1,4,2-Diazaphospholothiazoles and -pyridines by a Hantzsch-Type Condensation Using Chloromethyldichlorophosphane

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Received November 17, 1994

Key Words: Anellated azaphospholes / Hantzsch-type [3 + 2] cyclocondensation / Chloromethyldichlorophosphane / Regioselectivity / ^{31}P-, ^{1}H-, ^{13}C-NMR spectra

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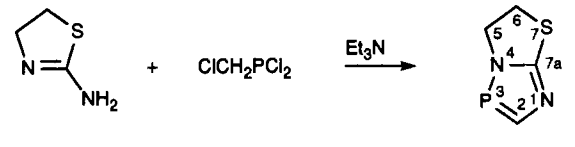
The [3 + 2] cyclocondensation of 2-amino-1,3-thiazoline, 2-aminopyridines, 2- and 4-aminopyrimidines, 2-aminopyrazine, and 2-aminoquinoline with chloromethyldichlorophosphane in the presence of triethylamine yields regiospecifically 5,6-dihydrothiazolo[2,3-e][1,4,2]diazaphosphole (**3**), 1,4,2-diazaphospholo[4,5-*a*]pyridines (**12**), 1,4,2-diazaphospholo[4,5-*a*]pyrimidines (**15**), 1,4,2-diazaphospholo[4,5-e]pyrimidine (**17**), 1,4,2-diazaphospholo[4,5-*a*]pyrazine (**19**), and [1,4,2]diazaphospholo[4,5-*a*]quinoline (**22**), respectively. Using 2-amino-1,3-thiazole (**4**) and 2-aminobenzothiazoles **8**, we obtained mixtures of the 1,5- and 4,5-anellated 1,4,2-diazaphospholes **5/6**, **9a/10a** and **9b/10b**, while in the case of the methyl derivative **8c** only the [1,4,2]diazaphospholo[5,4-*b*][1,3]benzothiazole **10c** was formed. In the reaction of 2-aminothiazole and 2-aminopyrazine with chloromethyldichlorophosphane the bis(diazaphospholo)-substituted chloromethylphosphanes **7** and **20** could be detected. The new anellated 1,4,2-diazaphospholes are colorless to pale yellow crystalline moisture-sensitive solids.

Many azaphospholes have been synthesized in the last 25 years, mostly by [4 + 1] cyclocondensation reactions or by [3 + 2] cycloaddition reactions[1,2]. These syntheses often parallel those of azoles: When carboxylic acid derivatives are used for condensation to yield azoles, phosphorus trihalides or trisamides take their part in azaphosphole syntheses. When acetylenes are employed in the synthesis of azoles involving cycloaddition, phosphaalkynes are used instead for azaphospholes. A further route to azaphospholes by a condensation reaction may be understood as a parallel of the Hantzsch thiazole synthesis, with the part of the α-haloketone played by chloromethyldichlorophosphane. Starting from thioamides, we thus obtained 1,3,4-thiazaphospholes and starting from amidines, we obtained 1,4,2-diazaphospholes. Only this route does give access to representatives containing an unsubstituted carbon ring member adjacent to phosphorus (i.e. in the 5- or 3-position)[3]. The present paper describes the synthesis of anellated 1,4,2-diazaphospholes starting from heterocycles containing an amidine system, i.e. 2-aminopyridines and 2-amino-1,3-thiazoles, and in one case a 2-aminothiazoline.

Syntheses

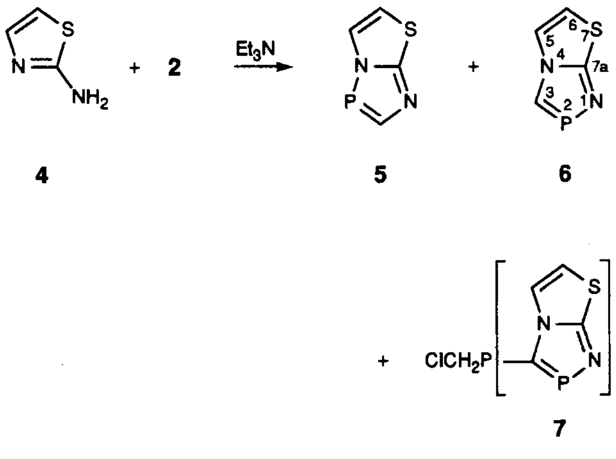
The condensation of equimolar amounts of 2-amino-1,3-thiazoline with chloromethyldichlorophosphane in the presence of a threefold molar amount of triethylamine in acetonitrile proceeds regiospecifically to give 5,6-dihydro[1,3]-thiazolo[2,3-*e*][1,4,2]diazaphosphole (**3**).



