Synthesis and some properties of phosphorus-substituted azomethines

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A series of phosphorus(III)-substituted azomethines and enamines were synthesized by the reaction of lithium salts of aldimines and ketimines with derivatives of phosphorus(III) acids. Some properties of the compounds synthesized were studied.

Key words: azomethines, aldimines, ketimines, phosphorus(111), phosphorylation, ambident systems.

We have shown previously¹ that the reaction of PCl_3 with lithium salts of azomethines results in C-dichlorophosphinoaldimines and -ketimines. Based on the latter, we have synthesized C-phosphorus(III)-substituted azomethines containing various substituents at the P atom and started a study of their properties. However, dichlorophosphino-substituted imines are highly unstable and cannot be widely used in syntheses of phosphorylated azomethines and enamines.

In the present work, we studied the reaction of lithium salts of aldimines and ketimines with phosphorus(III) acid chlorides for the purpose of elaborating a general method for synthesizing C-phosphory-lated azomethines and enamines. Lithium salts of azomethines are known to be ambident systems, and their phosphorylation, like the phosphorylation of enolates of carbonyl compounds,^{2,3} can occur either at the C or at the N atom to give C- or N-substituted azomethines and enamines. In view of this, it was

interesting to study the dependence of the direction of the reactions of lithium derivatives of azomethines with phosphorus acid chlorides on various factors: structure of the starting azomethine, nature of substituents at the P atom, and the character of the solvent used.

Azomethines were metallated with lithium diethylamide in hexane for 0.5-1.5 h at 0 °C.



The phosphorylation of the resulting lithium salts was carried out at -70 °C. The reaction was monitored by IR spectroscopy. It was found that the reaction of lithium derivatives of aldimines with chlorophosphines in non-polar solvents affords exclusively α -C-phosphorus-substituted azomethines (2) in 80% yield. It is note-



Scheme 1

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Scheme 2





3: $R^1 = H$, $R^2 = Me(a)$; $R^1 = Et$, $R^2 = Pr(b)$

Table 1. Physicochemical constants and elemental analysis data for α -C-phosphorus(III)-substituted azomethines (2-4)

Com- pound	Com-Yield B.p./°C n_D^{20} ³¹ P NMR, pound (%) (p/Torr) δ v_i		IR, v/cm ⁻¹	$\begin{array}{ccc} IR, & A:B\\ v/cm^{-1} & (\%) \end{array}$			Found (%) Calculated			
		[M.p./°C]					С	Н	Р	
2a	80	115-117 (1)	1.5100	5.8,	1630 (C=C);	46 : 54	69.62	11.17	12.25	C ₁₄ H ₂₈ NP
				-2.0,	1680 (C=N);		69.50	11.60	12.80	
				-24.0	3300 (NH)					
2b	75	73-75(1)	1.4862	3.0,	1630 (C=C);	38:62	<u>63.00</u>	11.54	<u>13.42</u>	$C_{12}H_{26}NP$
				-2.4,	1680 (C=N);		62.30	11.25	13.40	
				-26.0	3300 (NH)					
2c	65	82-84 (1)	1.4893	21.3.	1630 (C=C);	5:95	<u>68.73</u>	12.04	13.25	$C_{13}H_{28}NP$
				-14.1	3300 (NH)		68.12	12.22	13.53	
2d	55	87-90 (1)	1.4882	22.39,	1630 (C=C);	24:76	<u>69.33</u>	12.25	11.54	$C_{14}H_{30}NP$
				16.38,	1670 (C=N);		69.14	12.35	11.76	
				-12.32	3350 (NH)					
2e	60	92-95 (1)	1.4684	33.0	1670 (C=N)	100:0	<u>69.73</u>	12.43	11.85	C14H30NP
							69.14	12.35	11.76	
2f	35	[62]		24.0,	1610 (C=C);	20:80	<u>69.53</u>	12.30	11.59	$C_{14}H_{30}NP$
				16.8,	1660 (C=N);		69.14	12.35	11.76	
				-8.0	3200 (NH)					
2g	30	140-142 (0.04)	1.5034	59.9	1665 (C=N)	100:0	<u>69.98</u>	<u>12.77</u>	11.64	C ₁₆ H ₃₄ NP
							70.80	12.62	11.41	
2h	69	[34]		11.0	1660 (C=N)	100:0	<u>76.66</u>	8.42	<u>9.25</u>	$C_{20}H_{26}NP$
							77.17	8.36	9.97	
3a	50	103-105 (1)	1.5123	-10.4,	1615 (C=C);	39:61	<u>69.90</u>	11.75	12.23	C15H30NP
				0.0,	1665 (C=N);		70.59	11.76	12.16	
				-23.2	3350 (NH)					
3 b	57	118-120 (0.012)	1.5114	13.8	1670 (C=N)	100:0	<u>73.37</u>	12.12	10.01	$C_{19}H_{38}NP$
							73.31	12.22	9.97	
4a	60	115-117 (0.015)	1.5242	-20.2	1615 (C=C);	0:100	72.63	<u>11.46</u>	10.99	C ₁₇ H ₃₂ NP
					3400 (NH)		72.60	11.39	11.03	
4b	65	123-125 (0.015)	1.5239	-12.9	1605 (C=C);	0:100	73.15	11.53	<u>10.51</u>	$C_{18}H_{34}NP$
					3370 (NH)		73.06	11.77	10.34	
4c	58	110-112 (1.5)	1.5039	-21.3	1610 (C=C);	0:100	<u>70,28</u>	11.65	12.04	C ₁₅ H ₃₀ NP
					3350(NH)		70.59	11.76	12.16	
4d	49	102-104 (1)	1.5043	-8.5	1620 (C=C);	0:100	<u>70.99</u>	11.90	<u>11.43</u>	$C_{16}H_{32}NP$
					3400 (NH)		71.38	11.90	11.52	

