Russian Journal of Organic Chemistry, Vol. 39, No. 6, 2003, pp. 797–807 . Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 6, 2003, pp. 847–856.

Hydrophosphorylation of Terminal Alkynes Catalyzed by Palladium

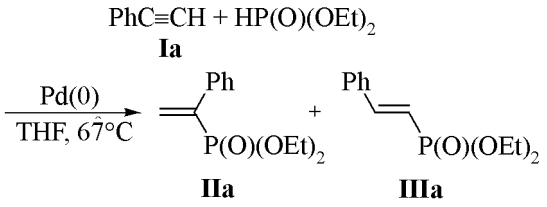
N. S. Gulykina, T. M. Dolgina, G. N. Bondarenko, and I. P. Beletskaya

Moscow State University, Moscow, 119899 Russia

Received September 27, 2002

Abstract—A series of new 1-aryl-, 1-heteroaryl-, and 1-alkylethenylphosphonates was prepared by hydrophosphorylation of terminal acetylenes catalyzed by palladium. A stable in air complex $Pd_2(dba)_3 \cdot CHCl_3$ was applied as catalyst. The reaction mechanism is discussed.

α,β-Unsaturated phosphonates are of significant interest for they have found wide application both in industry and medical chemistry [1, 2]. They underlie preparation, e.g., of incombustible and self-extinguishing polymers [3], antibiotics [4], cersatile biologically active compounds [5]. We showed recently that 1-arylethenylphosphonic acids and their esters are convenient intermediates for preparation of 1-arylethylphosphonates which exhibit immunosuppressor properties of central type action [6, 7]. A lot of preparation procedures for α,β-unsaturated phosphonates are published but they mostly concern the synthesis of vinylphosphonates with a stong electron-withdrawing group in the α-position [8]. Among the synthetic methods for ethenylphosphonates with an aryl or alkyl substituent in the α-position may be cited dehydration of saturated α-hydroxyphosphonic acids [3, 9–11] or their esters [12–17], catalyzed by Cu(I)- [18, 19] or Ni(II) [20] Arbuzov reaction of trialkylphosphites with vinyl halides, catalyzed by Pd(0) Michaelis–Becker reaction of phosphorous acid dialkyl esters with vinyl bromides [21, 22] or with vinyl triflates [23], addition of trialkyl phosphites [24] or phosphorous acid dialkyl esters [25] to α-nitroolefins followed by elimination of nitrous acid [26, 27], addition of potassium diethylphosphite to phenyl-β-styryl sulfone with subsequent elimination of benzenesulfinic acid [28], thermal decomposition of alkyl (1-diethoxyphosphoryl-1-phenylalkyl) sulfoxides [29], olefination of acylphosphonates with methylenetriphenylphosphorane by Wittig reaction [30, 31], photolysis of dimethyl 1-diazo-2-phenylethylphosphonate [32], addition of trimethylsilyldiazomethane to phosphorylated aryl- and vinylketenes followed by decarbonylation [33], and the reaction of Ivanov reagent prepared from diethyl 1-benzylphosphonate with formaldehyde [34]. In 1996 L.-B. Han and T. M. Tanaka demonstrated that in the presence of palladium complexes dimethyl- and diethylphosphoric acids added to aromatic and aliphatic terminal acetylenes [35]. In contrast to Pudovik reaction proceeding along ionic or radical mechanism [36] the hydrophosphorylation of terminal acetylenes catalyzed by palladium occurrs in keeping with Markownikoff rule affording prevailingly α-substituted ethenylphosphonates. At the use as catalyst of *cis*-$PdMe_2(PPh_2Me)_2$ the regioselectivity of the process attains 90% [35]. In this paper we report on continuation of the study of the new promising synthetic method for α-aryl- and α-alkyl-ethenylphosphonates in order to find a convenient catalytic system for preparative procedures. A range of substrates was also extended to include in particular heteroarylacetylenes and arylacetylenes containing in the ring strong electron-withdrawing substituents. The preliminary results of our studies were published before [37]. In the selection of an optimal catalytic system phenylacetylene (**Ia**) was used as model substrate. As catalyst was applied stable in air complex $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of mono- or bidentate phosphine ligands, or $Pd(PPh_3)_4$. A mixture of 1.1 mmol of phenylacetylene, 1 mmol of diethylphosphorous acid, palladium catalyst (3 mol% of Pd), and phosphine in 1 ml of anhydrous THF was heated to 67°C in a sealed ampule. The reaction progress was monitored by ^{31}P NMR measuring the $HP(O)(OEt)_2$ conversion by decrease in the signal at δ 6.9 ppm and the formation of two regioisomers of



1070-4280/03/3906-0797$25.00 © 2003 MAIK "Nauka/Interperiodica"

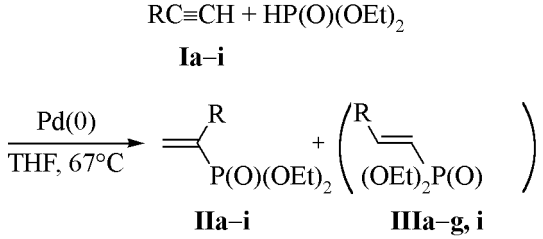
the reaction product **IIa** and **IIIa** by increase in the signals at δ 16.5 and 18.8 ppm respectively [38].

The results obtained listed in Table 1 show that at the use as catalyst of $Pd(PPh_3)_4$ the reaction is completed in 9 h and affords products **IIa**) and **IIIa** in 90 and 10% yield respectively (run no. 1). The same selectivity of reaction was observed at the use of $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of triphenylphosphine (runs nos. 2 and 3); therewith the catalytic activity of $Pd_2(dba)_3 \cdot CHCl_3$ depended on the amount of the added ligand. In the presence of 1.5 mol% of $Pd_2(dba)_3 \cdot CHCl_3$ and 12 mol% of PPh_3 (P/Pd = 4) in 9 h the overall yield of products **IIa** and **IIIa** was 87% (run no. 2), i.e. the efficiency of this system was comparable with that of $Pd(PPh_3)_4$. The reduction of triphenylphosphine amount to 6 mol% (P/Pd = 2) resulted in decrease of the overall product yield within the same time to 76% (run no. 3). The same trend was observed at the use of a bidentate ligand dppp: in the presence of 1.5 mol% of $Pd_2(dba)_3 \cdot CHCl_3$ and 6 mol% of dppp (P/Pd = 4) the overall yield of products **IIa** and **IIIa** in 9 h was 79% (run no. 4) and considerably decreased (52% in 35 h) at reduction by half of the ligand amount (P/Pd = 2) (run no. 5); therewith the hydrophosphorylation was stereospecifical: Regioisomer **IIIa** formed only in trace amount. The reaction is highly regiospecific at the use of dppe, but the process is very slow (runs nos. 6 and 7).