1 **2** **3**

When 2-amino-1,3-thiazole or 2-amino-1,3-benzothiazoles are used for the cyclocondensation, mixtures of isomeric anellated 1,4,2-diazaphospholes, resulting from both orientations of the CP unit in **2** with respect to the NCN fragment in the aminothiazole, are generally obtained.

Thus, the reaction of 2-amino-1,3-thiazole with **2** leads to thiazolo[2,3-*e*][1,4,2]diazaphosphole **5** (70%) and thiazolo[3,2-*d*]-1,4,2-diazaphosphole (**6**) (10%). The bis(diazaphospholyl)phosphane **7**, δ^{31}P(CDCl$_3$) = 254.3 (σ^2-P),



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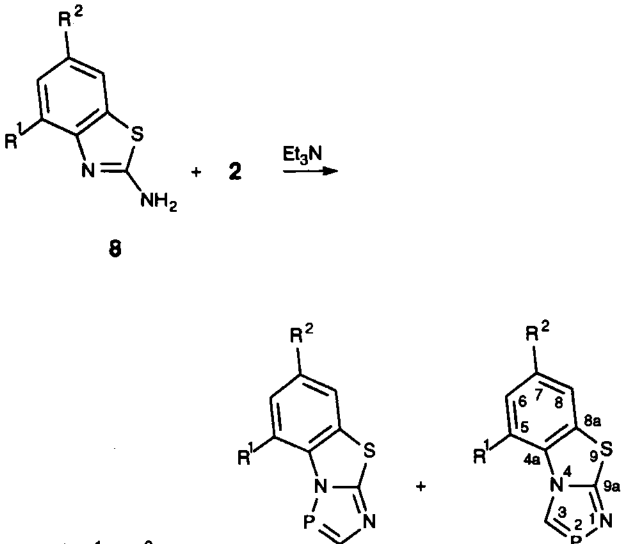
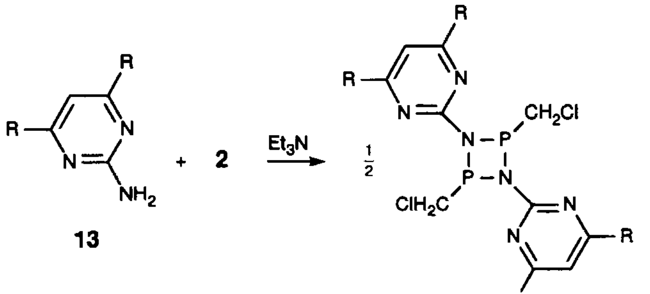
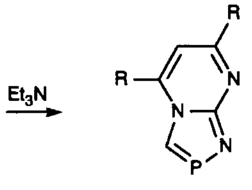


	R¹	R²				
a	H	H	**9a**	23%	**10a**	77%
b	H	OMe	**9b**	33%	**10b**	67%
c	Me	H	**9c**	-	**10c**	100%



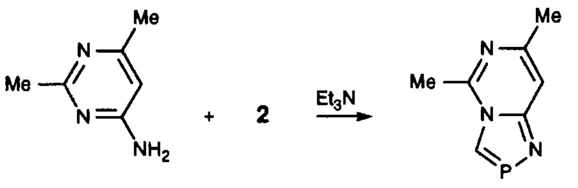
	R
a	H
b	Me

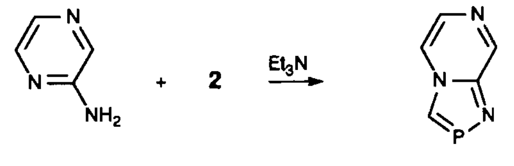


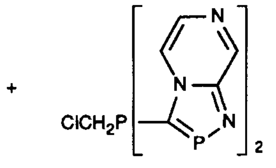
-47.5 (σ^3-P), $^2J_{PP} = 11.3$ Hz, formed by reaction of **6** with excess **2**, was detected as a minor side product (up to 5%) by ^{31}P-NMR spectroscopy.

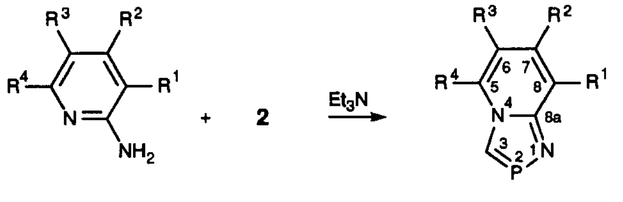
The regioselectivity of the condensation of 2-aminobenzothiazoles with **2** is remarkably influenced by the substituents on the benzene ring. Thus, the reaction of 2-aminobenzothiazole **8a** as well as its 6-methoxy derivative **8b** with **2** gives each a mixture of the isomeric [1,4,2]diazaphospholo[5,1-*b*][1,3]benzothiazole **9** and -[5,4-*b*][1,3]benzothiazole **10**, the latter being the major product in both cases. The reaction of 2-amino-4-methylbenzothiazole with **2**, however, is regiospecific again although the orientation of **2** in this case is reversed as compared to that in its reaction with 2-aminothiazoline.

