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Phosphirenes and Azaphosphetines: X. 1-Aza-2-phosphabutadienes in Electrophilic Addition of P-Haloiminophosphines to 1-Alkoxyacetylenes: Synthesis and Chemical Properties*

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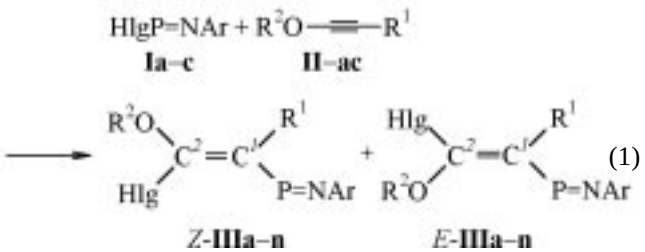
Abstract—Reaction of P-chloro-, P-bromo-, and P-iodoiminophosphines with 1-alkoxyacetylenes proceeds as an electrophilic regioselective addition across the triple bond with conservation of biscoordinate phosphorus providing 1-aza-2-phosphabutadienes. The stereochemistry of the resulting product depends on the character of the alkyl and alkoxy substituents in the alkyne, on the halogen in the iminophosphine, on the polarity of the solvent and the concentration of reagents. The azaphosphabutadienes easily enter into [2+1]-cycloaddition with the second equiv of alkyne to furnish P-alkenyl-substituted phosphirenes. They also add hydrogen halides to the P=N bond forming acyl halides of alkenylphosphonous acids amides. The possibility of Z/E-isomerization of the alkenyl moiety in all the compounds synthesized was investigated.

λ^3-Iminophosphines due to a specific position of n_p and π-orbitals of the P=N moiety may possess dual reactivity with respect to alkynes: the cycloaddition may occur both along [2+1] and [2+2] route [1, 2]. A presence of a halogen substituent at the biscoordinate phosphorus atom extends the possible range of reactions by the electrophilic addition to the triple bond of alkyne. In the preceding communications we described the reactions of P-chloroiminophosphine (**Ia**) with alkoxyacetylenes [3], alkyldialkylaminoacetylenes [4], and of P-bromoiminophosphine (**Ib**) with alkyldialkylaminoacetylenes [5]. In all cases the reaction gave rise to products of electrophilic addition across the triple bond with conservation of the biscoordinate phosphorus. The primary products were the corresponding 1-aza-2-phosphabutadienes. The stability of 1-aza-2-phosphabutadiens obtained was quite different: for instance, the azaphosphabutadienes prepared from 1-alkoxyalkynes were reasonably stable even at heating, whereas their analogs synthesized from 1-dialkylaminoalkynes were detected only at low temperatures. Since in [3] we studied only the reaction between 1-alkoxyalkynes with *N*-(2,4,6-tri-*tert*-butylphenyl)-P-chloroiminophosphine, it was of interest to extend the range of alkynes and P-haloiminophosphines under investigation by changing the halogen nature aiming at revealing the general laws of the process, first of all the stereochemistry of addition and the possibility of isomerization of azaphosphabutadienes and the products of their transformation that retained the alkenyl fragment. Besides the α-bromovinyl ethers and α-bromoenamines that are produced in reaction of P–Br bond with nucleophilic acetylenes are practically interesting as synthetic equivalents of synthons of C=COR and C=CNR_2 type due to the ease of cleavage of the C(sp^2)–Br bond under the reaction conditions.

In the present study we investigated the reaction of P-chloro- (**Ia**), P-bromo- (**Ib**), and P-iodoimino-



(1)

I, Hlg = Cl (**a**), Br (**b**), I (**c**); **II**, R^1 = Me (**a**), Et (**b, c**), *i*-Pr (**d**), H (**e**); R^2 = **Me (a, b)**, Et (**c–e**); **III**, Hlg = Cl (**a–e**), Br (**f–j**), I (**k–n**); R^1 = **Me (a, f, k)**, Et (**b, c, g, h, l, m**), *i*-Pr (**d, i, n**), H (**e, j**); R^2 = Me (**a, b, f, g, k, l**), Et (**c–e, h–j, m, n**); Ar = 2,4,6-tri-*tert*-butylphenyl.

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Table 1. Ratio of *Z*- and *E*-isomers , and ^{31}P NMR spectra of azaphosphabutadienes **IIIa**–**n**

Imino-phosphine, Hlg	Alkyne, R^1,R^2	Azaphospha-butadiene	Solvent	Concent-ration, mol l^{-1}	*Z/E* ratio[a]	δ_P, ppm (hexane)	
						Z	*E*
Ia	**IIa**	**IIIa**	Hexane	1	4/96 (10/90)	406.9	402.8
Cl	Me,Me			1	42/58 (55/45)		
				1	77/23		
				0.1	35/65		
			Benzene	1	30/70		
			CH_2Cl_2	1	47/53		
			CH_3CN–CH_2Cl_2	1	50/50 (58/42)		
Ia	**IIb**	**IIIb**	Hexane		100/0	411.3	
Cl	Et,Me		Benzene	1	100/0		
			CH_2Cl_2	1	100/0		
			CH_3CN–CH_2Cl_2	1	100/0		
Ia	**IIc**	**IIIc**	Hexane	1	50/50	411.8	412.2
Cl	Et,Et			0.1	100/0		
			Benzene	1	82/18		
			CH_2Cl_2	1	100/0		
			CH_3CN–CH_2Cl_2	1	93/7		
Ia	**IId**	**IIId**	Hexane	1	100/0	407.8	
Cl	*i*-Pr,Et		CH_2Cl_2	1	100/0		
Ia	**IIe**	**IIIe**	CH_2Cl_2	1	100/0	357.9[b]	
Cl	H,Et						
Ib	**IIa**	**IIIf**	Hexane	1	25/75	412.1	400.9
Br	Me,Me			0.1	83/17		
			CH_2Cl_2	1	40/60		
Ib	**IIb**	**IIIg**	Hexane	1	75/25	416.1	411.2
Br	Et,Me			0.1	100/0		
			CH_2Cl_2	1	100/0		
				0.1	100/0		
			CH_3CN–CH_2Cl_2	1	70/30		
				0.1	80/20		
Ib	**IIc**	**IIIh**	Hexane	1	65/35	419.7	414.8
Br	Et,Et			0.1	80/20		
			CH_2Cl_2	1	8/12		
Ib	**IId**	**IIIi**	Hexane	1	100/0 (90/10)	413.4	411.7
Br	*i*-Pr,Et			0.1	100/0		
			CH_2Cl_2	1	100/0		
Ib	**IIe**	**IIIj**	CH_2Cl_2	1	100/0	361.0[b]	
Br	H,Et			0.1	100/0		
Ic	**IIa**	**IIIk**	Benzene	1	54/46	423.9[c]	402.1
I	Me,Me						
Ic	**IIb**	**IIIl**	Benzene	1	93/7	427.4[c]	413.7
I	Et,Me						
Ic	**IIc**	**IIIv**	Hexane	1	42/58	428.2[c]	414.8
I	Et,Et		Benzene	1	95/5		
Ic	**IId**	**IIIn**	Benzene	1	100/0	425.2[c]	
I	*i*-Pr,Et						