Totally inactive as catalysts were the following complexes: $(PhCN)_2PdCl_2$, *p*-$NO_2C_6H_4PdI(PPh_3)_2$, $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of $AsPh_3$ or CH_3CN (used as solvent), and also $Ni(acac)_2$ that catalyzed diphenylphosphine addition to phenylacetylene [39].

The attempt to replace diethyl phosphite as phosphorylating agent by $HP(O)(OSiMe_3)_2$ failed likely by sterical reasons. The successful modification in this case promised easy conversion under very mild conditions of the trimethylsilyl esters obtained into the corresponding α,β-unsaturated phosphonic acids by mere methanolysis. To our regret, in reaction of phenylacetylene with $HP(O)(OSiMe_3)_2$ in the presence of $Pd(PPh_3)_4$ under standard conditions after 9.5 h we observed formation of no more than 26% of the product [δ –0.8 ppm (THF)]; further heating resulted in separation of a colorles flocculent precipitate, and the reaction stopped.

We involved into the hydrophosphorylation reaction aromatic and aliphatic acetylenes **Ia–i**.



Pd(0) = $Pd(PPh_3)_4$ (3 mol%) or $Pd_2(dba)_3 \cdot CHCl_3$ (1.5 mol%) and PPh_3 (12 mol%); R = Ph (**a**), 4-MeOC6H4 (**b**), 6-MeO-2-Nf (**c**), ferrocenyl (**d**), 3-pyridyl (**e**), 3-quinolyl (**f**), 6-quinolyl (**g**), Bu (**h**24)), *t*-Bu (**i**).

Table 1. Hydrophosphorylation of phenylacetylene (**Ia**)[a]

Run no.	Catalyst (amount)	Time, h	Overall products yield (**IIa** and **IIIa**), % (^{31}P NMR)	Selectivity (**IIa**)/(**IIIa**) (^{31}P NMR)
1	$Pd(PPh_3)_4$	6	91	90/10
	(3 mol%)	9	100	
2	Pd2(*dba*)3 · $CHCl_3$/PPh_3	6	71	90/10
	(1.5 mol%)/(12 mol%)	9	87	
3	Pd_2(*dba*)3 · $CHCl_3$/PPh_3	6	60	89/11
	(1.5 mol%)/(6 mol%)	9	76	
4	Pd2(*dba*)$_3$ · $CHCl_3$/*dppe*	9	79	>98/2
	(1.5 mol%)/(6 mol%)			
5	$Pd_2(dba)_3 \cdot CHCl_3$/*dppe*	18	37	>98/2
	(1.5 mol%)/(3 mol%)	3	52	
6	$Pd_2(dba)_3 \cdot CHCl_3$/*dppe*	9	6	–
	(1.5 mol%)/(6 mol%)			
7	$Pd_2(dba)_3 \cdot CHCl_3$/*dppe*	15	41	95/5
	(1.5 mol%)/(3 mol%)	35	56	

[a] 1.1 mmol of PhC≡CH, 1 mmol of $HP(O)(OEt)_2$, 1 ml of THF, 67°C.

Table 2. Hydrophosphorylation of terminal alkynes RC≡CH **Ia**–**i** with diethyl phosphite catalyzed by palladium

Compd. no.	R	Catalyst[a]	Reaction time, h	$HP(O)(OEt)_2$ conversion, % (^{31}P NMR)	Isomer ratio (**II**)/(**III**) (^{31}P NMR)	Preparative yield of **II**, %
Ia	Ph	A	9	100	90/10	75
Ib	4-$MeOC_6H_4$	B	10	84		
			14	91		
			29	91	94/6	65
Ic	6-MeO-2-Nf	B	17	78		
			28	88		
			37	88	93/7	73
Id	Ferrocenyl	B	39	89	91/9	–
Ie	3-Pyridyl	B	26	83	80/20	59
If	3-Quinolyl	B	30	77		
			68	89		
			114	89	80/20	58
Ig	6-Quinolyl	B	45	44		
			117	73	82/18	48
Ih	Bu	A	12	100	100/0	82
Ih	Bu	B	27	100	100/0	76
Ii	*t*-Bu	C	73	79		
			120	97	34/66b	–

[a] A is $Pd(PPh_3)_4$ (3 mol%); B is $Pd_2(dba)3\cdot CHCl_3$ (1.5 mol%), PPh_3 (12 mol%); C is $Pd(PPh_3)_4$ (10 mol%).
[b] According to ^1H NMR.

Table 3. ^1H and ^{31}P NMR spectra of α-substituted diethyl ethenylphosphonates $CH_2=C(R)P(O)(OEt)_2$ **IIa**–**i**

	R	^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)					^{31}P NMR spectrum, δ, ppm (solvent)
		trans-PC=CH, d.d (1H)	*cis*-PC=CH, d.d (1H)	R	OCH_2CH_3		
					CH_2,m (4H)	CH_3, t (6H)	
IIa	Ph	6.16 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 45.7)	6.34 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 22.2)	7.34 m (3H, Harom), 7.53 m (2H, Harom)	4.11	1.29 ($^3J_{HH}$ 7.2)	16.5 (THF), 17.0 (MeOH), 16.8 ($CDCl_3$)
IIb	4-$MeOC_6H_4$	6.06 ($^2J_{HH}$ 1.3, $^3J_{HP}$ 45.8)	6.20 ($^2J_{HH}$ 1.3, $^3J_{HP}$ 21.6)	3.76 s (3H, OCH_3), 6.83 d (2H, C^3H+C^5H, $^3J_{AB}$ 8.8), 7.44 d.d (2H, C^2H+C^6H, $^3J_{AB}$ 8.8, $^4 3J_{HP}$ 1.2)	4.05	1.24 ($^3J_{HH}$ 7.0)	16.9 (THF), 17.8 (MeOH)
IIc	6-MeO-2-	6.27 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 45.8)	6.38 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 21.9)	3.93 s (3H, OCH_3), 7.12 d (1H, C^5H, $^4 4J_{HH}$ 2.4), 7.16 d.d (1H, C^7H, $^3J_{HH}$ 8.8, $^4 4J_{HH}$ 2.4), 7.62 m (1H, C^3H, $^3J_{HH}$ 8.8), 7.72 d (1H, C^4H, $^3J_{HH}$ 8.8), 7.75 d (1H, C^8H, $^3J_{HH}$ 8.8), 7.98 br.s (1H, C^1H)	4.13	1.30 ($^3J_{HH}$ 7.0)	16.7 (THF), 17.3 (MeOH)
IId	Fc	6.08 br. ($^3J_{HP}$ 43.9) ($^3J_{HP}$ 21.1)	6.05 br.	4.02 br. (5H, C_5H_5), 4.16 br. (2H, Harom), 4.49 br. (2H, H arom)	4.02 br.	1.26 br.	16.8 (THF), 17.2 (MeOH), 16.1 (Et2O)
IIe	3-Pyridyl	6.21 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 45.2)	6.42 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 21.8)	7.30 d.d (1H, C^5H, $^3J_{HH}$ 8.0, $^3J_{HH}$ 4.8), 7.89 m (1H, C^4H, $^3J_{HH}$ 8.0), 8.59 br.d (1H, C^6H, $^3J_{HH}$ 4.8), 8.72 br.s (1H, C^2H)	4.13	1.31 ($^3J_{HH}$ 7.0)	15.6 (THF), 15.45 ($CDCl_3$)

Table 3. Contd.