The cyclocondensation of 2-aminopyridines and related aminoazines with **2** yields regiospecifically 4,5-anellated 1,4,2-diazaphospholes. Starting from the 2-aminopyridines

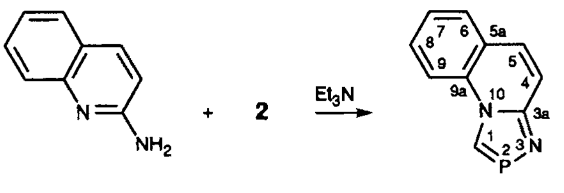








	R¹	R²	R³	R⁴
a	H	H	H	H
b	Me	H	H	H
c	H	Me	H	H
d	H	H	Me	H
e	H	H	H	Me



11a–e, we obtained the 1,4,2-diazaphospholo[4,5-*a*]pyridines **12a–e**[4].

2-Aminopyrimidines **13** react analogously to form 1,4,2-diazaphospholo[4,5-*a*]pyrimidines **15**. In the case of **13b**, the diazadiphosphetidine **14b** was identified as an intermediate by its ^{31}P-NMR signal ($\delta = 188.9$) and by the chracteristic pattern of the ^{1}H-NMR signal of the *P*-methylene protons ($\delta = 4.72$, X part of $AA'X_2X'_2$ spin system, $N = 12.9$ Hz)[3], when the reaction was performed with less than three equivalents of Et_3N. Upon addition of more Et_3N **14b** was converted completely to **15b**. This observation suggests, that in all cases the formation of the 1,5-anellated 1,4,2-diazaphospholopyridines by this method proceeds via diazadiphosphetidines in analogy to **14b**.

The reaction of 4-aminopyrimidine **16**, 2-aminopyrazine **18**, and 2-aminoquinoline **21** with **2** under similar conditions gives 1,4,2-diazaphospholo[4,5-*c*]pyrimidine (**17**), -[4,5-*a*]pyrazine (**19**), and -[4,5-*a*]quinoline (**20**), respectively. In the synthesis of **19** the bis(diazaphospholyl)-substituted phosphane **20**, $\delta^{31}P(CDCl_3) = 239.5$ (σ^2-P), -56.4 (σ^3-P), $^2J_{PP} = 9.2$ Hz, was identified as a minor side product (yield up to 8%).

Table 1. ^{31}P-, ^{1}H-, and ^{13}C-NMR data for the thiazolodiazaphospholes **3**, **5**, and **6** (in $CDCl_3$, coupling constants J in Hz)

		3[a]	**5**	**6**
δ^{31}P		194.0	191.9	223.8
δ^1H	2,3-H	9.06[b]	9.28	8.32
	^2J(P,H)	54.8	56.8	31.2
	^6J(2-H,6-H)	0.4	0.9	
	5-H	4.33	6.95	6.38
	$^{3,4}J$(P,H)		3.6	1.3
	^3J(5-H,6-H)	7.3	5.0	4.8
	6-H	3.80	6.18	6.06
	$^{4,5}J$(P,H)		1.4	2.1
δ^{13}C	C-2,3	178.2	177.2	151.1
	^1J(P,C)	54.0	57.9	66.7
	^1J(C,H)	183.7	182.8	183.2
	C-5	49.0	118.9	119.3
	^2J(P,C)	10.5	8.1	
	^1J(C,H)	147.7	195.6	195.6
	^2J(C,H)	2.7	6.6	5.9
	C-6	35.4	115.3	114.8
	^3J(P,C)		27.8	
	^1J(C,H)	146.0	194.5	193.4
	^2J(C,H)	2.7	9.9	9.5
	C-7a	163.2	164.5	155.6
	^2J(P,C)	3.5		18.3

[a] J(H,H) were obtained from a J-resolved 2D ^{1}H-NMR spectrum. – [b] ^5J(2-H,5-H) = 0.4 Hz.

The isolated anellated 1,4,2-diazaphospholes (see Table 5) are colorless to pale yellow crystalline solids having a characteristic odor; they are soluble in benzene, diethyl ether and polar aprotic organic solvents. They are highly sensitive to moisture[4] but can be stored at ambient temperature under dry argon.