[a] The isomers ratio after keeping the solution for several weeks at room temperature is given in parentheses.

[b] In dichloromethane.

[c] In C_6D_6.

phosphines (**Ic**) with internal alkylalkoxyacetylenes **IIa–d**, and with terminal ethoxyacetylene **IIe**. All reactions proceed under mild conditions (20°C, *c* 0.1–1 mol l^{-1}) and furnish the corresponding 1-aza-2-phosphabutadienes **IIIa–n** in high yield (equation 1). As solvents were used hexane, benzene, dichloromethane, and acetonitrile.

As in the previous study [3] here occurred the electrophilic addition of haloderivatives of biscoordinate phosphorus to the triple bond of nucleophilic phosphines with conserved coordination of the phosphorus and with formation of 1-aza-2-phosphabutadienes **IIIa–n**. The reaction afford the products in 90–95% yield save the reaction with terminal ethoxyacetylene **IIe** where arises an extremely reactive azaphosphabutadiene **IIId** which undergoes further transformations. In a series of halides of biscoordinate phosphorus containing Cl, Br, I the rate of addition considerably grows: the time of reaction completion decreases from tens of minutes to several seconds, The use of more polar solvent accelerates the reaction. The yields of azaphosphabutadienes **IIIk–n** are reduced by formation of addition products with hydrogen iodide due to the extremely easy hydrolysis of the P–I bond in the initial P-iodoiminophosphine.

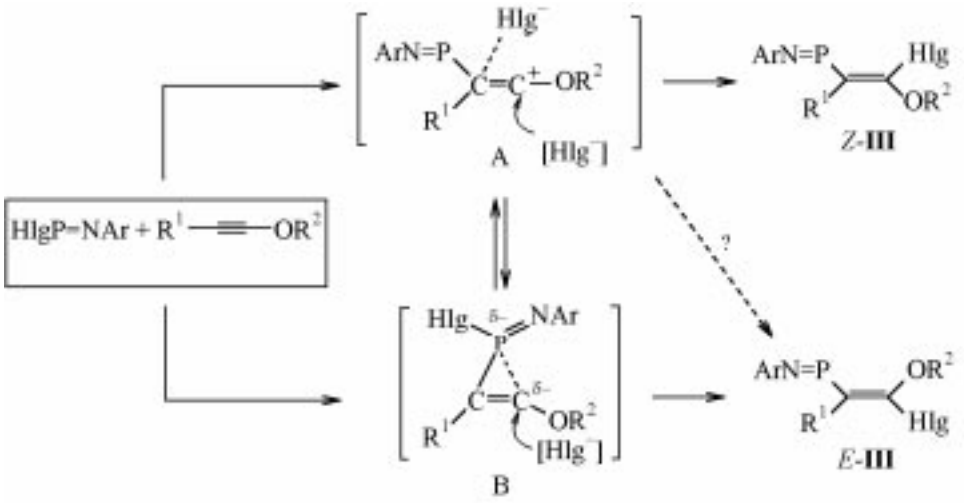
The structure of azaphosphabutadienes **III** is confirmed by the data of ^{31}P and ^{13}C NMR and UV spectroscopy (Table 1). In the ^{31}P NMR spectra of the compounds a downfield signal of biscoordinate phosphorus at δ_P 358–428 ppm characteristic of iminophosphines is present [6, 7]. A characteristic feature of the azaphosphabutadienes synthesized is also a strong absorption in the visible spectral range (λ_{max} 530–540 nm) revealed as a violet color. These compounds are very sensitive to traces of moisture and protoncontaining substances, but they are stable both in solution and in a free state under inert atmosphere even when heated.

An important feature of P-haloiminophosphines addition to 1-alkoxyalkynes is the regioselectivity of the process; but in a general case the reaction is not stereoselective: as a rule form azaphosphabutadiene isomers **III** with *Z*- and *E*-configuration of the alkenyl fragment.

In the ^{13}C NMR spectrum of the *Z*-isomer the coupling constants of phosphorus and carbon from the alkenyl fragment $^2J_{PC^2}$ is larger than the corresponding constant in the spectrum of the *E*-isomer (28–44 Hz and 7–20 Hz respectively). In the ^{31}P NMR spectra the signal of the *Z*-isomer is located downfield with respect to that of the *E*-isomer ($\Delta\delta$ +0.5–+22 ppm). In our preceding communication [3] we established that formerly revealed rules on difference in $^2J_{PC}$ for *Z*- and *E*-isomers of phosphorus-substituted vinyl ethers [8, 9] are valid also for compounds of biscoordinate phosphorus.