worthy that for $\mathbb{R}^1 = H$ (2a-d, f), prototropic azomethine-enamine rearrangement readily occurs to give a mixture of a C-phosphorylated azomethine (A) and a C-phosphorus-containing enamine (B) (Scheme 1) as the reaction product. The reaction of dialkylchlorophosphines with a series of ketimines under similar conditions also results in *C*-substituted azomethines and enamines (Scheme 2).

The composition and structure of the resulting compounds were confirmed by ^{31}P , ^{1}H , and ^{13}C NMR and

Com- pound		¹³ C-{ ¹ H} NMR							¹ H NMR					
	C=N-		P- <u>C</u> H-C=		Me3C CH-N-			-CH=N-			CHC≠			
•	δ	² J _{PC}	δ	1JPC	õ		δ	³ Ј _{РН}	³ Ј _{НН}	δ	² <i>J</i> _{PH}			
2a	159.00	14.05	30.74	23.20		55.49	7.61	2.42	5.85	2.32	2.34			
2b	156.54	14.82	31.74	23.73	58.00		7.53	2.20	6.00	2.32	2.80			
2c	157.85	14.90	32.58	24.08	57.65		7.63	1.80	5.50	2.30	2.53			
2d	161.51	7.35	44.70	14.00	56.12	_	7.62	2.00						
2e	157.34	8.52	38.65	23.70	56.25	_	7.66	2.34	5.44	2.45	4.28			
2f	162.26	17.50	43.32	33.20	55.56	-	7.75	2.00	_					
3a	164.30	10.62	38.41	25.04		51.46		~~		2.30	3.60			

Table 2. Spectroscopic parameters of compounds 2a-f, 3a (phosphorus-substituted azomethines)

IR spectra as well as by elemental analyses (Tables 1-3). According to ³¹P, ¹H, and ¹³C NMR spectroscopic data, the enamine form B of compounds 2a-d,f and 3a,b is a mixture of Z- and E-isomers, the latter of which predominates (see Tables 1-3). The cyclic compounds (4a-d) have the structure of C-phosphorylated enamines. The ³¹P NMR spectra of compounds 2, 3, and 4 contain signals at δ from 33 to -26 depending on the size of the substituent at the P atom and on the structure of the starting azomethine. Based on the ratio of integral intensities of signals of the azomethine and enamine forms in the 1H and 13C NMR spectra, the signals in the ³¹P NMR spectra were assigned to the azomethine form A or to the E- and Z-isomers of the enamine form B. For example, the signals corresponding to the C atom of the azomethine group (CH=N) of form A in the ¹³C NMR spectra of compounds 2 and 3 are observed as a doublet at δ 156-167 with ${}^{2}J_{PC}$ = 7-14 Hz. For the enamine form of compounds 2a-d,f, 3a,b, and 4a-d (E- and Z-isomers), the C atom adjacent to the N atom is displayed as two doublets at δ 141–161 (=CH–N) with ²J_{PC} = 56–57 Hz (*E*);