Table 2. ^{31}P-, ^{1}H-, and ^{13}C-NMR data for the diazaphospholo benzothiazoles **9** and **10** (in $CDCl_3$, coupling constants J in Hz)

		9a	**9b**	**10a**	**10b**	**10c**[a]
δ^{31}P		184.7	184.2	223.4	221.7	220.4
δ^1H	2,3-H	9.35	9.33	9.24	9.18	9.53
	^2J(P,H)	56.6	57.0	30.8	30.6	32.0
	5-H	7.68[b]	7.61	7.61	7.48	
	^3J(5-H,6-H)	7.8	8.9	7.8	8.8	
	^4J(5-H,7-H)	1.3		1.5		
	6-H	7.31	6.96	7.31	6.97	7.17[c]
	^3J(6-H,7-H)	7.8		7.6		7.5
	^4J(6-H,8-H)	1.5	2.5	1.2	2.4	1.7
	7-H	7.38		7.37		7.20
	^3J(7-H,8-H)	7.8		7.8		7.5
	8-H	7.65	7.17	7.55	7.13	7.46[d]
	CH_3		3.84		3.84	2.78
δ^{13}C	C-2,3	177.1	176.5	149.8	149.5	153.3
	^1J(P,C)	56.9	56.8	66.8	67.4	64.0
	C-4a	137.1	131.2	131.4	126.0	131.1
	^2J(P,C)	7.6	7.6			
	C-5	115.0	116.2	113.5	114.6	124.8
	$^{3,4}J$(P,C)	3.8	3.7		0.9	1.4
	C-6	126.4	114.0	126.3	113.7	129.0
	C-7	125.6	157.7	125.8	157.8	125.2
	^6J(P,C)			1.4	1.5	1.4
	C-8	124.0	108.0	124.4	108.4	122.0
	^5J(P,C)			1.4	1.5	1.4
	C-8a	131.1	132.0	130.7	132.3	130.9
	C-9a	159.6	159.2	153.5	152.9	154.0
	^2J(P,C)	3.3	2.7	19.4	18.9	18.5
	CH_3		55.9		55.9	19.8

[a] C-3: ^1J(C,H) = 183.4 Hz; C-4a: ^3J(C,6-H) = ^3J(C,8-H) = 7.6, ^3J(C,CH_3) = 4.2 Hz; C-5: ^2J(C,CH_3) = 6.2, ^3J(C,H) = 8.1 Hz; C-6: ^1J(C,H) = 161.1, ^3J(C,8-H) = 8.5, ^3J(C,CH_3) = 5.2 Hz; C-7: ^1J(C,H) = 162.3 Hz; C-8: ^1J(C,H) = 161.1, ^3J(C,H) = 8.1 Hz; C-8a: ^3J(C,H) = 9.5 Hz; C-9a: ^3J(C,H) = 10.4 Hz. – [b] ^4J(P,H) = 0.7, ^5J(5-H,8-H) = 0.4 Hz. – [c] ^6J(P,H) = 0.8 Hz. – [d] ^6J(P,H) = 0.5 Hz.

Regioselectivity

As mentioned in the introduction, the present method parallels the synthesis of anellated imidazoles involving [3 + 2] cyclocondensation of heterocycles like 2-aminopyridines with α-halocarbonyl compounds[5]. The regiochemistry of the two condensations may therefore also be compared. 2-Aminopyridines and 2-amino-1,3-thiazoles have been shown to exist predominantly in the amino form[6]. Although they exhibit ambident nucleophilic reactivity their cyclocondensation with α-halocarbonyl compounds has been reported to proceed regiospecifically, the carbon atom of the carbonyl end being bound to the nitrogen atom of the amino group[7]. In the proposed mechanism of the reaction, the first step involves quaternization of the ring nitrogen, which is followed by cyclization of the resulting 2-aminocycloiminium salt[5]. The initial formation of the cycloiminium salt is supported by the isolation of the corresponding salts in the reactions of 2-amino-1,3-thiazole[8] and 2-aminopyridine[9] with ω-bromoacetophenone.

Table 3. ^{31}P- and ^{1}H-NMR data for the diazaphospholo pyridines **12**, pyrimidines **15** and **17**, pyrazine **19**, and quinoline **22** (in $CDCl_3$, coupling constants *J* in Hz)

		12a[a]	**12b**	**12c**	**12d**	**12e**[b]	**15a**	**15b**	**17**	**19**	**22**[b,c]
δ^{31}P		195.0	195.6	198.1	197.6	194.8	197.0	198.0	204.5	207.9	194.3
δ^{1}H	3-H	8.87	8.90	8.85	8.77	8.85	8.94	8.86	8.90	8.97	9.49
	^{2}J(P,H)	29.8	29.3	29.8	30.3	30.4	28.1	28.6	30.1	29.5	29.6
	^{5}J(3-H,8-H)	1.2		0.9		0.9			1.1		0.9
	5-H	8.14	8.05	8.06	7.92		8.51[d]			8.13[e]	
	^{3}J(5-H,6-H)	6.8	6.8	7.0			6.8			4.6	
	6-H	6.73	6.67	6.63		6.67[f]	6.90	6.72[e]		7.84	
	^{3}J(6-H,7-H)	6.8	6.8			6.8	4.1				
	^{4}J(6-H,8-H)	1.2		1.7		1.4					
	7-H	7.17	7.02		7.02	7.20[g]	8.68				7.45
	^{3}J(7-H,8-H)	9.2			9.3	9.1					9.6
	8-H	7.52		7.35[h]	7.41	7.52[i]			7.20	9.03	7.44
	CH_3		2.59	2.36	2.22	2.60		2.68	2.85		
								2.58	2.50		