The *Z/E* isomer ratio in the products of reaction (1) depend on the halogen nature in the iminophosphine, on the substituents at the triple bond of the alkyne, on the solvent used, and on concentration of reagents (Table 1). At more bulky substituents R^1, and in reaction carried out in dilute solution the content of *Z*-isomer grows, especially in azaphosphabutadienes **IIIf–i** (Hlg = Br). On the contrary we did not find any connection between the polarity of the solvent and changes in isomer ratio. In the most cases studied the reproducibility of the *Z/E* ratio in the reaction products is fairly good, with exception of two reactions, those of P-chloroiminophosphine **Ia** with methylmethoxyacetylene **IIa**, and with ethylethoxyacetylene **IIc** (Table 1). For instance, in reaction carried out in hexane for different runs with compounds **Ia** and **IIa** the *Z/E* ratio varied from 0/100 to 77/23, and with compounds **Ia** and **IIc** from 50/50 to 100/0. The monitoring of the addition with the use of ^{31}P NMR spectroscopy showed that the *Z/E* ratio of the arising azaphosphabutadienes **III** remained constant throughout the process. On completion of the reaction the isomer ratio did not change even at replacing the solvent. The slight isomerization was found only with azaphosphabutadiene **IIIi**. Thus just at the end of reaction between alkoxyacetylene **IId** and P-bromoiminophospine exclusively *Z*-isomer of the corresponding azaphosphabutadiene is present in the reaction mixture (δ_P 413.4 ppm), and after standing for several weeks at 20°C in hexane or benzene solution forms up to 10% of the *E*-isomer (δ_P 411.7 ppm).

The slow interconversion of *Z*- and *E*-isomers after the end of reaction is an evidence of kinetic control in the azaphosphabutadienes formation. The growing amount of *Z*-isomer in the series of R^1 = Me, Et, *i*-Pr may indicate that the addition proceeds through an intermediate A, and the nucleophile attack occurs in the plane of CCP atoms, prevailingly from the side of less bulky substituent (in this case it is the iminophosphine substituent). Yet it cannot be excluded that the *E*-isomer forms through phosphirenium intermediate B or through intermediate A at the nucleophile attack from the side of a small alkyl substituent (R^1 = Me). It is also presumable that intermediate A and phosphirenium ion B are in equilibrium, and all the above cited processes are concurrent (equation 2).



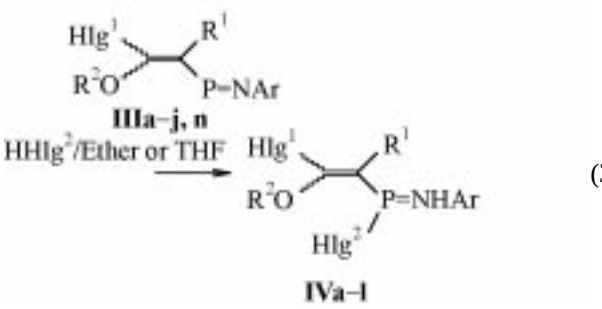
(2)

Table 2. ^{13}C NMR spectral data (taken in C_6D_6) of azaphosphabutadienes **III**, δ_C, ppm (J_{PC}, Hz)[a]

Compd. no.	= CP	= C(OR)	R^1	R^2	C^1(Ar)	C^2(Ar)	C^3(Ar)	C^4(Ar)	*o*-*t*-Bu	*p*-*t*-Bu
***Z*-IIIa**		162.3 (35.8)	12.6	57.9	150.6 (15.2)	134.2 (10.6)	121.8	142.7	C 36.4 CH_3 33.0	C 34.8 CH_3 32.1
***E*-IIIa**	132.9 (67.3)	163.6 (17.0)	11.4 (1.4)	57.9	150.4 (12.1)	133.8 (11.0)	121.8	143.0	C 36.3 CH_3 33.0	C 34.8 CH_3 32.1
***Z*-IIIb**	135.1 (58.1)	163.0 (37.4)	CH_2 20.0 CH_3 14.3	58.0	150.7 (16.4)	134.6 (10.3)	121.8	142.7	C 36.4 CH_3 33.0	C 34.8 CH_3 32.1
***Z*-IIIc**	135.5 (57.9)	162.1 (36.6)	CH_2 20.1 CH_3 14.3	CH_2 67.7 CH_3 14.6	150.9 (15.9)	134.7 (9.2)	121.9	142.8	C 36.5 CH_3 33.0	C 34.8 CH_3 32.1
***E*-IIIc**	139.6 (66.4)	163.0 (15.3)	CH_2 20.7 CH_3 13.9	CH_2 67.7 CH_3 14.6	150.8 (15.6)	134.7 (9.2)	121.9	143.1	C 36.4 CH_3 33.0	C 34.7 CH_3 32.1
***Z*-IIIe**	113.2 (79.4)	162.8 (24.4)	–	CH_2 68.1 CH_3 13.8	150.8 (13.8)	134.1 (10.7)	121.7	142.8	C 36.3 CH_3 32.4	C 34.8 CH_3 32.1
***Z*-IIIf**	134.0 (50.5)	156.3 (35.0)	13.8	60.0	150.4 (13.7)	133.9 (9.6)	121.8	142.8	C 36.4 CH_3 33.0	C 34.8 CH_3 32.2
***E*-IIIf**	137.3 (70.5)	159.7 (13.3)	15.9	61.7	150.1 (11.4)	133.3 (10.8)	121.8	143.0	C 36.3 CH_3 33.1	C 34.8 CH_3 32.1
***Z*-IIIg**	138.4 (56.3)	157.6 (41.3)	CH_2 21.3 CH_3 14.4	60.2	150.5 (15.1)	134.5 (9.4)	121.8	142.8	C 36.4 CH_3 33.1	C 34.8 CH_3 32.2
***E*-IIIg**	142.2 (69.0)	159.8 (13.8)	CH_2 22.4 CH_3 14.6	61.6	150.4 (15.7)	134.3 (12.1)	121.8	143.0	C 36.4 CH_3 33.1	C 34.8 CH_3 32.1
***Z*-IIIh**	138.5 (58.7)	156.3 (41.2)	CH_2 21.4 CH_3 13.5–14.5	CH_2 70.0	150.5 (13.8)	134.3 br	121.6	142.9	C 36.4 CH_3 33.1	C 34.5 CH_3 32.2
***E*-IIIh**		158.7 (7.6)	CH_2 22.5 CH3 13.5–14.5	CH_2 70.8	150.4 (15.2)	134.3 br	121.6	142.6	C 36.4 CH_3 33.1	C 34.5 CH_3 32.2
***Z*-IIIi**	142.7 (58.0)	157.8 (44.8)	CH 28.2 CH_3 21.0	CH_2 70.2 CH_3 14.5	150.1 (14.3)	134.1 (9.0)	121.8	142.8	C 36.4 CH_3 33/0	C 34.8 CH_3 32.1
***Z*-IIIn**	146.2 (53.8)	144.0 (50.1)	CH 30.2 CH_3 24.5 21.2	CH_2 73.4 CH_3 14.1	150.0 (16.1)	134.3 (10.9)	121.8 (2.0)	142.8	C 36.4 CH_3 33.0	C 34.7 CH_3 32.1

[a] ^{13}C NMR spectrum of compound **IIId** was published in [3].

