phosphorus in the systems known so far the shifts range from 50 to 180 [1]. The shifts observed for **3** and **7** extend this range to lower field. As can be seen from Table 2, the ^{31}P NMR shift of an 1,3-azaphosphole clearly depends on the ring annulated to its 1,5-bond. For a given substitution, it always decreases in the order

benzothiazole > thiazoline > pyridine

with roughly $\Delta\delta \approx 10$ for each step.

As has already been mentioned in the case of the 2-phosphaindolizines [3], the phosphorus shift also reflects the influence of substituent R^2, decreasing in the order

COPh > CN > CO_2Et > $C_6H_4NO_2$-*p* > C_6H_4Me-*p*

The exchange of COPh for CO_2Et causes an upfield shift of roughly $\Delta\delta \approx 20$. The observed order is also the order of decreasing CH acidity under the influence of the substituents in question [21].

Replacement of Me for PCl_2 in the 1-position of **3b** (→ **4**) is accompanied by a significant downfield shift (Table 2). Similar shifts are known for the 2-phosphaindolizine series. $\delta(PCl_2)$ = 156.7 and ^2J(P,P) = 107.4 Hz of **4** are also comparable to the data of 1-dichlorophosphino-2-phosphaindolizines [20].

The NMR signals of the ring protons of compounds **7** (Table 3) are assigned starting with that of 5-H at lowest field. The assignment of the ^{13}C NMR signals of the benzo ring of **7** is based on comparisons and is in accord with the long range coupling ^5J(P,C) observed for C-6. In the case of **7e** even a coupling ^6J(P,C) is observed for C-7. The coupling ^4J(P,C) for the *o*-C of COPh is found to be remarkably large in **7d** as well as in the corresponding 2-phosphaindolizines [3].

EXPERIMENTAL

All operations involving phosphorus-containing compounds are carried out in dry equipment under nitrogen. ^{31}P NMR: Jeol FX-90-Q and GSX-270 at 36.2 and 109.7 MHz. ^1H NMR: Jeol FX-90-Q and EX-400 at 90 and 400 MHz. ^{13}C NMR: Jeol EX-400 at 100.5 MHz. The chemical shifts refer to 85% H_3PO_4 (external) or TMS (internal).

2,3-Dialkylthiazolinium Bromides (**2**)

0.04 mol alkyl bromide are added. On stirring the resulting solution for 3 days at ambient temperature (~25°C) a solid or syrupy mass is obtained, which is separated, washed with dry diethyl ether, and dried.

3-(2-Ethoxy-2-oxoethyl)-2-methylthiazolinium Bromide **2a.** 84% yield, pale yellow solid, mp 114–

115°C. ^{1}H NMR (d^6-DMSO): δ = 0.95 (t, ^3J = 6.5 Hz, 3H, $OCH_2\underline{CH_3}$), 2.47 (s, 3H, 2-CH_3), 3.63 (t, ^3J = 9.6 Hz, 2H, 4-H), 3.96 (q, ^3J = 6.5 Hz, 2H, OCH_2), 4.56 (t, ^3J = 9.6 Hz, 2H, 5-H), 4.88 (s, 2H, NCH_2).

3-(2-Ethoxy-2-oxoethyl)-2-ethylthiazolinium Bromide **2b**. 72% yield, reddish brown syrupy mass. ^{1}H NMR (d^6-DMSO): δ = 1.21 (t, ^3J = 6.8 Hz, 3H, OCH_2CH_3), 1.26 (t, ^3J = 7.0 Hz, 3H, 2-CH_2CH_3), 2.96 (q, ^3J = 7.0 Hz, 2H, CH_2), 3.79 (t, ^3J = 9.5 Hz, 2H, 5-H), 4.19 (q, ^3J = 6.8 Hz, 2H, OCH_2), 4.88 (t, ^3J = 9.5 Hz, 2H, 4-H), 5.13 (s, 2H, NCH_2).

2-Ethyl-3-phenacylthiazolinium Bromide **2c.** 70% yield, reddish brown syrupy mass. ^{1}H NMR (d^6-DMSO): δ = 0.78 (t, ^3J = 7.0 Hz, 3H, CH_3), 2.54 (t, ^3J = 8.2 Hz, 2H, 5-H), 3.01 (q, ^3J = 7.0 Hz, 2H, $C\underline{H_2}CH_3$), 3.72 (t, ^3J = 8.2 Hz, 2H, 4-H), 4.15 (s, 2H, NCH_2), 7.4-8.0 (m, 5H, aromatic H).