 ${}^{2}J_{PC} = 19$ Hz (Z), while the C atom adjacent to the P atom (P--CH=) manifests itself as two doublets at δ 82--104 with ${}^{1}J_{PC} = 6.6-6.8$ Hz (E) and 10 Hz (Z). The 1 H NMR spectra display signals of the azomethine group proton at δ 7.5-7.7 (CH=N), while the vinylic protons (Z- and E-isomers) in the enamine form manifest themselves as two groups of signals at δ 4.0-6.0 (P--CH=) and two groups of signals at δ 6.0-6.5 (=CH--N). The assignment of signals to the E- and Z-isomers was based on the coupling constants of the vicinal protons: ${}^{3}J_{HH} = 14-20$ Hz (E-isomer); ${}^{3}J_{HH} = 6-12$ Hz (Z-isomer).

The IR spectra of compounds 2-4 contain an intense absorption band at $1630-1605 \text{ cm}^{-1}$, which corresponds to vibrations of the C=C bond, and an intense band at $1680-1660 \text{ cm}^{-1}$ corresponding to the C=N bond, as well as a medium-intensity band at 3300 cm^{-1} from the vibrations of the NH group. The ratio of tautomeric forms A and B is determined by the structure of the azomethine and the substituents at the P atom (see Table 1). It should be noted that neither prolonged storage of C-substituted compounds (2a-d,f,3a,b) nor

Table 3. Spectroscopic parameters of compounds 2-4 (phosphorus-substituted enamines)

Com-	Isomer	Content		130	2-{ ¹ H} N	MR				¹ H N	MR*			
pound		(%)	P	CH=	=CH-	-NH	Me <u>3C</u> ,		P-CH	===	(CH-N		
-			δ	JPC	δ	² J _{PC}	δ	δ	$^{2}J_{\rm PH}$	$^{3}J_{\rm HH}$	δ	${}^{3}J_{\rm PH}$	³ Ј _{НН}	
2a	E	69	83.80	6.80	147.50	57.51		4.23	6.67	14.73	6.56	8.34	12.33	
	Ζ	31	86.42	10.02	148.10	19.35		4.07	6.22	9.24	6.57	17.17	12.15	
2b	Ē	73	88.75	6.60	148.28	56.60	51.69	4.36	6.40	15.60	6.59	8.56	12.25	
	Ζ	27	89.23	10.00	147.50	19.20	51.58	4.08	6.35	8.20	6.62	17.60	12.00	
2c	Ε	93	95.93	9.80	142.35	68.30	50.44				6.56	12.30	12.30	
	Z	7	96.46	11.32	144.39	23.70	50.12	_		—	6.62	17.85	12.10	
2đ	Ē	93	102.37	11.70	141.77	61.90	50.89	-	—		6.66	12.50	12.50	
	Z	7	100.08	13.50	143.67	19.60	50.53	_	_		6.78	18.05	12.35	
2f	Ē	93	89.83	6.78	147.82	62.28	54.80	4.64	6.50	14.23	6.58	11.70	11.70	
	Z	7	90.32	10.93	148.54	21.85	54.75	4.42	5.74	9.30	6.69	13.92	10.21	
3a	Ē	91	82.60	6.00	153.17	32.50		4.03	6.80			-		
	Z	9	88.46	6.62	156.96	19.40		3.98	6.40					
4a	Z	100	98.71	7.31	153.35	21.30		-					-	
4b	Z	100	97.99	9.92	160.39	25.90					~~~			
4c	ī	100	104.61	6.80	155.29	10.70	51.53	—	-		-			
4d	Ĩ	100	104.59	9.40	161.52	24.62	51.78	-	—		-		-	

* The NH group signals in the ¹H NMR spectrum are at δ 3.7-4.6.



the presence of acid or basic catalysts affect the attained ratio of isomeric compounds A and B, which seems to indicate that the formation of equilibrium mixtures of isomers takes place.