We studied some chemical properties of the azaphosphabutadienes synthesized. In some cases the reactions discussed below can complicate the preparation of pure azaphosphabutadienes: the azaphosphabutadienes readily take up hydrogen halides to furnish acyl halides of alkenylphosphonous acids anilides **IVa–l** (equation 3).



(3)

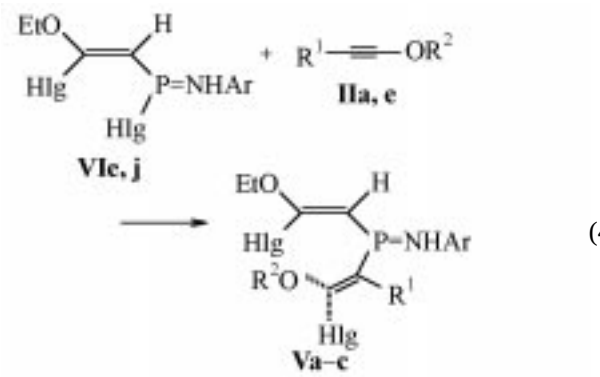
IV, Hlg^1 = Cl (**a**–**e**), Br (**f**–**j**), I (**k, l**); Hlg^2 = Cl (**a**–**e, l**), Br (**f**–**j**), I (**k**); R^1 = Me (**a, f**), Et (**b, c, g, h**), *i*-Pr (**d, i, k, l**), H (**e, j**); R^2 = Me (**a, b, f, g**), Et (**c**–**e, h**–**l**).

Compounds **IV** obtained are light-yellow solids, stable under inert atmosphere. In their ^{31}P NMR spectra phosphorus signals appear at δ_P 11–146 ppm. The configuration of the double bond was established from the values of coupling constants $^2J_{PC}$ in the ^{13}C NMR spectra: for the *Z*-isomers it equals to 45–69 Hz, for the *E*-isomers to 8–27 Hz (Table 2). The chemical shift of phosphorus in compounds **IV** depends on the double bond configuration, and the signal from *Z*-isomer is always by 2–10 ppm downfield with respect to that of *E*-isomer. Same as in the other compounds containing P–Hlg bond the phosphorus chemical shift in acyl halides **IV** is affected by the solvent used: in going from hexane to dichloromethane the signals shift downfield by 6–8 ppm.

The experimental data testify to the possibility of interconversion of *E*- and *Z*-isomers of compounds **IV** at heating or at storage. For instance, on prolonged heating to 100°C of acyl chloride **IVa** in a sealed tube the ratio (*Z*-**IVa**)/(*E*-**IVa**) changed from 100/0 to 60/40. From the pure *Z*-isomer of **IIIb** adduct **IVb** is formed with a small impurity of *E*-isomer (less than 10%). This isomerization occurs also in reaction of compound **IIIi**: from a pure *Z*-isomer already at room temperature arises a mixture of isomers with (*Z*-**IVi**)/(*E*-**IVi**) up to 60/40.

Relatively easy isomerization is obviously due to heterolysis of the C(sp^2)–Hlg bond, especially characteristic of the products of hydrogen halides addition to azaphosphabutadiene **IIIn** with the most labile halogen–carbon bond. In this case the *Z*/*E* ratio in the obtained adducts **IVk, l** in no way correlates with that in the initial azaphosphabutadiene, and it suffers notable further changes on standing of the solution for several days.

An interesting feature of adducts **IVe, j** obtained proceeding from the terminal ethoxyacetylene consists in their capability to take up the second molecule of 1-alkoxyacetylene. Therewith the addition occurs at the triple bond of alkyne providing anilides of dialkenylphosphonous acids **Va–c** (equation 4).

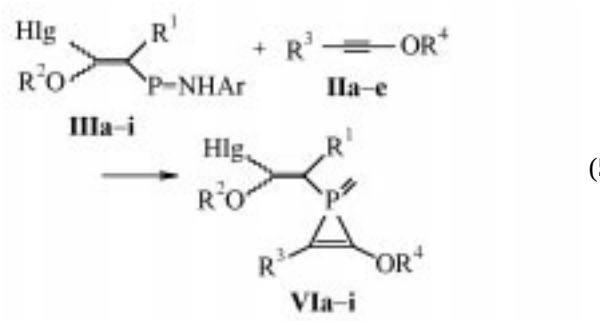


(4)

V, Hlg = Cl (**a, c**), Br (**b**); R^1 = H (**a, b**), Me (**c**); R^2 = Et (**a, b**), Me (**c**).

The addition proceeds regioselectively and to a significant extent stereoselectively: reaction with ethoxyacetylene affords exclusively *Z*,*Z*-isomers of adducts **Va, b**, and with methylmethoxyacetylene forms a mixture of *Z*,*Z*- and *Z*,*E*-isomers in 3 : 1 ratio. The elevated reactivity of acyl halides **IVe, l** results in decrease in their yield due to a fast formation of adducts **V**.

An important feature of azaphosphadienes **III** is their analogy in the chemical sense to phosphinidene. Therefore they are prone to [2+1]-cyclization reac-



(5)

VI, R^1 = Me (**a, f**), Et (**b, c, g, h**), *i*-Pr (**d, i**), H (**e**); R^2 = Me (**a, b, f, g**), Et (**c**–**e, h, i**); R^3 = Me (**a, e, f**), Et (**b, c, g, h**), *i*-Pr (**d, i**); R^4 = Me (**a, b, e, f, g**), Et (**c, d, h, i**).

tions with alkynes. In this respect they are similar to the other P-alkyl- and P-aryl-substituted iminophosphines that form phosphirenes in reactions with acetylenes [10–16] or dimerize to afford three-membered rings [2]. We found that under mild conditions azaphosphabutadienes **III** enter into [2+1]-cycloaddition with the second molecule of alkoxyacetylene yielding the corresponding P-alkenyl-λ^5-phosphirenes **VI** (equation 5).