[a] From ref.[4]. – [b] *J*(H,H) were obtained from a *J*-resolved 2D ^{1}H-NMR spectrum. – [c] The data in the fields of 3-H, 7-H, and 8-H in the Table correspond to those of 1-H, 5-H, and 4-H in **22**, respectively; ^{6}J(1-H,5-H) = 0.4, ^{5}J(5-H,9-H) = 1.0 Hz; 6-H: δ = 7.68, ^{3}J(6-H,7-H) = 7.9, ^{4}J(6-H,8-H) = 1.5, ^{5}J(6-H,9-H) = 0.5 Hz; 7-H: δ = 7.37, ^{3}J(7-H,8-H) = 7.3, ^{4}J(7-H,9-H) = 1.0 Hz; 8-H: δ = 7.55, ^{3}J(8-H,9-H) = 8.5 Hz; 9-H: δ = 7.86. – [d] ^{4}J(P,H) = 1.0 Hz, ^{4}J(5-H,7-H) = 2.2 Hz. – [e] ^{5}J(5-H,8-H) = 1.2 Hz. – [f] ^{4}J(6-H, CH_3) = 0.9 Hz. – [g] ^{5}J(7-H,CH_3) = 0.4 Hz. – [h] ^{4}J(8-H,CH_3) = 1.2 Hz. – [i] ^{6}J(8-H,CH_3) = 0.6 Hz.

Table 4. ^{13}C-NMR data for the diazaphospholopyridines **12**, pyrimidines **15** and **17**, pyrazine **19**, and quinoline **22** (in $CDCl_3$, coupling constants *J* in Hz)

	12a[a]	**12b**	**12c**	**12d**	**12e**	**15b**	**17**	**19**	**22**[b]
C-3	151.2	152.0	150.8	150.7	147.3	146.3	147.1	151.1	149.3
^{1}J(P,C)	65.5	65.6	65.6	65.4	63.8	63.8	64.5	71.1	64.3
^{1}J(C,H)	181.9	180.9	181.9	181.0	181.3	182.7		182.6	180.3
^{3}J(C,H)[c]	1.7		2.1					0.9	
C-5	127.8	126.0	126.8	125.6	136.1	143.8	147.0	120.7[d]	133.2
^{3}J(P,C)	2.3		2.5		2.6	3.5	2.9		1.7
^{1}J(C,H)	181.9	184.6	183.6	181.0				186.5	
C-6	112.7	112.8	115.4	122.5	112.3	109.2		129.6	123.2
^{4}J(P,C)	1.5		1.3		1.9	1.9		1.2	0.7
^{1}J(C,H)	166.9	166.3	164.9		167.4	167.5		186.8	
^{2}J(C,H)	3.4, 1.7		4.9	6.6[e]	1.1			5.5	
^{3}J(C,H)	8.9		7.9	6.6	8.1, 4.8[e]			13.1	
C-7	126.5	125.0	137.7	129.7	126.4	161.5	150.1		128.1
^{1}J(C,H)	163.3	162.4		162.1	164.9				165.0
^{2}J(C,H)	1.2		6.7[e]			6.4[e], 2.3			
^{3}J(C,H)	7.8	6.6, 4.6[e]	6.7	7.6, 4.7[e]					5.6
C-8	119.3	128.9	117.8	118.5	117.1[f]		109.1	144.9[g]	118.9
^{3}J(P,C)	8.6	9.1	7.6	8.5	9.2		7.3	10.2	7.4
^{1}J(C,H)	167.2		165.4	167.8	168.3			189.4	170.0
^{3}J(C,H)	8.4		5.7, 5.7[e]		7.3			11.3	
C-8a	152.1	152.8	152.6	151.3	153.1	153.6	152.8	146.8	151.2
^{2}J(P,C)	14.2	15.3	13.7	14.2	14.0	16.1	13.9	14.2	14.3
^{3}J(C,H)	13.2, 8.5		8.8, 4.9			9.1			
CH_3		18.1	20.9	17.6	19.5	24.4, 19.5	22.7, 21.8		
^{1}J(C,H)		128.1	127.6	128.0	129.0	128.0, 130.0			
^{3}J(C,H)		6.1	5.1, 3.8	3.8	4.0	1.7, 3.8			