	R	^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)					^{31}P NMR spectrum, δ, ppm (solvent)
		trans-PC=CH, d.d (1H)	*cis*-PC=CH, d.d (1H)	R	OCH_2CH_3		
					CH_2,m (4H)	CH_3, t (6H)	
IIf	3-Quinolyl	6.35 ($^2J_{HH}$ 1.2, $^3J_{HP}$ 45.2)	6.51 ($^2J_{HH}$ 1.2, $^3J_{HP}$ 22.0)	7.58 d.d.d (1H, C6H, $^3J_{HH}$ 8.0, $^3J_{HH}$ 7.0, $^4J_{HH}$ 1.2), 7.74 d.d.d (1H, C^7H, $^3J_{HH}$ 8.4, $^3J_{HH}$ 7.0, $^4J_{HH}$ 1.2), 7.86 br.d (1H, C^5H, $^3J_{HH}$ 8.0), 8.11 br.d (1H, C8H, $^3J_{HH}$ 8.4), 8.39 s (1H, C4H), 9.03 s (1H, C^2H)	4.17	1.32 ($^3J_{HH}$ 7.0)	15.7 (THF), 15.6 ($CDCl_3$)
IIg	6-Quinolyl	6.32 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 45.2)	6.46 ($^2J_{HH}$ 1.4, $^3J_{HP}$ 22.0)	7.43 d.d (1H, $^3J_{HH}$ 8.4, $^3J_{HH}$ 4.4, C^3H), 7.88 d.d.d (1H, C^7H, $^3J_{HH}$ 8.8, $^4J_{HH}$ 2.0, $^43J_{HP}$ 1.0), 8.06 m (1H, C^5H), 8.11 d (1H, C^8H, $^3J_{HH}$ 8.8), 8.20 d.d (1H, C^4H, $^3J_{HH}$ 8.4, $^4J_{HH}$ 1.6), 8.93 d.d (1H, C^2H, $^3J_{HH}$ 4.4, $^4J_{HH}$ 1.6)	4.16	1.31 ($^3J_{HH}$ 7.0)	16.0 (THF), 16.3 ($CDCl_3$)
IIh	Bu	5.72[a] ($^2J_{HH}$ 1.4, $^3J_{HP}$ 49.0, $^3J_{HP}$ 22.9)	5.99[a] ($^4J_{HH}$ 1.6) ($^2J_{HH}$ 1.4,	0.88 t (3H, CH3, $^3J_{HH}$ 7.4), 1.32 m (2H, C_3H_2), 1.47 quintet (2H, C2H2, $^3J_{HH}$ 7.5), 2.20 m (2H, C1H2, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.6, $^3J_{HP}$ 13.3)	4.04	1.29 ($^3J_{HH}$ 7.0)	18.7 (THF), 21.9 (MeOH)
IIi	*t*-Bu	5.77[b] ($^3J_{HP}$ 47.9) ($^3J_{HP}$ 23.3)	5.95[b]	1.15 s (9H, CH_3)	3.98	1.24 ($^3J_{HH}$ 7.2)	18.9 (THF)

[a] Multiplet. [b] Doublet.

The results obtained are compiled in Table 2. The hydrophosphorylation of aryl- and heteroarylacetylenes **Ib–g** was carried out using as catalyst the stable in air $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of triphenylphosphine. We did not attain a complete conversion of the diethylphosphite: The reaction stopped when conversion of $HP(O)(OEt)_2$ reached 73–91%. As in the case of phenylacetylene (**Ia**) the main reaction products were diethyl 1-arylethenylphosphonates **IIa–g** which were isolated in 49–75% yield. Their structure and composition were confirmed by NMR and IR spectra and by elemental analyses.

In the ^{1}H NMR spectra of compounds **IIa–g** (Table 3) vinyl protons signals appear as doublets of doublets with the geminal coupling constant $^2J_{HH}$ 1.2–1.4 Hz and characteristic coupling constants with phosphorus nucleus: $^3J_{HP}$ *cis* 21.1–22.2 and $^3J_{HP}$ *trans*.

In the ^{13}C NMR spectra of compounds **IIa–c, h** the characteristic doublet of the carbon directly linked to the phosphorus appears in the region 138.7–139.6 ppm; the coupling constant $^1J_{CP}$ amounts to 170.8–178.2 Hz.

In the IR spectra of compounds **IIa–c, h** a characteristic group of strong bands is observed corresponding to the vibrations of the diethoxyphosphoryl fragments [41]: a broad band of ν(P=O) in the region 1234–1255 cm^{-1}, usually two bands in the region 1024–1055 cm^{-1} from O–C vibrations, and a band of C–C vibrations at 962–968 cm^{-1}.

The formation of isomeric *trans*-diethyl-2-arylethenylphosphonates **IIIa–g** was registered by spectral methods. In the ^{31}P NMR spectra of the reaction mixtures the minor isomers **IIIa–g** are observed in the region 17.8–19.8 ppm, whereas the signals of the major isomers **IIa–g** are displaced upfield by 2.2–2.9 ppm (in all likelihood due to the anisotrotic effect of the aromatic ring) and appear in the region 15.5–16.9 ppm. For acetylenes **Ia–d** the fraction of minor isomers amounted to 6–10% and increased up to 18-20% for acetylenes **Ie–g** containing electron-withdrawing heteroaromatic substituents.