This reaction proceeds selectively in solvents of different polarity (hexane, benzene, dichloromethane). Its rate is considerably affected by the bulk of the alkyl substituent at the triple bond: in a series of R^1 = Me, Et, *i*-Pr the time required for completion of reaction, e.g., for compounds **VIf–i**, grows from 24 h to 14 days (*c* 1 mol l^{-1}, hexane). The forming phosphirenes are sufficiently stable under inert atmosphere both in solution and in free state, but are very prone to hydrolysis; besides in the case Hlg = Br they gradually decompose at prolonged storage giving an intractable mixture of products. The chemical shift of the phosphorus signal in the ^{31}P NMR spectrum is in upfield region characteristic of this type compounds (δ_P –68–-81 ppm, hexane). In the ^{13}C NMR spectra appear downfield signals of carbon atoms from the cycle with attached alkoxy group (δ_C 163–166 ppm, $^1J_{PC}$ 7–27 Hz). Another characteristic spectral feature of phosphirene ring is small values of direct coupling constants phosphorus–carbon for endocyclic carbon atoms ($^1J_{PC}$ 0–27 Hz) (cf. with data from [17–20]) whereas for the exocyclic carbon atoms the direct coupling constants phosphorus–carbon have large values ($^1J_{PC}$ 145–175 Hz). The phosphorus signal of phosphirene with the *Z*-configuration of the alkenyl fragment is always by several ppm downfield with respect to the corresponding signal of phosphirene with the *E*-configuration.

In the most cases the *Z/E* isomer ratio in phosphirenes **VI** (Hlg = Cl) corresponds to that in the initial azaphosphabutadienes **III** with exception of reaction product of compound **IIIa** with methylmethoxyacetylene **IIa**. Here in the course of reaction the *Z/E* ratio decreases (for instance, from 3:1 to 1:1, or fro 1:1 to 1:2, or from 1:2 to 1:4). For phosphirenes **VIf–h** already after the end of the cycloaddition a slow conversion was observed of *E*-isomers into *Z*-isomers. In contrast initial (*Z*-**IIIi**) isomer with isopropylethoxyacetylene furnished a mixture of *Z*- and *E*-isomers that on standing at room temperature after 3 weeks contains already 65% of *E*-isomer.

Table 3. ^{31}P NMR data for compounds **IVa–l** and **VIa–i** (spectra recorded in hexane)

Azaphosphabutadiene	Adduct with hydrogen halide	δ_P, ppm		Phosphirene	δ_P, ppm	
		Z	*E*		*Z*	*E*
IIIa	**IVa**	114.8	111.3	**VIa**	–78.2	–80.7
IIIb	**IVb**	117.1		**VIb**	–75.7	
		122.5[a]	118.7[a]		–75.8[b]	–79.9[b]
IIIc	**IVc**	117.1	114.2	**VIc**	–75.4	–78.2
IIId	**IVd**	124.0		**VId**	–70.6	
IIIe	**IVe**	118.2[b]		**VIe**	–75.2[b]	
IIIa	**IVf**	124.0	116.0	**VIf**	–75.6[d]	–80.1[d]
IIIb	**IVg**	125.8	116.9	**VIg**	–73.7	–79.9
IIIc	**IVh**	128.0	120.3	**VIh**	–75.4	–80.5
IIId	**IVi**	130.6	128.0	**VIi**	–68.1	–73.8
IIIe	**IVj**	131.8[b]				
IIId	**IVk**	146.3[d]	139.7[d]			
IIId	**IVl**	127.8[c]	122.0[c]			

[a] In acetonitrile.
[b] In dichloromethane.
[c] In C_6D_6.
[d] In benzene.

EXPERIMENTAL

All operations concerning reaction performance and handling the compounds obtained during registering NMR spectra were carried out under atmosphere of dry argon and with the use of anhydrous solvents. ^{31}P NMR spectra were taken on spectrometers Varian FT-80A and Varian VXR-400 (operating frequencies 32.2 and 161.9 MHz respectively, reference 85% H_3PO_4), ^1H and ^{13}C NMR spectra were registered on spectrometer Varian VXR-400 (operating frequencies 400 and 100.6 MHz respectively, reference TMS). P-chloroiminophosphine (**Ia**) was prepared by a procedure described in [21], P-bromoiminophosphine (**Ib**) and P-iodoiminophosphine (**Ic**) by a method from [22]. Alkoxyacetylenes were obtained by procedure from [23].

General procedure for preparation of 3-alkyl-4-alkoxy-1-(2,4,6-tri-*tert*-butylphenyl)-4-halo-1-azaphosphabuta-1,3-dienes (IIIa–n). To a solution of 1 mmol of P-haloiminophosphine **I** in 1–10 ml of solvent (hexane, benzene, dichloromethane, acetonitrile–dichloromethane mixture, 5:1) at room temperature was added 1 mmol of an appropriate alkyne **II**, and the mixture was kept from 5 min to 1 h (*c* 1 mol l^{-1}) or 24–48 h (*c* 0.1 mol l^{-1}) at room temperature. The solution became dark-violet. The

Table 4. ^{13}C NMR spectra (in C_6D_6) of compounds **IV**: δ_C, ppm (J_{PC}, Hz)