The direction of phosphorylation of Li-salts of azomethines does not depend on steric hindrance in the molecules of azomethine and phosphorylating reagent. For example, the phosphorylation of sterically hindered *N*-tert-butylisobutylideneamine with chlorodi(tert-butyl)phosphine also occurs exclusively at the C atom, although in this case the yield of the phosphorylated azomethine 2g does not exceed 30%.

To reveal the effect of the nature of substituent at the P atom in acid halide on the direction of the reactions in question and to synthesize C-substituted azomethines containing various substituents at the P atom, we studied the reaction of Li-salts of azomethines with phosphonous and phosphorous acid chlorides. It was shown that the reaction in hexane at -70 °C gives exclusively C-phosphorylation products. For example, the reaction of lithium salts of aldimines with phosphonous and phosphorous chlorides resulted in the corresponding phosphinamides (5a-c) and phosphonamides (5d-j) in 30-70% yields (Scheme 3).

The composition and structure of the resulting compounds were confirmed by elemental analyses and by ¹H, ³¹P, ¹³C NMR and IR spectroscopy (Tables 4-6). The spectroscopic data confirmed that all of the compounds 5, except for 5c,g,j, like analogous compounds containing alkyl substituents at the P atom, are mixtures of two tautomeric forms, *i.e.*, an azomethine form A and an enamine form B. Phosphinites and phosphonites 5 are unstable, and their prolonged storage or repeated distillation result in polycondensation in the case of diethylamide substituents at the P atom (compounds 5a-d, i) or partial disproportionation in the case of alkoxy substituents (compounds 5e-h), to give trialkyl phosphites. It should be stressed that the formation of N-isomers was not observed in any of the reactions studied.

Thus, we have shown that neither increase in the steric hindrance in the azomethine molecule, nor changes of the size and nature of the substituents at the P atom, affect the direction of the reaction. In all cases, only C-phosphorus-substituted azomethines are formed (or mixtures of phosphorylated azomethines and enamines).

Since the direction of reactions involving ambident systems is known to depend on the polarity and solvating ability of the solvent used, we studied the possibility of formation of N-phosphorylated enamines by carrying out the reactions of lithium salts of azomethines with phosphonous and phosporous chlorides in solvents of different polarity, as well as in the presence of tetramethylethylenediamine (TMEDA). The reactions of anions of the type 1 with chlorodiisopropylphosphine or dibutylphosphorochloride in dimethoxyethane (DME) or in the presence of TMEDA were found to result in mixtures of C- and N-phosphorylated isomeric com-

Scheme 4





Com- pound	Yield (%)	B.p./°C (p/Torr)	<i>n</i> _D ²⁰	³¹ Ρ NMR, δ	IR, v/cm ⁻¹	<u>Fou</u> Calc	nd culated (%)	Molecular formula
						C	Н	P	
5a	49	118-120 (1.5)	1.4795	61.8, 63.8, 54.6	1680, 1620, 3350	<u>63.29</u> 63.93	<u>11.85</u> 11.89	<u>12.74</u> 12.70	C ₁₃ H ₂₉ N ₂ P
5b	30	115—117 (1)	1.4905	63.8, 64.4, 53.8	1670, 1620, 3350	<u>66.36</u> 66.66	<u>11,19</u> 11.48	<u>11.43</u> 11.48	C ₁₅ H ₃₁ N ₂ P
5c	57	73-74 (0.011)	1.4671	88.5	1660	<u>66.45</u> 66.18	<u>12.08</u> 12.13	<u>11.36</u> 11.40	C ₁₅ H ₃₃ N ₂ P
5d	30	135-137 (1)	1.4930	135.0, 137.3, 130.5	1650, 1620, 3300	<u>60.75</u> 61.75	<u>10.62</u> 10.66	<u>11.40</u> 11.39	$C_{14}H_{29}N_2OP$
5e	40	125—127 (2)	1.4735	175.9. 168.9	1675, 1625, 3320	<u>60.92</u> 61.09	<u>10.78</u> 10.91	<u>11.32</u> 11.27	C ₁₄ H ₃₀ NO ₂ P
5f	51	125-126 (1)	1.4800	175.2, 170.5	1680, 1630, 3350	<u>63.56</u> 63.81	<u>10.46</u> 10.63	<u>10.46</u> 10.29	C ₁₆ H ₃₂ NO ₂ P
5g	60	88-90 (0.012)	1.4342	186.5	1660	<u>63.50</u> 63.37	$\frac{11.25}{11.22}$	<u>10.18</u> 10.23	$C_{16}H_{34}NO_2P$
5h	50	115-117 (1)	1.4645	171.5, 165.9	1675, 1630, 3350	<u>61.35</u> 61.54	<u>10.25</u> 10.26	<u>11.28</u> 11.36	C ₁₄ H ₂₈ NO ₂ P
51	70	Decomposes	-	85.0, 88.7, 83.2	1670, 1625, 33000		-		C ₁₅ H ₃₄ N ₃ P
5j	50	73-76 (0.015)	1.4748	111.8	1655	<u>63.15</u> 63.79	<u>11.82</u> 11.96	<u>10.37</u> 10.30	C ₁₆ H ₃₆ N ₃ P