Compounds **IIIe–g** were isolated and characterized by ^{1}H and ^{31}P NMR spectra (Table 4). The vinyl protons appear in the spectra as doublet of doublets; their assignment was done basing on the coupling

Table 4. ^{1}H and ^{31}P NMR spectra of α-substituted diethyl ethenylphosphonates *trans*-RCH=CHP(O)(OEt)$_2$ **IIIe–g, i**[a]

	R	^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)					^{31}P NMR spectrum, δ, ppm (solvent)
		trans-C=CHP, d.d (1H)	*cis*-HC=CP, d.d (1H)	R	OCH_2CH_3		
					CH_2,m (4H)	CH_3, t (6H)	
IIIe	3-Pyridyl	6.37 ($^3J_{HH}$ 17.6, $^2J_{HP}$ 16.8)	7.50 ($^3J_{HH}$ 17.6, $^3J_{HP}$ 22.5)	7.34 d.d (1H, C5H, $^3J_{HH}$ 7.8, $^3J_{HH}$ 4.8), 7.82 d.t (1H, C4H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8), 8.61 d.d (1H, C6H, $^3J_{HH}$ 4.8, $^4J_{HH}$ 1.8), 8.74 br. (1H, C^2H)	4.16	1.37 ($^3J_{HH}$ 7.2)	17.8 (THF), 17.6 ($CDCl_3$)
IIIf	3-Quinolyl	6.52 ($^3J_{HH}$ 17.6, $^2J_{HP}$ 16.8)	7.67 ($^3J_{HH}$ 17.6 $^3J_{HP}$ 22.8)	7.59 d.d.d (1H, C6H, $^3J_{HH}$ 8.0, $^3J_{HH}$ 7.2, $^4J_{HH}$ 0.6), 7.76 d.d.d (1H, C^7H, $^3J_{HH}$ 8.8, $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.4), 7.86 br.d (1H, C^5H, $^3J_{HH}$ 8.0), 8.12 br.d (1H, C8H, $^3J_{HH}$ 8.8), 8.22 s (1H, C^4H), 9.09 br. (1H, C^2H)	4.19 ($^3J_{HH}$ 7.2, $^3J_{HP}$ 8.0)	1.39 ($^3J_{HH}$ 7.2)	18.0 (THF), 17.8 ($CDCl_3$)
IIIg	6-Quinolyl	6.42 ($^3J_{HH}$ 17.2, $^2J_{HP}$ 17.2)	7.68 ($^3J_{HH}$ 17.2 $^3J_{HP}$ 22.4)	7.45 d.d (1H, C^3H, $^3J_{HH}$ 8.0, $^3J_{HH}$ 4.0), 7.89 s (1H, C^5H), 7.90 d (1H, C^7H, $^3J_{HH}$ 8.4), 8.12 d (1H, C^8H, $^3J_{HH}$ 8.4), 8.19 d (1H, C^4H, $^3J_{HH}$ 8.0), 8.94 d.d (1H, C^2H, $^3J_{HH}$ 4.0, $^4J_{HH}$ 2.0)	4.18	1.38 ($^3J_{HH}$ 7.0)	18.5 (THF), 18.6 ($CDCl_3$)
IIIi	*t*-Bu	5.46 ($^3J_{HH}$ 17.5, $^2J_{HP}$ 20.0)	6.69 ($^3J_{HH}$ 17.5, $^3J_{HP}$ 22.9)	0.98 s (9H, CH_3)	3.98	1.24 ($^3J_{HH}$ 7.2)	19.1 (THF)

[a] ^{31}P NMR spectrum (THF), δ, ppm: 18.8 (**IIIa**), 19.8 (**IIIb**), 19.4 (IIIc), 19.7 (**IIId**).

constants with the phosphorus nucleus [40]. The observed constant $^3J_{HP}$ equals to 22.4–22.8 Hz and is close to the $^3J_{HP}$ *cis* value in compounds **IIa–g**. *trans*-Configuration was unambiguously proved by the value of the vicinal coupling constant $^3J_{HH}$ 17.2–17.6 Hz [42].

Aliphatic 1-hexyne **Ih** cleanly reacted with diethylphosphorous acid: 100% conversion of $HP(O)(OEt)_2$ was reached at the use as catalyst both $Pd(PPh_3)_4$ and $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of PPh_3. The reaction in both cases was regiospecific and afforded (*O,O*-diethyl)-1-butylethenylphosphonate **IIh** as the sole reaction product isolated in 82 and 76% yield respectively. The structure and composition of compound **IIh** were confirmed by spectral data and elemental analysis (see Table 3 and EXPERIMENTAL).

With the sterically overloaded tert-butylacetylene **Ii** the reaction rate was significantly slower, and the amount of $Pd(PPh_3)_4$ required was increased to 10 mol%. The reaction afforded predominantly **IIIi** isomer.

The interesting feature in the spectral characteristics of isomers **IIi** and **IIIi** consists in small difference between the corresponding chemical shifts in ^{31}P NMR spectra (Tables 3 and 4): The respective chemical shifts differ only by 0.2 ppm. This fact supports the assumption on the aninisotropic effect of aromatic rings on the phosphorus resonance in the pairs (**IIIa–g**)/(**IIa–g**). The vinyl protons signals belonging to isomer **IIi** (Table 3) appear as doublets with characteristic coupling constants $^3J_{HP}$. No coupling of geminal protons revealed in compounds **IIa–h** was observed in the spectrum of compound **IIi** apparently due to decrease in the HCH bond angle caused by the bulky *tert*-butyl substituent [40].

It was noted before [40], that the presence of electron-withdrawing substituents in β-substituted ethenylphosphonates reduced the value of coupling constant $^2J_{HP}$. Actually, in the ^{1}H NMR spectrum of isomer **IIIi** (Table 4) the constant $^2J_{HP}$ amounts to 20.0 Hz against 16.8–17.2 Hz for ethenylphosphonates **IIIe–g** which contain a heteroaromatic substituent in the β-position.

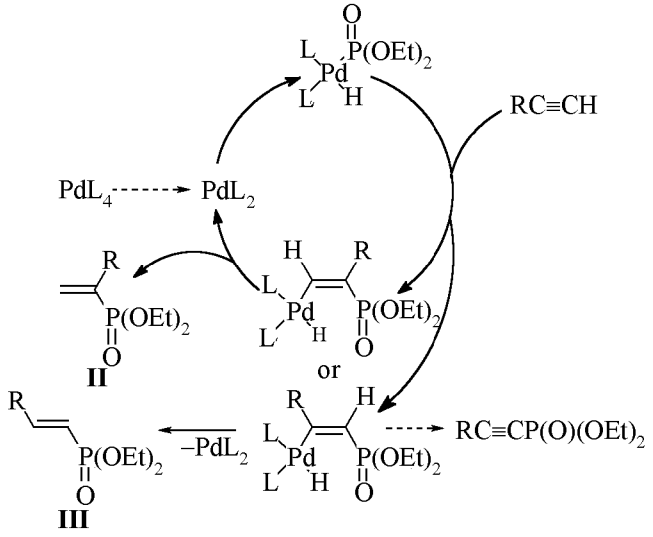
In contrast to hydrophosphorylation of arylacetylenes **Ib, c** containing a π-donor group MeO in the ring, the reaction of aliphatic 3-methoxy-1-propyne with diethyl phosphite proceeds very slowly. We

obtained less than 10% of reaction product [δ 16.6 ppm (THF)] after heating the reaction mixture for 30 h under standard conditions in the presence of $Pd(PPh_3)_4$.