Compd. no.	=CP	=C(OR)	R^1	R^2	C^1(Ar)	C^2(Ar)	C^3(Ar)	C^4(Ar)	*o*-*t*-Bu	*p*-*t*-Bu
***Z*-IVa**	115.2 (23.7)	147.1 (58.1)	13.7	59.2	135.7 (19.6)	147.0 (8.0)	124.4 (2.4)	146.8 (2.7)	C 37.0 CH_3 34.0 (4.6)	C 35.2 CH_3 31.9
***E*-IVa**	117.6 (36.3)	149.0 (27.1)	13.7	60.0	135.7 (19.9)	147.2 (4.9)	124.3 (2.0)	146.9 (2.7)	C 37.1 CH_3 33.9 (4.8)	C 35.2 CH_3 31.9
***Z*-IVb**	120.5 (24.4)	148.3 (59.5)	CH_2 20.2 CH_3 14.4	58.0	135.7 (19.1)	146.0 (94.0)	124.4 (2.4)	146.1 (2.2)	C 37.1 CH_3 34.1 (4.5)	C 35.1 CH_3 31.9
***Z*-IVc**	121.2 (26.3)	147.5 (59.3)	CH_2 21.6 CH_3 14.6	CH_2 67.1 CH_3 14.8	135.9 (19.2)	146.1 (5.0)	124.4 (3.1)	146.2 (2.8)	C 37.1 CH_3 34.1 (4.7)	C 35.1 CH_3 31.6
***f*-IVc**		148.7 (19.6)	CH_2 21.6 CH_3 14.6	CH_2 68.0 CH_3 13.7	135.9 (19.2)	146.9 (4.2)	124.2	146.7	C 37.0 CH_3 33.9 (4.7)	C 35.1 CH_3 31.6
***Z*-IVd**[a]	124.2 (26.0)	147.2 (60.3)	CH 30.4 CH_3 22.9 21.4	CH_2 67.2 CH_3 14.9	135.5 (19.0)	146.2 (5.1)	124.4 (2.7)	146.2	C 37.1 CH_3 34.1 (4.5)	C 34.8 CH_3 31.9
Compd. no.	=CP	=C(OR)	R^1	R^2	C^1(Ar)	C^2(Ar)	C^3(Ar)	C^4(Ar)	*o*-*t*-Bu	*p*-*t*-Bu
***Z*-IVe**	103.2 (22.9)	152.6 (45.8)	–	CH_2 66.8 CH_3 14.5	135.8 (15.3)	147.5 (4.5)	124.0	146.9	C 37.2 CH_3 34.0 (4.0)	C 35.2 CH_3 31.9
***Z*-IVf**		140.9 (60.4)	11.8	60.6 (1.5)	139.8 (10.8)	146.3 (5.2)	124.5 (2.5)	146.5 (2.8)	C 37.3 CH_3 34.2 (4.7)	C 35.3 CH_3 32.0
***E*-IVf**	121.1 (44.2)	143.4 (21.4)	11.9	60.6 (1.5)	139.8 (10.8)	146.8 (5.2)	124.4 (2.2)	146.9 (2.7)	C 37.2 CH_3 34.1 (4.8)	C 35.2 CH_3 31.9
***Z*-IVg**	124.6 (29.0)	142.5 (69.0)	CH_2 23.0 CH_3 13.7	60.5	135.1 (18.3)	145.5 (5.5)	124.6 (2.6)	146.7 (3.7)	C 37.4 CH_3 34.3 (4.3)	C 35.2 CH_3 31.9
***E*-IVg**	126.2 (50.9)	138.5 (26.4)	CH_2 23.1 CH_3 13.7	60.5	135.1 (18.3)	146.5 (5.2)	124.7 (2.5)	146.7 (3.4)	C 37.3 CH_3 34.1 (4.9)	C 35.1 CH_3 31.8
***Z*-IVh**	125.1 (29.0)	140.6 (68.7)	CH_2 23.2 CH_2 69.1 CH_3 14.0–15.7		135.1 (18.3)	145.5 (6.1)	124.6	146.0 (3.0)	C 37.4 CH_3 34.4 (4.5)	C 35.2 CH_3 32.0
***E*-IVh**	125.7 (48.9)	136.4 (7.6)	CH_2 23.2 CH_2 68.1 CH_3 14.0–15.7		135.1 (18.3)	145.5 (6.1)	124.5	146.5	C 37.3 CH_3 34.2 (4.6)	C 35.1 CH_3 32.1
***Z*-IVi**		141.0 (76.3)	CH 28.0 CH_3 22.2 22.1	CH_2 69.4 CH_3 14.7	139.7 (10.7)	145.7 (6.1)	124.7 (2.9)	147.3 (4.6)	C 37.3 CH_3 34.3 (4.4)	C 35.2 CH_3 32.1
***E*-IVi**		136.1 (19.1)	CH 27.3 CH_3 21.8 21.6	CH_2 70.0 CH_3 15.1	139.7 (10.7)	146.0 (3.1)	124.6 (3.1)	146.9	C 37.1 CH_3 34.0 (4.4)	C 35.1 CH_3 32.0
Z-IVl	132.2 (28.2)		CH 29.7 CH_3 22.8 21.2	CH_2 72.2 CH_3 14.1	134.4 (16.6)	145.9 (5.1)	124.8	145.0 (5.6)	C 37.4 CH_3 34.4 (4.0)	C 35.1 CH_3 31.9
***E*-IVl**	135.8 (50.1)	126.2 (7.2)	CH 28.7 CH_3 23.3 21.5	CH_2 72.0 CH_3 14.0	135.2 (18.6)	145.9 (3.3)	124.4	145.0 (5.6)	C 37.2 CH_3 34.3 (4.0)	C 35.1 CH_3 31.9

[a] In $CDCl_3$.

Table 5. ^{31}P and ^{13}C NMR spectra (in C_6D_6) dialkenylphosphonous acids anilides **V**: δ_P, ppm, δ_C, ppm (J_{PC}, Hz)

Compd. no.	δ_P	=CH	=C(OEt)	=CR^1	=C(OR^2)	EtO	R^1	R^2	C^1(Ar)	C^2(Ar)	C^3(Ar)	C^4(Ar)	*o*-*t*-Bu	*p*-*t*-Bu
Z,*Z*-**VIa**	23.8	102.4 (15.3)	151.7 (39.7)	102.4 (15.3)	151.7 (39.7)	CH_2 67.6 CH_3 14.3	–	CH_2 67.6 CH_3 14.3	140.6 (18.3)	145.4 (2.0)	123.2	144.4	C 36.7 CH_3 33.4 (3.0)	C 34.9 CH_3 31.8
Z,*Z*-**VIb**	33.0[a]	108.0 (13.7)	144.5 (48.8)	108.0 (13.7)	144.5 (48.8)	CH_2 67.8 CH_3 14.4	–	CH_2 67.8 CH_3 14.4	140.7 (18.3)	145.5 (3.1)	123.2	144.4	C 36.7 CH_3 33.4 (4.6)	C 34.7 CH_3 31.9
Z,*Z*-**VIc**	29.2	100.4 (21.3)	151.9 (44.3)	115.1 (12.2)	146.9 (50.3)	CH_2 67.6 CH_3 14.0	11.2	57.8	141.0 (27.4)	145.6	123.2	145.0 (3.1)		
Z,*E*-**VIc**	28.9	101.2 (19.8)	151.4 (44.0)	116.5 (26.5)	147.3 (24.0)	CH_2 67.8 CH_3 13.8	11.3	58.9	140.9 (26.5)	145.6	123.2	145.0 (3.1)		

[a] ^{31}P NMR spectrum recorded in CH_2Cl_2, ^{13}C NMR spectrum in $CDCl_3$.