Table 4. Physicochemical constants, IR and ³¹P NMR spectroscopic and elemental analysis data for compounds 5a--j

Table 5. ¹³C-{¹H} spectroscopic data (δ , J/Hz) for phosphonites and phosphinites 5

Com-	Phosphorus-substituted azomethines									
pound	-CI	I=N-	_	P <u>C</u>	= 1	Me <u>3C,</u>				
	δ	$^{2}J_{PC}$		5	$^{1}J_{1}$	PC	δ			
5 a	153.26	12.2	0 43	43.94		.50	55.91			
5c	162.61	6.1	0 43	.22	28	.80	56.39			
5e	151.94	9.4	0 34	.75	32	.60	51.01			
5g	160.94	5.2	0 44	.65	14	.50	56.48			
5j	163.36	3.9	030	.11	7	.42	56.63			
Com-	PI	nosphor	us-subs	titute	d en	amines	5			
pound	Isomer	P0	CH=	=(сн-	NH-	Me <u>3C</u> ,			
-	(percen- tage (%))	ô	'J _{PC}	 δ		² <i>J</i> _{PC}	δ			
5a	E (88) Z (12)	92.58 94.08	13.00 14.85	148 146	3.29 5.40	56.25 15.00	50.87 50.38			
5e	E (100)	96.70	13.40	149	9.16	51.70	50.20			

pounds (2, 5, 6), in which the content of the latter was 30-60%, depending on the phosphorylating reagent and the solvent used (Scheme 4).

The structure of the resulting N-isomers (**6a,b**) was confirmed by IR as well as ${}^{31}P$ and ${}^{13}C$ NMR spectra (cf. Ref. 1). The IR spectra of the compounds obtained

contain, in addition to the C=N absorption band at $1680-1670 \text{ cm}^{-1}$ corresponding to the azomethine form of C-isomers, an absorption band at $1640-1630 \text{ cm}^{-1}$ characteristic of N-isomers. The ¹³C NMR spectra of a mixture of compounds **6a,b** contain signals corresponding to the C=C double bond in N-phosphorylated enamines (**6**) at $\delta 120-130 \text{ with } {}^{2}J_{PC} = 5-8 \text{ Hz} (=CH-N)$ and at $\delta 130-145 \text{ with } {}^{3}J_{PC} = 0-1 \text{ Hz} (Me_2C=)$. It is noteworthy that the ratio of C- and N-isomers was not changed by distillation or upon prolonged storage of the reaction mixture at ~20 °C in the presence of catalysts (R₂PCI; CdI₂), which suggests that these compounds are formed under kinetic control conditions and have sufficiently high energetic barrier for interconversions.

We also studied the reactions of the α -C-phosphorus(III)substituted azomethines synthesized with some electrophilic and nucleophilic reagents. To synthesize new α -C-phosphorus(IV)substituted derivatives of azomethines, we carried out oxidation, addition of sulfur, and alkylation of compounds of the type 2 and 5 and obtained a series of compounds with a four-coordinate P atom in the molecule (Scheme 5).

The physicochemical parameters and data from elemental analyses, IR, ³¹P, and ¹³C NMR spectra are presented in Tables 6 and 7. It should be noted that compounds 7-10 incorporating a four-coordinate P atom in the molecule and a reactive H atom at the α -C



* Compound 7d exists only in the azomethine form.

atom are C-phosphorus(IV)-substituted enamines, whereas C-phosphorus(IV)-substituted azomethine are only formed in trace amounts in these cases.