The experimental material collected by now is not sufficient for formulation of a detailed reaction mechanism. The key stages of the reaction are evidently oxidative addition of dialkylphosphorous acid to the zero-valent palladium, insertion of acetylene, and reductive elimination of the product. The oxidative addition of a P-H bond to complexes $Pd(PCy_3)_2$, $Pt(PEt_3)_3$ and $RhCl(PPh_3)_3$ was established in [35, 43, 44]. The question is still open whether acetylene inserts into Pd-H or Pd-P bond. In hydrophosphorylation of olefins catalyzed by palladium the participation of the P–H bond was proved [43]. It was established [44] that hydrophosphorylation of terminal acetylenes catalyzed by rhodium occurred with alkyne insertion into the Rh–H bond. However in this case the main reaction product was a β-substituted ethenylphosphonate (regioselectivity over 98%) whose formation was expected by steric reasons.

The possibility of the alternative path, insertion into the metal phosphorus bond was demonstrated on hydrophosphination of acrylonitrile catalyzed by platinum [45, 46]. This notion was suggested in discussing the mechanism of diphenylphosphine oxide addition to acetylenes in the presence of diphenylphosphinic acid catalyzed by palladium [47]. The possibility of acetylene insertion into the Pd–P bond is directly proved by results obtained in [48] on addition of $Ph_2P–PPh_2$ to terminal acetylenes catalyzed by $Pd(PPh_3)_4$.

It was reported in [49] that at bis-hydrophosphorylation of arylacetylenes in boiling toluene catalyzed by palladium were isolated as side products the corresponding 2-arylethynylphosphonates. This fact is a serious argument supporting the insertion mechanism into the Pd–P bond for the only possibility of 2-arylethynylphosphonate formation is the β-hydride elimination from the corresponding intermediate.



Regretfully in neither of reaction we studied we detected formation of $RC≡CP(O)(OEt)_2$ likely because of using milder conditions in carrying out the processes. Nonetheless, the assumed scheme is in agreement with the found in our study deceleration of reaction at increased bulk of a substituent not only in the initial acetylene but also at the phosphorus atom [at the use of $HP(O)(OSiMe_3)_2$].

In the framework of this scheme the introduction into the molecule of acetylene RC≡CH of electron-withdrawing substituents causing formation of a partial positive charge on the β-carbon should decrease both the reaction rate and selectivity. This assumption was confirmed at the use of heteroarylacetylenes **Ie–g**.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometer Varian VXR-400 at operating frequencies 400 and 101 MHz respectively. ^{31}P NMR spectra were recorded on spectrometers Varian FT-80A or Brucker 80-WP at operating frequency 32.4 MHz. Chemical shifts are given in the δ-scale relative to TMS or 85% H_3PO_4. In some cases the chemical shifts were measured from the signals of residual protons or the carbon atom of $CDCl_3$ (7.25 and 77.0 ppm respectively). IR spectra were measured on a Fourier spectrometer IKAR (ZAO "Mikrotekh", Russia), resolution 1 cm^{-1}, number of scans 30.

THF was boiled and distilled in succession from KOH and Na and then stored on sodium benzophenone ketyl. Before use it was degassed and distilled through a vacuum manifold into a cooled reaction ampule. The preparative column chromatography was carried out using silica gel L40/100 or Silpearl (Chemapol) and aluminum oxide (neutral, Brockmann activity II grade, Reanal).

3-Ethynylquinoline (If). To a solution of 1.0 ml (7.4 mmol) of 3-bromoquinoline, 107 mg (0.15 mmol) of Pd(PPh3)2Cl2, 59 mg (0.31 mmol) of CuI, 1.6 ml (11.5 mmol) of Et_3N (freshly distilled from NaOH) in 3.8 ml of anhydrous THF while stirring under atmosphere of dry argon was slowly added dropwise a solution of 1.3 ml (9.2 mmol) of trimethylsilylacetylene in 0.7 ml of THF. The reaction mixture gradually

turned dark, and a voluminous precipitate separated. After the stirring at room temperature was continued for 24 h the reaction mixture was evaporated in a vacuum, the residue was diluted with water and extracted with Et_2O. The ether extracts were washed with saturated water solution of NaCl, and dried on $MgSO_4$. The solvent was distilled off in a vacuum, and the residue was submitted to chromatography on silica gel using as eluent a mixture of petroleum ether and dichloromethane gradually increasing the eluent polarity. We obtained 1.59 g (96%) of trimethylsilylethynylquinoline. R_f 0.25 (Silufol UV 254, CH_2Cl_2). ^{1}H NMR spectrum (CDCl3), δ, ppm: 0.31 s (9H, CH_3), 7.56 m (1H, C^6H), 7.72 m (1H, C^7H), 7.77 d (1H, C^5H, $^3J_{HH}$ 8.4 Hz), 8.09 d (1H, C^8H, $^3J_{HH}$ 8.4 Hz), 8.26 s (1H, C4H), 8.92 s (1H, C^2H).

To a solution of 1.59 g (7.1 mmol) of 3-trimethylsilylethynylquinoline in 5 ml of anhydrous MeOH under atmosphere of dry argon was added 1.93 g (14.0 mmol) of K_2CO_3. After stirring at room temperature for 2 h the reaction mixture was filtered and evaporated on a rotary evaporator. The residue was diluted with ether and submitted to chromatography on Al_2O_3. We obtained 0.71 g (66%) of compound **If**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.30 s (1H, C≡CH), 7.51 m (1H, C^6H), 7.69 m (2H, C^5H + C^7H), 8.08 d (1H, C8H, $^3J_{HH}$ 8.0 Hz), 8.21 s (1H, C^4H), 8.93 s (1H, C^2H).