2-Ethyl 3-p-tolylthiazolinium Bromide **2d.** 82% yield, brown solid, mp 148–150°C. ^{1}H NMR (d^6-DMSO): δ = 1.47 (t, ^3J = 7.4 Hz, 3H, $CH_2C\underline{H_3}$), 2.39 (s, 3H, CH_3), 3.24 q, ^3J = 7.4 Hz, 2H, $C\underline{H_2}CH_3$), 3.91 (t, ^3J = 9.4 Hz, 2H, 5-H), 4.76 (t, ^3J = 9.4 Hz, 2H, 4-H), 5.32 (s, 2H, NCH_2), 7.2–7.5 (m, 4H, aromatic H).

1,3-Azaphospholo[5,1-b]thiazolines (**3, 4**)

To 0.02 mol thiazolinium bromide **2** in 50 mL dry acetonitrile 0.02 mol freshly distilled PCl_3 are added, and the suspension is cooled to 0–5°C. A solution of 11.2 mL (0.08 mol) triethylamine in 15 mL acetonitrile is slowly added to the well-stirred suspension while the temperature is maintained at 0–5°C. An exothermic reaction sets in and the reaction mixture turns orange. It is allowed slowly to come to ambient temperature and then heated to 60–70°C for 8–12 hours. The solvent is removed under vacuum and the residue extracted three times with 70 mL diethyl ether overnight. The combined filtrates are concentrated to about 40 mL and left in the refrigerator. The products precipitate from the solution, and they are separated and dried. For ^{31}P NMR see Table 2 and text.

3-Ethoxycarbonyl-1-methyl-1,3-azaphospholo-[5,1-b]thiazoline **3b**. 47% yield, reddish brown solid, mp 62–64°C. ^{1}H NMR ($CDCl_3$): δ = 1.27 (t, ^3J(H, H) = 7.5 Hz, 3H, $OCH_2C\underline{H_3}$), 2.12 (d, ^3J(P, H) = 10.0 Hz, 3H, CH_3), 3.73 (t, ^3J(H, H) = 7.5 Hz, 2H, 6-H), 4.24 (q, ^3J(H, H) = 7.5 Hz, 2H, OCH_2), 4.67 (dt, ^3J(H, H) = 7.5, ^4J(P, H) = 2.5 Hz, 5-H. Anal. Calcd. for $C_9H_{12}O_2NSP$ (229.2): C, 47.16; H, 5.28; N, 6.16. Found: C, 46.20; H, 5.80; N, 5.80.

3-Benzoyl-1-methyl-1,3-azaphospholo[5,1-b]thiazoline **3c**. 54% yield, reddish brown syrupy mass. ^{1}H NMR ($CDCl_3$): δ = 2.18 (d, ^3J(P, H) = 10.0 Hz, 3H, CH_3), 3.79 (t, ^3J(H, H) = 7.0 Hz, 2H, 4-H), 4.84 (dt, ^3J(H, H) = 7.0, ^4J(P, H) = 3.0 Hz, 2H, 5-H), 7.3–7.9 (m, 5H, aromatic H).

1-Methyl-3-p-tolyl-1,3-azaphospholo[5,1-b]-thiazoline **3d**. 43% yield, pale yellow solid, mp

TABLE 4 Physical and ^{1}H NMR Data of 2,3-Dialkylbenzothiazolium Bromides **6** (in d^6-DMSO)

	R^1 R^2	*Yield (%)* *mp (°C)*	δ ^{1}H *J(H, H) [Hz]*
6a	H CO_2Et	95 170–171	1.22 (t, ^3J = 8.0, 3H, CH_2CH_3), 3.41 (s, 3H, 2-CH_3), 4.22 (q, ^3J = 8.0, 2H, OCH_2), 6.00 (s, 2H, NCH_2), 7.5–8.3 (m, 4H, aromatic H)
6b	H COPh	58 196–197	3.14 (s, 3H, CH_3), 6.89 (s, 2H, NCH_2), 7.3–8.3 (m, 9H, aromatic H)
6c	Me CO_2Et	74 154–155	1.18 (t, ^3J = 8.0, 3H, 2-CH_2CH_3), 1.49 (t, ^3J = 8.0, 3H, OCH_2CH_3), 3.68 (q, ^3J = 8.0, 2H, 2-CH_2), 4.17 (q, ^3J = 8.0, OCH_2), 6.00 (s, 2H, NCH_2), 7.3–8.5 (m, 4H, aromatic H)
6d	Me COPh	60 159–160	1.53 (t, ^3J = 8.0, CH_3), 3.58 (q, ^3J = 8.0, 2H, 2-CH_2), 7.07 (s, 2H, NCH_2), 7.5–8.5 (m, 9H, aromatic H)
6e	Me CN	57 153–154	1.58 (t, ^3J = 8.0, 3H, CH_3), 3.63 (q, ^3J = 8.0 2H, 2-CH_2), 7.6–8.6 (m, 6H, NCH_2 and aromatic H)
6f	Me $C_6H_4NO_2$-*p*	55 167–168	1.31 (t, ^3J = 8.0, 3H, CH_3), 3.32 (q, ^3J = 8.0, 2H, 2-CH_2), 7.3–8.5 (m, 10H, NCH_2 and aromatic H)