The study of the reactions of α -C-phosphorus(III)substituted azomethine derivatives of the type 2-5 with alkyl, phenyl, diethylamido, or alkoxy groups at the P atom with some nucleophilic reagents (alcohol, amine) made it possible to estimate the comparative stability of P-C bonds in the above compounds as a function of the type of substituent at the P atom. For example, the reaction of phosphonites of the type 5e-g with butanol for 1 day at ~20 °C or with diethylamine for 5 h at 100 °C results in complete cleavage of the P-C bonds to give the corresponding phosphites (Scheme 6).



 $X = BuO, Et_2N; R^1, R^2 = H, Me$

In the case of α -C-phosphorus(11)substituted azomethines with alkyl or phenyl groups at the P atom, the cleavage of the P-C bond in the presence of water, alcohols, or amines does not occur even on heating for 10 h at 100-110 °C. Phosphonamides 5i,j are stable against the action of diethylamine when heated for 10 h at 110-120 °C. It was shown that the reaction of phosphonamide **5j** with two equivalents of butanol at 110-120 °C for 2 h mostly occurs as the cleavage of the P-N bonds to give phosphonite **5g** as the main product (Scheme 7).



Thus, the direction and ease of the reaction of α -C-phosphorus(III)substituted azomethine derivatives with

Table 6. ¹H NMR spectroscopic data (δ , J/Hz) for compounds 5

Com-		Phos	phoru	s-subst	ituted	azomet	nines		
pound			CH=	N—		P-CH	IC=		
		δ	³ Ј _{РН}	3 ј	нн	δ	$^{2}J_{\rm PH}$		
5a		7.57	3.5	0 6	.40	2.20	2.60		
5b	7.60		2.0	0.					
5c	7.40		5.0	0 6	.00	2.20	2.35		
Com-		Phe	osphor	us-sub	stitute	d enami	nes		
pound	Iso-		P-CF	I=	=CH-N -NH				
	mer	δ	²J _{PH}	³ J _{HH}	δ	${}^{3}J_{\rm PH}$	³ <i>J</i> _{HH} δ		
5a	E	4.50	6.35	15.80	6.50	11.20	12.13 4.50		
	Ζ	4.38	6.20	8.70	6.65	16.90	12.00 4.50		
5b	Ē	4.80	6.55	15.35	7.00	11.54	12.35 4.80		
	Z	4.45	6.30	8.95	7.10	17.25	12.15 4.80		

Com- pound	Yield (%)	B.p./°C (<i>p</i> /Torr) [M.p., °C]	IR, v/cm ⁻¹	³¹ P NMR, δ	<u>Found</u> (%) Calculated			Molecular formula
					C	Н	P	
7 a	65	136-140 (2.5 • 10 ⁻²)	1640,	62.1	<u>57.95</u>	10.40	12.35	C ₁₂ H ₂₆ NSP
			3300		58.14	10.53	12.55	
7 b	85	[65]	1630,	68.6	<u>59.90</u>	<u>10.93</u>	<u>11.77</u>	C ₁₃ H ₂₈ NSP
			3330		59.77	10.73	11.88	
7c	81	[5759]	1635,	68.3	<u>61,23</u>	<u>11.05</u>	11.25	$C_{14}H_{30}NSP$
			3350		61.09	10.91	11.27	
7d	73	$123 - 125 (1.2 \cdot 10^{-2})$	1650	74.5	<u>60.95</u>	<u>10.70</u>	<u>11.10</u>	C ₁₄ H ₃₀ NSP
					61.09	10.91	11.27	
82	91	$106 - 108 (3 \cdot 10^{-2})$	1685,	61.5	64.56	11.47	11.96	C ₁₄ H ₃₀ NOP
			1210		64.86	11.58	11.96	
8b	90	$103 - 105 (1.1 \cdot 10^{-2})$	1650,	57.7	63.48	11.34	12.35	C13H28NOP
			3220		63.67	11.42	12.56	
9a	76	[107-109]	1640.	35.4	43.74	8.37	8.85	C13H29NPI
		. ,	3350		43.69	8.12	8.68	13 17
9b	98	[113-115]	1635.	40.1	45.09	8.23	8.36	C14H21NPI
	,,,	(3350		45.28	8.36	8.36	1451
90	80	[116]	1630	39.9	46.57	8.50	8.29	C ₁₄ H ₂₂ NPI
		[]	3340		46.75	8.57	8.05	
9d	57	[130]	1640.	40.6	57.95	9.85	8.78	C17HasNPO2CI
~ 4	2.	[]	3370		58 04	9.96	8 82	- 1735 2
10	60	$98 - 100 (1.8 \cdot 10^{-2})$	1635	53.0	56.00	10.22	13.43	CuH ₂ NO ₂ P
10	50	Jo-100 (1.0 10)	3340		56.65	10.30	13.30	011112411021