6-Ethynylquinoline (Ig) was prepared in a way similar to the synthesis of compound **If**. The 6-trimethylsilylethynylquinoline was obtained in 56% yield from 1.043 g (5.01 mmol) of 6-bromoquinoline, 71 mg (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 39 mg (0.20 mmol) of CuI, 1.05 ml (7.5 mmol) Et_3N, and 0.85 ml (6.0 mmol) of trimethylsilylacetylene in 3 ml of anhydrous THF. Reaction time 24 h. The product was submitted to chromatography on silica gel using as eluent a mixture of petroleum ether and ethyl acetate gradually increasing the eluent polarity. R_f 0.4 (Silufol UV-254, petroleum ether–EtOAc, 2 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.29 s (9H, CH3), 7.41 d.d (1H, C^3H, $^3J_{HH}$ 8.4, $^3J_{HH}$ 4.0 Hz), 7.74 d (1H, C^7H, $^3J_{HH}$ 8.8 Hz), 7.97 s (1H, C^5H), 8.03 d (1H, C^8H, $^3J_{HH}$ 8.8 Hz), 8.10 d (1H, C^4H, $^3J_{HH}$ 8.4 Hz), 8.90 br.d (1H, C^2H).

To a solution of 0.535 g (2.37 mmol) of 6-trimethylsilylethynylquinoline in 0.4 ml of Et_2O and 1.8 ml of MeOH under argon atmosphere was added 0.149 g (1.08 mmol) of K_2CO_3. After stirring at room temperature for 2.5 h the reaction mixture was diluted with water and extracted wuth Et_2O. The ether extracts were washed with saturated water solution of NaCl, and dried on $MgSO_4$. The solvent was distilled off in a vacuum, and the residue was submitted to chromatography on silica gel using as eluent Et_2O. We obtained 0.332 g (91%) of compound **Ig**. R_f 0.7 (Silufol UV-254, Et_2O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.20 s (1H, C–CH), 7.42 d.d (1H, C^3H, $^3J_{HH}$ 8.4, $^3J_{HH}$ 4.4 Hz), 7.76 d.d (1H, C^7H, $^3J_{HH}$ 8.8, $^4J_{HH}$ 2.0 Hz), 7.99 d (1H, C^5H, $^4J_{HH}$ 2.0 Hz), 8.05 d (1H, C^8H, $^3J_{HH}$ 8.8 Hz), 8.11 d.d (1H, C^4H, $^3J_{HH}$ 8.4, $^4J_{HH}$ 1.6 Hz), 8.92 d.d (1H, C^2H, $^3J_{HH}$ 4.4, $^4J_{HH}$ 1.6 Hz).

4-Methoxyphenylacetylene (Ib) [50], 6-methoxy-2-ethynylnaphthalene (**Ic**) [51], ethynylferrocene (**Id**) [52], 3-ethynylpyridine (**Ie**) [53], *tert*-butylacetylene (**Ii**) [54], trimethylsilylacetylene [55], $Pd(PPh_3)_4$ [56], and $Pd_2(dba)_3 \cdot CHCl_3$ [57] were synthesized by published procedures. The other reagents that were commercially available were purified before use by distillation in a flow of dry argon or by recrystallization.

(*O,O*-Diethyl)-1-phenylethenylphosphonate (IIa). A mixture of 1.14 g (11.2 mmol) of phenylacetylene (**Ia**), 1.38 g (10.0 mmol) of diethyl phosphite, and 0.34 g (0.3 mmol) of $Pd(PPh_3)_4$ in 10 ml of anhydrous THF was heated in a sealed evacuated ampule at 67°C for 15 h. The ampule was opened, the solvent was removed on a rotary evaporator, the residue was distilled in a vacuum in an argon flow. We obtained 1.80 g (75%) of phosphonate **IIa** as a yellowish viscous fluid. bp 112–115°C (10^{-1} mm Hg) [20, 24, 26, 28]. IR spectrum (from film), ν, cm^{-1}: 2981, 2906, 1494, 1444, 1392, 1261, 1234, 1162, 1099, 1051, 1024, 962, 846, 781, 713. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.1 d (CH_3, $^3J_{CP}$ 6.3 Hz), 62.1 d (OCH_2, $^2J_{CP}$ 5.5 Hz), 127.3 d ($C^{2'}$ + $C^{6'}$, $^3J_{CP}$ 5.1 Hz), 128.1 s ($C^{4'}$), 128.3 s ($C^{3'}$ + $C^{5'}$), 131.6 d ($C^{2'}$, $^2J_{CP}$ 8.1 Hz), 136.6 d ($C^{1'}$, $^2J_{CP}$ 12.1 Hz), 139.6 d (CP, $^1J_{CP}$ 174.2 Hz).

(*O,O*-Diethyl)-1-(4-methoxyphenyl)ethenylphosphonate (IIb) was prepared similarly to **IIa** from 1.06 g (8.0 mmol) of 4-methoxyphenylacetylene (**Ib**), 1.1 ml (8.5 mmol) of $HP(O)(OEt)_2$, 126 mg (122 mol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 252 mg (0.96 mmol) of PPh_3 in 8 ml of anhydrous THF. Reaction time 29 h. We obtained 1.41 g (65%) of phosphonate **IIb** as a yellowish viscous fluid. bp 133–135°C (10^{-1} mm Hg), R_f 0.5 (Silufol UV-254, EtOAc). IR spectrum (from film), ν, cm^{-1}: 2983, 1604, 1511, 1295, 1255, 1180, 1025, 968, 836, 792. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.1 d (CH_2CH_3, $^3J_{CP}$ 6.1 Hz), 55.1 s (OCH_3), 62.0 d (OCH_2, $^2J_{CP}$ 5.6 Hz), 113.6 s ($C^{3'}$ + $C^{5'}$), 128.5 d

($C^{2'}$ + $C^{6'}$, $^3J_{CP}$ 5.9 Hz), 129.9 d (C^2, $^2J_{CP}$ 8.1 Hz), 133.5 d ($C^{1'}$), 138.7 d (CP, $^1J_{CP}$ 178.2 Hz), 159.5 s (COMe). Found, %: C 58.22; H 7.09; P 11.71. $C_{13}H_{19}O_4P$. Calculated, %: C 57.77; H 7.09; P 11.46.