94–96°C. ^{1}H NMR ($CDCl_3$): δ = 2.07 (s, 3H, CH_3), 2.23 (d, ^3J(P, H) = 8.0 Hz, 3H, 1-CH_3), 3.62 (t, ^3J(H, H) = 6.8 Hz, 2H, 6-H), 4.24 (dt, ^3J(H, H) = 6.8 Hz, ^4J(P, H) unresolved, 2H, 5-H), 7.1–7.6 (m, 4H, aromatic H). Anal. Calcd. for $C_{13}H_{14}NSP$ (217.3): C, 63.14; H, 5.71; N, 5.66. Found: C, 61.20; H, 5.20; N, 5.30.

1-Dichlorophosphino-3-ethoxycarbonyl-1,3-azaphospholo[5,1-b]thiazoline **4**. As above from **2a**, 2 equivalents PCl_3 and 5 equivalents Et_3N after 12 hours at ambient temperature, 40% yield, yellow syrupy mass. ^{1}H NMR ($CDCl_3$): δ = 1.38 (t, ^3J(H, H) = 8.0 Hz, 3H, CH_3), 3.93 (t, ^3J(H, H) = 8.0 Hz, 2H, 6-H), 4.37 (q, ^3J(H, H) = 8.0 Hz, 2H, OCH_2), 4.82 (tdd, ^3J(H, H) = 8.0, ^4J(P, H) = 1.7, ^5J(P, H) = 1.0 Hz, 2H, 5-H).

2,3-Dialkylbenzothiazolium Bromides (6)

A solution of 0.04 mol of 2-alkylbenzothiazole and 0.04 mol alkyl bromide in 45 mL of absolute ethanol is refluxed for 6 days followed by evaporation of the solvent and maceration of the residue with diethyl ether, when a cream colored solid is obtained (Table 4).

1,3-Azaphospholo[5,1-b]benzothiazoles (7)

To the well-stirred suspension of 0.02 mol of benzothiazolium bromide **6** in 50 mL acetonitrile 0.08 mol triethylamine is added slowly when an intense yellow color develops indicating the formation of the benzothiazolium *N*-ylide. Then 0.02 mol PCl_3 in 15 mL acetonitrile are slowly added maintaining the temperature of the reaction mixture at 0–5°C. An exothermic reaction sets in and the reaction mixture turns orange. It is allowed slowly to come to ambient temperature. After stirring for 12 hours or heating to 60–65°C for 5 hours in case of **6d,e**, the solvent is removed from the reaction mixture under reduced pressure and the residue extracted three times with 70 mL diethyl ether. The combined ether solutions are concentrated to about one fourth of their volume and left in the refrigerator when cream colored crystals are formed. The ether extract obtained from **6e** is completely dried and the residue is stirred two times with 30 mL hexane for 6 hours. The hexane insoluble solid is found to be **7e**. For NMR spectra see Tables 2 and 3.

3-Ethoxycarbonyl-1-methyl-1,3-azaphospholo-[5,1-b]benzothiazole **7c**. *57% yield, mp 99–100°C.*

3-Benzoyl-1-methyl-1,3-azaphospholo[5,1-b]benzothiazole **7d**. 24% yield, mp 146–147°C.

3-Cyano-1-methyl-1,3-azaphospholo[5,1-b]benzothiazole **7e**. 18% yield, mp 106–108°C.

Benzothiazolium N-(dichlorophosphino) Ylides (8)

2-Ethylbenzothiazolium N-(dichlorophosphino) cyanomethylide **8e**. On evaporation of the solvent from the hexane solution obtained above from the preparation of **7e**, an orange oily liquid is left that could not be crystallized, 24% yield. ^{1}H NMR ($CDCl_3$): δ = 1.38 (t, ^3J(H, H) = 8.0 Hz, 3H, CH_3), 3.13 (q, ^3J(H, H) = 8.0 Hz, 2H, CH_2), 7.2–8.1 (m, 4H, aromatic H). For ^{31}P NMR see Table 1.