[a] From ref.[4]. – [b] The data in the fields of C-3, C-5, C-6, C-7, C-8, and C-8a in the Table correspond to those of C-1, C-9a, C-5a, C-4, and C-3a in **22**. C-6: δ = 129.0, ^{1}J(C,H) = 160.9, ^{2}J(C,H) = 1.5, ^{3}J(C,H) = 7.9, 3.3 Hz; C-7: δ = 125.4, ^{6}J(P,C) = 1.0, ^{1}J(C,H) = 163.5, ^{3}J(C,H) = 7.9 Hz; C-8: δ = 129.3, ^{1}J(C,H) = 163.6, ^{3}J(C,H) = 8.5 Hz; C-9: δ = 116.4, ^{1}J(C,H) = 152.5, ^{3}J(C,H) = 7.7, ^{4}J(C,H) = 2.5, 1.3, 0.6 Hz. – [c] Coupling to 5-H. – [d] ^{2}J(C,H) = 12.8 Hz. – [e] Coupling to methyl protons. – [f] ^{2}J(C,H) = 0.9 Hz. – [g] ^{4}J(C,H) = 1.7 Hz.

Table 5. Yields, physical and analytical data for **3**, **9**, **10**, **12**, **15**, **17**, **19**, and **22**

	Colour m.p. [°C]	Yield [%]	Formula M	Calcd. Found C	H	N
3	colorless 47-48	53	$C_4H_5N_2PS$ 144.13	33.33 33.46	3.50 3.81	19.44 19.11
9a+10a	pale yellow 63-64	28	$C_8H_5N_2PS$ 192.17	50.00 49.50	2.62 3.55	14.57 14.18
9b+10b	pale yellow 94-95	38	$C_9H_7N_2POS$ 222.20	48.65 47.34	3.18 3.65	12.61 11.43
10c	pale yellow 116-117	16	$C_9H_7N_2PS$ 206.20	52.42 52.42	3.42 3.96	13.59 12.67
12b	colorless 83-85	62	$C_7H_7N_2P$ 150.12	56.01 56.31	4.70 4.91	18.66 17.80
12c	colorless 112-114	73	$C_7H_7N_2P$ 150.12	56.01 55.84	4.70 5.53	18.66 18.47
12d	colorless 94-95	67	$C_7H_7N_2P$ 150.12	56.01 56.03	4.70 4.57	18.66 18.27
12e	colorless 89-90	66	$C_7H_7N_2P$ 150.12	56.01 56.11	4.70 5.40	18.66 18.54
15b	pale yellow 161-162	41	$C_7H_8N_3P$ 165.13	50.91 50.87	4.88 4.54	25.45 25.21
17	pale yellow 153-155	24	$C_7H_8N_3P$ 165.13	50.91 50.81	4.88 5.57	25.45 25.28
19	pale yellow 135-137	47	$C_5H_4N_3P$ 137.08	43.81 43.66	2.94 3.02	30.65 30.48
22	pale yellow 82-83	76	$C_{10}H_7N_2P$ 186.15	64.52 64.28	3.79 4.09	15.05 15.16

Although the condensation of **2** and the condensation of α-halo carbonyl compounds can well be compared to each other in principle, the two reagents differ in the order of reactivity of their two electrophilic sites. In **2** the phosphorus atom is expected to be more electrophilic and to react first. The regiochemistry will thus depend on the relative reactivity of the amino group and the ring nitrogen atom towards this phosphorus atom. 2-Aminopyridines **11** as well as aminodiazines **13**, **16**, and **18** obviously attack **2** exclusively through their amino group. This step is confirmed by the observed formation of intermediate **14b**. In the case of thiazole and benzothiazole the ring nitrogen competes effectively for the phosphorus leading to a mixture of both isomers. Similar differences in the behavior of 2-aminopyridine and 2-aminothiazole have been observed before[10] and are explained on the basis of semiempirical CNDO/2 calculations, which reveal that the charge density at the ring nitrogen of 2-amino-1,3-thiazole is much higher than that at the ring nitrogen of 2-aminopyridine[11]. That no isomer **9c** is formed may be explained by the steric effect of the 4-methyl substituent which makes the adjacent ring nitrogen less easily accessible.

In the aminothiazoline **1** the two-coordinate nitrogen atom is no longer part of an aromatic system and proves to be more nucleophilic than the amino group nitrogen. It leads therefore selectively to the isomer **3**.

NMR Spectroscopy

The new anellated 1,4,2-diazaphospholes exhibit ^{31}P chemical shifts between $\delta = 180$ and 225 (Tables 1−3), i.e. in a range characteristic of $\delta^{31}P$ of azaphospholes with the dicoordinate phosphorus bound to one nitrogen and one carbon atom[12]. For the 1,5-anellated diazaphospholes **5** and **9** $\delta^{31}P$ appears at lower field as compared to the 4,5-anellated isomers **6** and **10** ($\Delta\delta \approx 35$). A similar dependency of $\delta^{31}P$ on the position of anellation was observed for 1,2-(4,5-) and 1,5-anellated 1,3-azaphospholes[2].