(*O,O*-Diethyl)-1-(6-methoxy-2-naphthyl)ethenylphosphonate (IIc) was prepared similarly to **IIa** from 0.351 g (1.93 mmol) of 6-methoxy-2-ethynylnaphthalene (**Ic**), 0.265 g (1.92 mmol) of $HP(O)(OEt)_2$, 31 mg (30 mol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 60 mg (0.23 mmol) of PPh3 in 1.9 ml of anhydrous THF. Reaction time 37 h. The solvent was removed on a rotary evaporator, the residue was submitted to chromatography on silica gel using as eluent ether–hexane mixture gradually increasing the eluent polarity. We obtained 0.448 g (73%) of phosphonate **IIc** as viscous yellow fluid. R_f 0,25 (Silufol UV-254, Et_2O). IR spectrum (from film), ν, cm^{-1}: 2985, 1627, 1604, 1483, 1438, 1390, 1255, 1205, 1164, 1049, 1025, 968, 856, 790, 754, 723. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.2 d (CH_2CH_3, $^3J_{CP}$ 6.3 Hz), 55.2 s (OCH_3), 62.2 d (OCH_2, $^2J_{CP}$ 5.7 Hz), 105.6 s ($C^{7'}$ or $C^{5'}$), 119.1 s ($C^{5'}$ or $C^{7'}$), 125.6 d ($C^{3'}$ or $C^{1'}$, $^3J_{CP}$ 6.0 Hz), 126.6 d ($C^{1'}$ or $C^{2'}$, $^3J_{CP}$ 6.0 Hz), 126.8 s ($C^{4'}$), 128.6 s ($C^{9'}$), 129.8 s ($C^{8'}$), 131.0 d (C^2, $^2J_{CP}$ 8.0 Hz), 131.7 d (C^4, $^2J_{CP}$ 12.1 Hz), 134.2 s ($C^{10'}$), 139.6 d (CP, $^1J_{CP}$ 175.0 Hz), 158.1 s (COMe). Found, %: C 63.83; H 6.68; P 9.69. $C_{17}H_{21}O_4P$. Calculated, %: C 63.74; H 6.61; P 9.67.

(*O,O*-Diethyl)-1-(ferrocenyl)ethenylphosphonate (IId) was prepared similarly to **IIa** from 0.630 g (3.00 mmol) of ethynylferrocene (**Id**), 0.416 g (3.01 mmol) of $HP(O)(OEt)_2$, 47 mg (45 mol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 103 mg (0.39 mmol) of PPh_3 in 3.5 ml of anhydrous THF. Reaction time 39 h. The solvent was removed on a rotary evaporator, the residue was submitted to chromatography on Al_2O_3 using as eluent benzene ether mixture gradually increasing the eluent polarity. We obtained unstable yellow-brown oily fluid, R_f 0.44 (Alufol, Et_2O).

(*O,O*-Diethyl)-1-(3-pyridyl)ethenylphosphonate (IIe) was prepared similarly to **IIa** from 0.197 g (1.91 mmol) of 3-ethynylpyridine (**Ie**), 0.236 g (1.71 mmol) of $HP(O)(OEt)_2$, 27 mg (26 mol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 55 mg (0.21 mmol) of PPh_3 in 1.7 ml of anhydrous THF. Reaction time 26 h. The solvent was removed on a rotary evaporator, the residue was submitted to chromatography on silica gel using as eluent benzene ethyl acetate mixture gradually increasing the eluent polarity. We obtained 0.242 g (59%) of phosphonate **IIe** as yellowish viscous fluid. R_f 0.45 (Silufol UV-254, C_6H_6–acetone, 1 : 1).

Besides 0.060 g (15%) of *trans*-(*O,O*-diethyl)-2-(3-pyridyl)ethenylphosphonate (**IIIe**) [58] was isolated, R_f 0.35 (Silufol UV-254, C_6H_6–acetone, 1$^: 1).

(*O,O*-Diethyl)-1-(3-quinolyl)ethenylphosphonate (IIf) was prepared similarly to **IIa** from 0.173 g (1.13 mmol) of 3-ethynylquinoline (**If**), 0.149 g (1.08 mmol) of $HP(O)(OEt)_2$, 17 mg (16.4 mol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 36 mg (137 mol) of PPh_3 in 1.1 ml of anhydrous THF. Reaction time 114 h. The solvent was removed on a rotary evaporator, the residue was submitted to chromatography on silica gel using as eluent hexane–ethyl acetate mixture gradually increasing the eluent polarity. We obtained 0.223 g (71%) of isomers **IIf** and **IIIf** mixture in the ratio of 84 : 16 (^{31}P NMR). R_f 0.4 (Silufol UV-254, EtOAc).

The separation of 133.5 mg of the isomer mixture obtained was carried out by preparative thin layer chromatography on Silufol plates (200 × 200 mm) at repeated treating with eluent (C_6H_6–acetone, 3 : 1). We obtained 110 mg (82%) of phosphonate **IIf**. Besides 19 mg (14%) of *trans*-(*O,O*-diethyl)-2-(3-quinolyl)ethenylphosphonate (**IIIf**) was isolated.

(*O,O*-Diethyl)-1-(6-quinolyl)ethenylphosphonate (IIg) was prepared similarly to compound **IIa** from 0.125 g (0.82 mmol) of 6-ethynylquinoline **Ig**, 0.108 g (0.78 mmol) of $HP(O)(OEt)_2$, 13 mg (12.5 μmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 25 mg (95 μmol) of PPh_3 in 1 ml of anhydrous THF. Reaction time 117 h. The solvent was removed on a rotary evaporator, the residue was submitted to chromatography on silica gel using as eluent hexane–ethyl acetate mixture gradually increasing the eluent polarity. We obtained 0.155 g (68%) of isomers **IIg** and **IIIg** mixture in the ratio of 4 : 1 (^{31}P NMR). R_f 0.35 (Silufol UV-254, EtOAc).

The separation of 132.5 mg of the isomer mixture obtained was carried out by preparative thin layer chromatography on Silufol plates (200 × 200 mm) at repeated treating with eluent (CCl_4–acetone, 3 : 1). We obtained 94.4 mg (71%) of phosphonate **IIg**. Besides 13 mg (10%) of *trans*-(*O,O*-diethyl)-2-(6-quinolyl)ethenylphosphonate (**IIIg**) was isolated.

(*O,O*-Diethyl)-1-butylethenylphosphonate (IIh) was prepared in the same way as compound **IIa** from 0.91 g (11.1 mmol) of hexyne-1, 1.38 g (10.0 mmol) of $HP(O)(OEt)_2$, and 0.38 g (0.3 mmol) of $Pd(PPh3)_4$ in 10 ml of anhydrous THF. Reaction time 12 h. We obtained 1.81 g (82%) of phosphonate **IIh** as colorless fluid, bp 59–61°C (10^{-1} mm Hg).

IR spectrum (from film), ν, cm^{-1}: 2970, 2935, 2880, 1450, 1395, 1255, 1240, 1185, 1165, 1100, 1055, 1030, 960, 795, 740. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.4 s ($C^{4'}$), 15.9 d (OCH_2CH_3, $^3J_{CP}$ 6.1 Hz), 21.8 s ($C^{3'}$), 29.7 d ($C^{2'}$, $^3J_{CP}$ 5.2 Hz), 31.4 d ($C^{1'}$, $^2J_{CP}$ 10.8 Hz), 61.2 d (OCH_2, $^2J_{CP}$ 5.4 Hz), 128.4 d (C^2, $^2J_{CP}$ 6.7 Hz), 139.1 d (CP, $^1J_{CP}$ 170.8 Hz). Found, %: C 54.49; H 9.64. $C_{10}H_{21}O_3P$. Calculated, %: C 54.53; H 9.61.