Table 6. ^{13}C NMR spectra (in C_6D_6) of phosphirenes **VI**: δ_C, ppm (J_{PC}, Hz)

Compd. no.	=CR^3	=COR^4	=CR^1	=COR^2	R^1	R^2	R^3	R^4	C^1(Ar)	C^2(Ar)	C^3(Ar)	C^4(Ar)	*o*-*t*-Bu	*p*-*t*-Bu
Z-**VIa**	125.0 (7.7)	166.0 (9.2)	111.8 (174.0)	145.4 (19.9)	15.5 (3.5)	58.0	11.4 (5.6)	59.4 (5.2)	142.9 (11.3)	143.1 (9.2)	121.5	139.6 (4.6)	C 36.5 CH_3 32.0	C 34.6 CH_3 32.2
E-**VIa**	124.7 (7.6)	165.5 (9.1)	111.3 (152.6)	149.2 (15.2)	16.6 (4.6)	58.9	11.3 (4.6)	59.8 (7.6)	142.9 (11.3)	143.1 (9.2)	121.5	139.6 (4.6)	C 36.5 CH_3 32.0	C 34.6 CH_3 32.2
Z-**VIb**	130.1 (7.6)	165.3 (13.7)	117.8 (168.6)	145.8 (21.4)	CH_2 23.5 (3.1) CH_3 14.6 (1.5)	58.1	CH_2 20.1 (4.6) CH_3 13.5 (4.6)	60.1 (8.4)	143.2 (6.9)	143.0 (10.0)	121.4 (4.6)	139.5 (5.3)	C 36.5 (1.5) CH_3 32.0	C 34.7 (1.6) CH_3 32.1
Z-**VIc**	129.4 (7.6)	164.6 (13.7)	118.6 (167.8)	144.7 (21.3)	CH_2 24.0 (3.0) CH_3 14.4 (5.1)	CH_2 67.2 CH_3 15.3	CH_2 20.2 (4.6) CH_3 13.3 (4.6)	CH_2 69.3 (7.7) CH_3 14.4 (5.1)	143.4 (2.6)	143.0 (9.1)	121.4 (4.6)	139.4 (4.6)	C 36.5 CH_3 32.2	C 34.6 CH_3 32.4
Z-**VId**[a]	134.7 (9.0)	166.1 (23.4)	122.8 (166.2)	145.6 (19.8)	CH 29.5 (2.8) CH_3 24.5	CH_2 67.8 CH_3 14.7	CH 27.8 (4.7) CH_3 21.8 (2.0)	CH_2 70.7 (7.7) CH_3 15.7	143.3 (6.3)	142.9 (6.3)	119.8 (6.4)	139.4 (4.7)	C 37.3 CH_3 32.0	C 36.5 CH_3 31.8

Table 6. (Contd.)

Compd. no.	=CR^3	=COR^4	=CR^1	=COR^2	R^1	R^2	R^3	R^4	C^1(Ar)	C^2(Ar)	C^3(Ar)	C^4(Ar)	*o*-*t*-Bu	*p*-*t*-Bu
***Z*-VIe**	122.8 (18.1)	162.9	89.7 (154.1)	153.4 (12.2)	–	CH_2 66.8 CH_3 14.4	11.3 (5.0)	60.7 (10.7)	143.6 (6.0)	142.9 (9.1)	121.4	139.6 (4.6)		
***Z*-VIf**	125.5 (8.1)	166.3 (9.9)	117.4 (175.5)	138.2 (21.5)	16.4 (5.2)	60.4	11.4 (4.9)	59.8 (8.8)	142.7 (8.4)	143.2 (10.4)	121.6 (4.6)	139.7 (6.0)	C 36.6 (2.3) CH_3 31.8	C 35.0 CH_3 32.0
***E*-VIe**	125.0 (8.5)	165.7 (9.2)	115.3 (145.5)	136.1 (1.8)	18.7 (6.1)	60.4	11.2 (5.2)	59.6 (9.9)	142.8 (8.6)	143.1 (10.1)	121.6 (4.6)	139.7 (6.0)	C 36.5 (2.2) CH_3 31.9	C 34.7 CH_3 32.0
***Z*-VIg**	130.2 (7.4)	165.5 (14.3)	120.5 (165.9)	138.7 (21.9)	CH_2 24.8 (5.0) CH_3 14.4 (4.1)	59.8	CH_2 20.1 (5.0) CH_3 13.6 (4.8)	60.1 (8.4)	143.0 (7.6)	142.9 (10.1)	121.4 (3.8)	139.5 (6.3)	C 36.5 (2.2) CH_3 32.0	C 35.1 CH_3 32.1
***E*-VIg**	130.5 (8.2)	164.9 (12.9)		135.2 (8.2)	CH_2 26.7 (4.0) CH_3 13.6	59.8	CH_2 17.9 (4.0) CH_3 13.2 (5.4)	60.1 (8.4)	143.0 (7.6)	142.9 (10.1)	121.4 (3.8)	139.6 (6.3)	C 36.5 (2.2) CH_3 31.9	C 35.0 CH_3 32.1
***Z*-VIh**	129.3 (7.6)	164.8 (15.3)	123.3 (170.9)	137.4 (22.9)	CH_2 25.2 (4.6) CH_3[b]	CH_2 69.1 CH_3[b]	CH_2 20.3 (3.0) CH_3 13.4 (3.1)	CH_2 69.3 (7.6) CH_3[b]	143.3 (7.6)	143.0 (10.7)	121.4 (3.1)	139.4 (4.6)	C 36.5 CH_3 32.0	C 34.6 CH_3 32.1
***E*-VIh**	130.0 (3.1)	163.8 (10.8)	121.5 (155.7)		CH_2 26.7 (4.0) CH_3[b]	CH_2 69.5 CH_3[b]	CH_2 20.3 (3.0) CH_3 13.6 (4.5)	CH_2 69.2 (10.7) CH_3[b]	143.3 (7.6)	143.0 (10.7)	121.4 (3.1)	139.4 (4.6)	C 36.5 CH_3 32.0	C 34.6 CH_3 32.1
***Z*-VIi**	133.4 (9.1)	166.0 (27.5)		138.5 (22.9)	CH 27.8 (4.6) CH_3[c]	CH_2 69.2 CH_3 14.6	CH 29.5 (3.0) CH_3[c]	CH_2 70.4 (6.2) CH_3 15.8	143.5 (7.6)	142.9 (10.7)	121.2 (4.9)	139.4 (5.0)	C 36.7 CH_3 32.2	C 34.7 CH_3 32.1
***E*-VIi**	133.1 (6.2)	166.4 (23.5)	124.2 (138.3)	136.0 (11.3)	CH 27.7 (3.3) CH_3[c]	CH_2 68.9 CH_3 14.5	CH 29.5 (3.0) CH_3[c]	CH_2 69.9 (7.7) CH_3 15.7	143.9 (10.8)	143.0 (12.3)	121.3 (6.3)	139.5 (6.2)	C 36.7 CH_3 32.2	C 34.7 CH_3 32.1