The assignment of the ^1H- and ^{13}C-NMR signals (Tables 1−4) is based on $^1H,^1H$ and $^1H,^{13}C$ shift-correlated 2D NMR spectra. In the case of the pair of isomers **9b/10b** the data assignment for the individual isomers results from a ^1H-NOESY experiment, showing a cross-peak between the signals of the proton at the diazaphosphole ring and 5-H only for **10b**.

Characteristic of the proton of the $-P{=}CH-$ moiety is a low-field NMR signal ($\delta = 8.3-9.5$) and a large two-bond coupling to phosphorus[13,15]. Remarkably, $^2J_{PH}$ of the 1,5-anellated diazaphospholes **3**, **5**, and **9** (54−57 Hz) is almost twice the coupling constant observed for the 4,5-anellated heterocycles (28−32 Hz). In both cases the values are of the same order of magnitude as found for monocyclic 1*H*- and 4*H*-1,4,2-diazaphospholes, respectively[3].

The ^{13}C-NMR signal for the *P*-bound carbon atom in the 4,5-anellated diazaphospholes ($\delta = 146-156$) is observed at higher field as compared to that of **3**, **5**, and **9** ($\delta = 176-178$), and P,C coupling to the carbon atoms of the diazaphosphole ring is larger for the former ($^1J_{PC} = 63-71$ Hz, $^2J_{PC} = 13-20$ Hz) than for the latter ($^1J_{PC} = 54-58$ Hz, $^2J_{PC} \leq 3.5$ Hz). Both couplings are in the order of magnitude generally encountered for azaphospholes[14,15].

Table 6. Mass spectral data for the diazaphospholo pyridines **12** (EI, 70 eV, 24 °C)

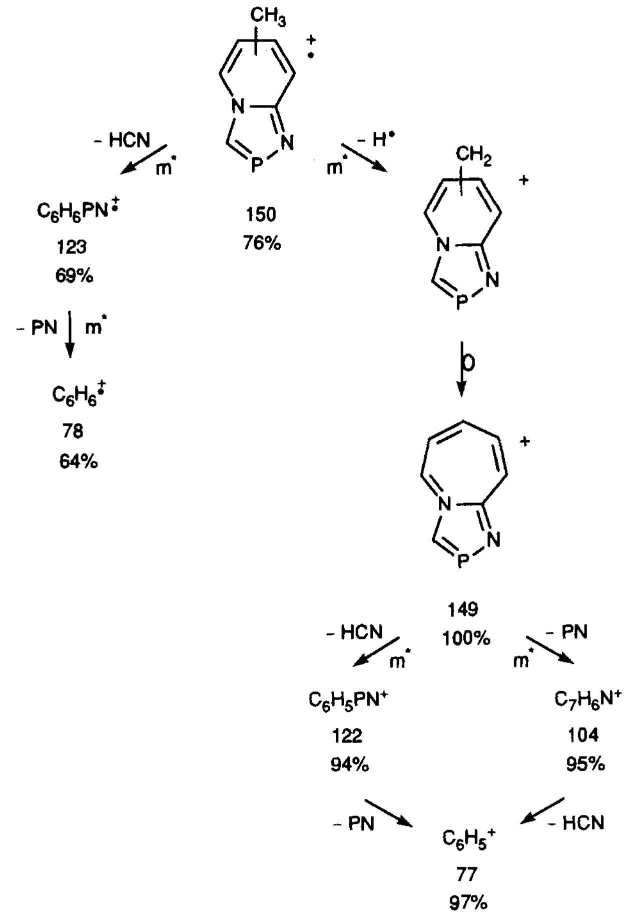
12a	137 (42) $[M+1]^+$, 136 (100) $[M]^+$, 109 (95), 91 (36), 70 (56), 64 (54)
12c	151 (90) $[M+1]^+$, 150 (76) $[M]^+$, 149 (100) $[M-1]^+$, 135 (12), 123 (69), 122 (94), 105 (84), 104 (95), 78 (64), 77 (97)
12d	151 (100) $[M+1]^+$, 150 (66) $[M]^+$, 149 (93) $[M-1]^+$, 135 (7), 123 (87), 122 (92), 105 (57), 104 (60), 78 (72), 77 (90)
12e	151 (48) $[M+1]^+$, 150 (100) $[M]^+$, 149 (53) $[M-1]^+$, 135 (4), 123 (61), 122 (75), 105 (30), 104 (52), 78 (55), 77 (31)

In the diazaphospholo-benzothiazoles **10** long-range P,C coupling to the carbon atoms of the benzo ring over 4, 5, and even 6 bonds is detected.