Table 7. Physicochemical constants, IR and ³¹P NMR spectroscopic and elemental analysis data for compounds 7-10

Table 8. ${}^{13}C-{}^{1}H$ NMR spectroscopic data (δ , J/Hz) for compounds 7–9

Com-	P-	-C=	=0	Me <u>3C</u> ,		
pound	δ	¹ J _{PC}	δ	$^{2}J_{PC}$	δ	
7a	66.34	70.40	150.81	14.20	51.13	
7b	85.46	87.20	146.13	19.50	51.30	
7c	92.42	82.80	145.69	20.10	51.32	
8a	74.55	113.90	148.27	8.40	50.26	
8b	74.05	112.12	146.68	8.02	50.20	
9b	66.59	98.60	144.68	22.05	51.82	
9c	80.73	93.60	146.43	19.60	52.98	

nucleophilic reagents is determined by the type of the nucleophile and substituents at the P atom.

Experimental

All reactions were conducted in a dry argon atmosphere and in dry solvents. ³¹P NMR spectra were recorded on a Varian FT-80A instrument using H_3PO_4 as the external standard. ¹H NMR spectra were recorded on a Tesla BS-497 spectrometer for solutions in deuteriobenzene relative to SiMe₄. IR spectra were obtained on an IKS-22 spectrophotometer using a NaCl cell, the layer thickness was 0.1 mm.

N-tert-Butyl-(2-diisopropylphosphino)ethylideneamine 2b. A solution of butyllithium (0.1 mol) in hexane was added at 20 °C to a solution of diethylamine (7.3 g, 0.1 mol) in hexane (70 mL). This resulted in precipitation of lithium diethylamide. The reaction mixture was stirred for 30 min, and then a solution of *tert*-butylethylideneamine (9.9 g, 0.1 mol) in hexane (15 mL) was added at 0 °C. After the lithium diethylamide had dissolved completely, the reaction mixture was cooled to -70 °C, and a solution of chlorodiisopropylphosphine (15.2 g, 0.1 mol) in hexane (20 mL) was added. The temperature was gradually increased to 20 °C, and the reaction mixture was stirred for an additional 2 h. The precipitate of lithium chloride was separated by centrifugation, the solvent was distilled off, and the residue was distilled *in vacuo*. The yield of compound **2b** was 16 g (75%).

Compounds 2a,c-h, 3a,b, 4a-d, and 5a-j were obtained in a similar way. The physicochemical constants and ³¹P. ¹H, and ¹³C NMR and IR spectroscopic data are presented in Tables 1--6.

Reaction of lithium derivatives of azomethines with Pri2PCl or (BuO)₂PCl in DME solution. A solution of a lithium azomethine derivative obtained from lithium diethylamide (2.37 g, 0.03 mol) and an azomethine (0.03 mol) in hexane according to the procedure described above for compound 2b was kept in vacuo to a constant pressure in order to remove the solvent. After that, dry DME (50 mL) was added, and then chlorodiisopropylphosphine (4.5 g, 0.03 mol) or dibutylphosphorochloride (6.4 g, 0.03 mol) was added at -70 °C. The temperature of the reaction mixture was increased to 20 °C, and stirring was continued for an additional 1 h. The solvent was distilled off, and the residue was distilled in vacuo to give a mixture of C-phosphorus-substituted azomethines and the corresponding N-phosphorylated enamines 6a,b. For compounds **2e**, **6a**, C: N = 70: 30, b.p. 68-70 °C (2 \cdot 10⁻²). IR, v/cm⁻¹: 1630 (C=C). ³¹P NMR, δ P 65.5; ¹³C{¹H} = 127.51 (=C-N), ${}^{2}J_{PC} = 8.7 \text{ Hz}; 131.01 \text{ (Me}_{2}\underline{C}), 55.13 \text{ (CMe}_{3}), {}^{2}J_{PC} = 13.6 \text{ Hz};$ for compounds 5g, 6b, C: N = 40:60; b.p. 110-115 °C (1 Torr). IR: 1640 (C=C). ³¹P NMR: 8P 146.