2-Ethylbenzothiazolium N-(dichlorophosphino) p-nitrobenzylide **8f**. The ether extract obtained from the attempted preparation of **7f** is completely dried followed by extraction of the residue two times with 30 mL hexane. Removal of the solvent from the extract affords an orange liquid, 21% yield. ^{1}H NMR ($CDCl_3$): δ = 1.40 (t, ^3J(H, H) = 8.0 Hz, 3H, CH_3), 3.08 (q, ^3J(H, H) = 8.0 Hz, 2H, CH_2), 7.2–8.3 (m, 8H, aromatic H). For ^{31}P NMR see Table 1.

ACKNOWLEDGMENT

This work was supported by the D.S.T., New Delhi, and by the Volkswagen Foundation, Germany.

REFERENCES

[1] A. Schmidpeter, K. Karaghiosoff, Heterophospholes, in M. Regitz, O. J. Scherer (eds): *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme Verlag, Stuttgart, p. 258 (1990).
[2] G. Märkl, λ^3-Phosphinines, in M. Regitz, O. J. Scherer (eds.): *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme Verlag, Stuttgart, p. 220 (1990).
[3] R. K. Bansal, K. Karaghiosoff, Neelima Gupta, A. Schmidpeter, C. Spindler, *Chem. Ber., 124*, 1991, 475.
[4] A. Schmidpeter, M. Thiele, *Angew. Chem., 103*, 1991, 333; *Angew. Chem. Int. Ed. Engl., 30*, 1991, 308.
[5] For recent patents in this field see: H. Hartmann, M. Weber, Ger. (East) DD 268,700; DD 268,701; DD 268,702; DD 268,703 (June 7, 1989) (*Chem. Abstr., 112* (1990) P 98839j; P 98840c; P 98841d; P 98842e).
[6] P. K. Claus, Azomethinylide, in Houben-Weyl: *Methoden der Organischen Chemie*, Vol. E14b, Thieme Verlag, Stuttgart, p. 74 (1990).
[7] H. W. Wanzlick, H. J. Kleiner, *Angew. Chem., 75*, 1963, 1204.
[8] I. Zugravescu, M. Petrovanu: *N-Ylid Chemistry*, McGraw-Hill, New York, pp. 126 and 157 (1976).
[9] J. R. Owen, *Tetrahedron Lett.*, 1969, 2709.
[10] R. K. Bansal, R. Mahnot, D. C. Sharma, K. Karaghiosoff, *Synthesis*, 1992, 267.
[11] H. Wenker, *J. Am. Chem. Soc., 57*, 1935, 1079.

[12] R. K. Bansal, unpublished observation.
[13] J. Luber, A. Schmidpeter, *J. Chem. Soc., Chem. Commun.*, 1976, 887.
[14] J. H. Weinmaier, G. Brunnhuber, A. Schmidpeter, *Chem. Ber., 113*, 1980, 2278.
[15] K. Karaghiosoff, C. Cleve, A. Schmidpeter, *Phosphorus Sulfur, 28*, 1986, 289.
[16] I. Ciocoiu, C. H. Budeanu, I. Zugravescu, *Bull. Inst. Politek. Iasi, Sect. 2, 24*, 1978, 109; *Chem. Abstr., 92* (1980) 41819s.
[17] S. Lochschmidt, A. Schmidpeter, *Phosphorus Sulfur, 29*, 1986, 73.
[18] Triphenylphosphonium dichlorophosphino benzylide Ph_3P^+—PhC^-—PCl_2 on addition of excess $AlCl_3$ analogously gives the *C*-phosphonio-*P*-chlorophosphaalkene Ph_3P^+—PhC=PClAlCl_4^-: A. Schmidpeter, G. Jochem, unpublished results; cf *Tetrahedron Lett. 33*, 1992, 471.
[19] A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, *Zh. Obshch. Khim., 59*, 1989, 719; *J. Gen. Chem. USSR, 59*, 1989, 636; A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, A. M. Pinchuk, *Zh. Obshch. Khim., 60*, 1990, 1752; *J. Gen. Chem. USSR, 60*, 1990, 1563.
[20] R. K. Bansal, C. Spindler, Neelima Gupta, V. Kabra, K. Karaghiosoff, A. Schmidpeter, *Heteroatom Chem.*, in press.
[21] J. March, *Advanced Organic Chemistry*, John Wiley and Sons, New York, 3rd. ed. 1985, p. 218.