[a] In CD_2Cl_2.

[b] Carbon atoms of CH_3 groups from ethyl and ethoxy substituents appear as a multiplet at 14–15 ppm.

[c] Carbon atoms of CH_3 groups from isopropyl substituents appear as a multiplet at 21–22 ppm.

Table 7. Elemental analyses of compounds **IIIf–i, IVf–i, Vb,** and **VIf–i**

Compd. no.	Found, %		Formula	Calculated, %	
	N	P		N	P
IIIf	2.98	6.87	$C_{22}H_{35}BrNOP$	3.18	7.03
IIIg	3.14	6.57	$C_{23}H_{37}BrNOP$	3.08	6.82
IIIh	3.20	6.11	$C_{24}H_{39}BrNOP$	3.00	6.62
IIIi	2.67	6.01	$C_{25}H_{41}BrNOP$	2.90	6.42
IVf	2.10	5.57	$C_{22}H_{36}Br_2NOP$	2.69	5.94
IVg	2.47	5.39	$C_{23}H_{38}Br_2NOP$	2.62	5.79
IVh	2.83	4.92	$C_{24}H_{40}Br_2NOP$	2.55	5.64
IVi	2.61	5.02	$C_{25}H_{42}Br_2NOP$	2.49	5.50
Vb	2.01	4.57	$C_{26}H_{42}Br_2NO_2P$	2.37	5.24
VIf	2.23	5.39	$C_{26}H_{41}BrNO_2P$	2.74	6.07
VIg	2.11	4.90	$C_{28}H_{45}BrNO_2P$	2.60	5.75
VIh	2.24	4.86	$C_{30}H_{49}BrNO_2P$	2.47	5.47
VIi	2.07	4.76	$C_{32}H_{53}BrNO_2P$	2.36	5.21

solvent was evaporated in a vacuum, the residue was maintained at a pressure 0.1 mm Hg, and a mixture of *Z*- and *E*-isomers of azaphosphabutadienes **III** was obtained as dark-violet solid in 90–95% yield [yields of azaphosphabutadienes **IIIk–n**, Hlg = I, were considerably less due to formation of side products, in particular, acyl halides **IV**, because the initial P-iodoiminophosphine (**Ic**) was extremely prone to hydrolysis]. The isomer ratio and ^{31}P NMR data are presented in Table 1, the data of ^{13}C NMR spectra in Table 2.

General procedure for preparation of acyl halides of 1-alkoxy-1-haloalken-2-ylphosphonous acids 2,4,6-tri-*tert*-butylanilides (IVa–l). Into a flask filled with argon was charged 1 mmol of azaphosphabutadiene **III** in 1–10 ml of solvent (hexane, benzene, dichloromethane, acetonitrile–dichloromethane mixture, 5:1), and 1 mmol of hydrogen halide dissolved in ethyl ether or THF was added. The violet color of the initial solution immediately disappeared. The solvent was removed in a vacuum, the residue was maintained under a pressure of 0.1 mm Hg to furnish a mixture of *Z*- and *E*-isomers of acyl halides **VI** as lightyellow oily substances in 90–98% yield. The isomer ratio and ^{31}P NMR data are given in Table 3, the ^{13}C NMR data in Table 4.

General procedure for preparation of (2-halo-2-ethoxycarbonyl) (2-halo-2-alkoxyalken-2-yl)phosphonous acids 2,4,6-tri-tert-butylanilides (Va–c). Into a flask filled with argon was charged 1 mmol of P-haloiminophosphine **Ia** or **Ib** in 1–10 ml of dichloromethane, 1 mmol of ethoxyacetylene (**IIe**) was added, the mixture was kept for 30 min till it turned bright violet, then 1 mmol of hydrogen chloride or bromide dissolved in ether or THF was added. After disappearance of the violet color 1 mmol of ethoxyacetylene (**IIe**) or methylmethoxyacetylene (**IIa**) was added. The mixture was kept for 1 h, then the solvent was removed in a vacuum, the residue was maintained under a pressure of 0.1 mm Hg, and dialkylphosphonous acids anilides **V** were obtained as light-yellow oily substances in 92%–96% yield. The ^{31}P and ^{13}C NMR data are listed in Table 5.

General preparation method for 1-(2,4,6-tri-*tert*-butylphenylamino)-1-(1-alkoxy-1-haloalken-2-yl)-2-alkyl-3-alkoxy-λ^5phosphirenes (VIa–i). Into a flask filled with argon was charged 1 mmol of azaphosphabutadiene **III** in 1 ml of solvent, and 1 mmol of alkyne **II** was added thereto. After the violet color of solution completely disappeared (depending on alkyne character it took from 1 to 12 days) the solvent was removed in a vacuum, the residue was maintained under a pressure of 0.1 mm Hg, and phosphirenes **VI** were obtained as yellow solids. The data of ^{31}P NMR spectra are presented in Table 3, those of ^{13}C NMR in Table 6.

The elemental analyses of all newly prepared compounds are listed in Table 7.

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