(2-tert-Butylaminovinyl)diisopropylphosphine sulfide (7a). Elementary sulfur (0.8 g, 0.025 mol) was added in portions with stirring to a solution of *N*-tert-butyl-(2-diisopropylphosphino)ethylideneamine **2b** (5.37 g, 0.025 g) in diethyl ether (20 mL). Self-heating of the reaction mixture to 35 °C was observed. The mixture was heated for 30 min and cooled to 20 °C. The ether was distilled off, and the residue was distilled in vacuo to give 4.5 g (75%) of compound 7a. Compounds 7b-d were obtained in a similar way. The physicochemical constants as well as spectroscopic and elemental analysis data are presented in Tables 7 and 8.

Diisopropyl(1-methyl-2-tert-butylaminovinyl)phosphine oxide (8b). N-tert-butyl-(2-diisopropylphosphino)ethylideneamine 2b (5.7 g, 0.025 mol) was oxidized with air oxygen at 20 °C for 3 days. The resulting viscous oil was distilled in vacuo. The yield of compound 8b was 6.1 g (90%).

Compound **8a** was obtained similarly. The physicochemical constants, spectroscopic parameters, and data of elemental analyses are presented in Tables 7 and 8.

Diisopropyl(methyl)-2-(*N*-terr-butylaminovinyl)phosphonium iodide (9a). A solution of freshly distilled methyl iodide (1.32 g, 0.0093 mol) in ether (5 mL) was added at 20 °C to a solution of *N*-tert-butyl-(2-diisopropylphosphino)ethylideneamine 2b (2.1 g, 0.093 mol) in ether (20 mL). This caused the temperature of the reaction mixture to increase to 35 °C. The phosphonium salt that formed precipitated as a yellow oil. The reaction mixture was stirred for an additional 2 h, the ether was decanted, and the phosphonium salt was reprecipitated from dichloromethane with pentane, yield 2.71 g (76%). Compounds 9b-d were obtained similarly. The physicochemical constants, elemental analysis data, as well as IR and ³¹P and ¹³C NMR spectroscopic data for phosphonium salts 9 are presented in Tables 7 and 8.

Synthesis of phosphinate 10. An excess of methyl iodide was added to a solution of compound 5e (12.2 g, 0.04 mol) in ether (30 mL), and the reaction mixture was refluxed for 3 h. The temperature of the reaction mixture was adjusted to 20 °C, the solvent was distilled off, and the residue was distilled *in vacuo*. The yield of compound 10 was 6.26 g (60%). The physico-

chemical constants, elemental analysis data, as well as IR spectroscopic data for compound 10 are presented in Table 7.

Reaction of phosphonites 5e,g with *n*-butanol. *n*-Butanol (2.2 g, 0.03 mol) was added to a phosphorus-substituted azomethine (0.03 mol). The reaction mixture was stirred at 20 °C for 24 h. Distillation gave tributyl phosphite⁴ and the corresponding azomethine in 80% yield.

Reaction of phosphonite 5g with diethylamine. A mixture of compound **5g** (6.1 g, 0.02 mol) and diethylamine (1.46 g, 0.02 mol) was heated for 5 h at 100 °C. The mixture was distilled to give 1.8 g (72%) of *N-tert*-butylisobutylideneamine and 2.3 g (70%) of dibutyldiethylphosphoramide.⁴

Reaction of phosphonite 5j with *n*-butanol. *n*-Butanol (3.0 g, 0.04 mol) was added to compound **5j** (6.0 g, 0.02 mol). The reaction mixture was stirred for 2 h at 110-120 °C and kept overnight at 20 °C. Distillation gave 4.5 g (75%) of compound **5g**.

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