Mass Spectrometry

The mass spectral fragmentation of **12a, c–e** (Table 6) resembles that of imidazo[1,2-*a*]pyridines[10]. The representatives having a methyl substituent on the pyridine ring undergo fragmentation by two parallel pathways as shown in Scheme 1 (the relative intensities given in Scheme 1 are those observed for **12c**). In the preferred mode, the methyl substituent of the molecular ion loses a hydrogen atom to form the [M − 1] ion which is expected to rearrange to the anellated azepinium ion[10]. The latter fragments further either by splitting off HCN or P≡N. Alternatively, the molecular ion loses HCN followed by the loss of P≡N. As expected, in the case of **12a**, the [M − 1] ion as well as the ions resulting from its subsequent fragmentation are not observed.

Scheme 1



We thank the *DAAD (Deutscher Akademischer Austauschdienst)* for a fellowship to N. G. and the *Volkswagen Stiftung* for financial support.

Experimental

All reactions were carried out in flame-dried glas flasks under dry oxygen-free argon using the Schlenk technique. Acetonitrile and diethyl ether were dried by conventional methods. Triethylamine was distilled from Na/benzophenone under argon. 2-Aminothiazoline, 2-aminothiazole, 2-aminobenzothiazoles, 2-aminopyridines, 2- and 4-aminopyrimidines, 2-aminopyrazine, and 2-aminoquinoline were commercially available and used without further purification. – Melting points were determined with a Lintström apparatus and are uncorrected. – ^{31}P NMR: Jeol GSX-270 at 109.7 MHz; ^1H and ^{13}C NMR: Jeol EX-400 at 399.8 MHz and 100.5 MHz, respectively; Chemical shifts refer to external 85% H_3PO_4 (^{31}P) and internal TMS (^1H, ^{13}C). – MS: Varian MS CH 7.

Chloromethyldichlorophosphane[3,16]: In a three-necked round-bottomed 0.5-l flask equipped with a reflux condenser, a mechanical stirrer, and a thermometer, chloromethyldichlorophosphane oxide (502.0 g, 306.8 ml, 3.0 ml) and P_4S_{10} (160.0 g, 0.36 mol) were heated to reflux temp. (180–190 °C) with stirring. After the temperature of the reaction mixture had reached 160 °C, P_4S_{10} dissolved and a clear dark brown solution formed. After refluxing for 6 h the reaction mixture was allowed to cool to ambient temp. overnight. Vacuum distillation yielded pure chloromethyldichlorophosphane sulfide (b.p. 90–105 °C/10–40 mbar) as a colorless oily liquid. Yield: 347.6 g (68.1%); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 74.7$ (s). To 154.6 g (0.843 mol) of chloromethyldichlorophosphane sulfide thus obtained, placed in a three-necked round-bottomed 0.5-l flask equipped with a 250 ml pressure-equalizing dropping funnel, a mechanical stirrer, and a thermometer, 170.5 g (210.0 ml, 0.843 mol) of tributylphosphane was added dropwise with stirring and cooling (ice bath) at such a rate that the temperature of the reaction mixture remained below 5 °C (about 1.5 h). The reaction mixture was allowed to warm to ambient temp. and chloromethyldichlorophosphane was condensed under reduced pressure (10^{-3} mbar) into a flask cooled with liquid nitrogen. Distillation of the crude product at normal pressure yielded pure chloromethyldichlorophosphane (b.p. 125–129 °C). Yield: 99.5 g (78%); $^{31}P\{^1H\}$ NMR: $\delta =$ 158.1 (s).

General Procedure for the Preparation of **3**, **5/6**, **9/10**, **12**, **15**, **17**, **19**, **22**: To a cooled (0–5 °C) and well-stirred solution of the 2-aminoheterocyclic compound (40 mmol) in acetonitrile (100 ml) chloromethyldichlorophosphane (6.05 g, 30 mmol) and subsequently a solution of triethylamine (12.14 g, 0.12 mmol) in acetonitrile (5 ml) were added dropwise. The reaction mixture turned pale yellow and a colorless precipitate of triethylammonium chloride formed. The reaction mixture was allowed to warm up to ambient temp. and stirring was continued for further 12 h (in the case of **3** and **9/10** for 3 h) until the reaction was complete (^{31}P NMR). The ammonium salt was separated by filtration and the solvent was removed in vacuo. The pale yellow solid residue was extracted with diethyl ether (2 × 100 ml). The ethereal extracts were combined and the solvent was evaporated to yield the azaphospholes as microcrystalline solids. ^{31}P-, ^{1}H-, and ^{13}C-NMR data are compiled in Tables 1−4. For yields, melting points and analytical data see Table 5, for mass spectral data see Table 6.

The reaction of **4** and **8a, b** with chloromethyldichlorophosphane by the procedure described above yielded mixtures of **5/6**, **9a/10a**, and **9b/10b**, respectively. From these mixtures the compounds were characterized by ^{31}P-, ^{1}H-, and ^{13}C-NMR spectroscopy.

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