Reaction of *tert*-butylacetylene with diethyl phosphite. A mixture of 0.091 g (1.11 mmol) of *tert*-butylacetylene, 0.138 g (1.0 mmol) of $HP(O)(OEt)_2$, 116 mg (0.10 mmol) of $Pd(PPh_3)_4$ in 1 ml of anhydrous THF was heated for 120 h in a sealed evacuated ampule to 67°C. The ampule was opened, the catalyst precipitated at cooling and was filtered off. The solvent was removed in a vacuum, the residue was analyzed by spectral methods. A mixture was obtained of (*O*,*O*-diethyl)-1-(tert-butyl)ethenylphosphonate **IIi** and *trans*-(*O*,*O*-diethyl)-2-(*tert*-butyl)ethenylphosphonate (**IIIi**) in 34 : 66 ratio (^1H NMR).

REFERENCES

1. Promonenkov, V.K. and Ivin, S.Z., *Usp. Khim.*, 1968, vol. 37, p. 1577.
2. *The Role of Phosphonates in Living Systems*, Hilderbrand, R.L., Boca Raton, FL: CRC Press, p. 1983.
3. UK Patent 2102427, 1983; *Chem. Abstr.*, 1983, vol. 99, 88368d.
4. Giordano, C. and Castaldi, G., *J. Org. Chem.*, 1989, vol. 54, p. 1470.
5. Engel, R., *Chem. Rev.*, 1977, vol. 77, p. 349.
6. Goulioukina, N.S., Dolgina, T.M., Beletskaya, I.P., Henry, J.-C., Lavergne, D., Ratovelomanana-Vidal, V., and Genet, J.-P., *Tetrahedron: Asymmetry*, 2001, vol. 12, p. 319.
7. Gulyukina, N.S., Dolgina, T.M., Bondarenko, G.N., Beletskaya, I.P., Bondarenko, N.A., Anri, Zh.-K., Lavern', D., Ratovelomanana-Vidal', V., and Zhene, Zh.-P., *Zh. Org. Khim.*, 2002, vol. 38, p. 600.
8. Minami, T. and Motoyoshiya, J., *Synthesis*, 1992, p. 333.
9. Worms, K.H. and Schmidt-Dunker, M., *Organic Phosphorus Compounds*, Kosolapoff, G.M. and Maier, L., Eds., New York: John Wiley, 1976, vol. 7, Ch. 18.
10. Conant, J.B. and Coyne, B.B., *J. Am. Chem. Soc.*, 1922, vol. 44, p. 2530.
11. German Patent 2060259, 1972; Chem. Abstr., 1972, vol. 77, 101895r.
12. Abramov, V.S., *Dokl. Akad. Nauk SSSR*, 1950, vol. 73, p. 487.
13. Yamashita, M., Morizane, T., Fujita, K., Nakatani, K., and Inokawa, S., *Bull. Chem. Soc. Jpn.*, 1987, vol. 60, p. 812.
14. Gomyo, T., Yoshida, H., Ogata, T., Inokawa, H., and Inokawa, S., *Nippon Kagaku Kaishi.*, 1974, p. 1093; *Ref. Zh. Khim.*, 1975, 2Zh347.
15. Pudovik, A.N., Gozman, I.P., and Nikitina, V.I., *Zh. Obshch. Khim.*, 1963, vol. 33, p. 3201.
16. PCT Int. Appl. Patent 9624599, 1996; Chem. Abstr., 1996, vol. 125, 222166x.
17. German Patent 1159443, 1963; *Chem. Abstr.*, 1964, vol. 60, 10718f.
18. Axelrad, G., Laosooksathit, S., and Engel, R., *PCT Int. Appl. J. Org. Chem.*, 1981, vol. 46, p. 5200.
19. Banerjee, S., Engel, R., and Axelrad, G., *Phosphorus and Sulfur.*, 1983, vol. 15, p. 15.
20. Tavs, P. and Weitkamp, H., *Tetrahedron*, 1970, vol. 26, p. 5529.
21. Hirao, T., Masunaga, T., Ohshiro, Y., and Agawa, T., *Tetrahedron Lett.*, 1980, vol. 21, p. 3595.
22. Hirao, T., Masunaga, T., Yamada, N., Ohshiro, Y., and Agawa, T., *Bull. Chem. Soc. Jpn.*, 1982, vol. 55, p. 909.
23. Holt, D.A. and Erb, J.M., *Tetrahedron Lett.*, 1989, vol. 30, p. 5393.
24. Krueger, W.E., McLean, M.B., Rizwaniuk, A., Maloney, J.R., Behelfer, G.L., and Boland, B.E., *J. Org. Chem.*, 1978, vol. 43, p. 2877.
25. Yamashita, M., Sugiura, M., Oshikawa, T., and Inokawa, S., *Synthesis*, 1987, p. 62.
26. Shin, C., Yonezawa, Y., Katayama, K., and Yoshimura, J., *Bull. Chem. Soc. Jpn.*, 1973, vol. 46, p. 1727.
27. Yamashita, M., Tamada, Y., Iida, A., and Oshikawa, T., *Synthesis*, 1990, p. 420.
28. Russell, G.A., Ngoviwatchai, P., *J. Org. Chem.*, 1989, vol. 54, p. 1836.
29. Porskamp, P.A.T.W., Lammerink, B.H.M., and Zwanenburg, B., *J. Org. Chem.*, 1984, vol. 49, p. 263.
30. Kojima, M., Yamashita, M., Yoshida, H., and Ogata, T., *Synthesis.*, 1979, p. 147.
31. Yamashita, M., Kojima, M., Yoshida, H., Ogata, T., and Inokawa, S., *Bull. Chem. Soc. Jpn.*, 1980, vol. 53, p. 1625.
32. Maas, G. and Regitz, M., *Chem. Ber.*, 1976, vol. 109, p. 2039.
33. Leost, F. and Doutheau, A., *Tetrahedron Lett.*, 1999, vol. 40, p. 847.
34. Blicke, F.F. and Raines, S., *J. Org. Chem.*, 1964, vol. 29, p. 2036.
35. Han, L.-B. and Tanaka, M., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 1571.

36. Semenzin, D., Etemad-Moghadam, G., Albouy, D., Diallo, O., and Koenig, M., *J. Org. Chem.*, 1997, vol. 62, p. 2414.
37. Beletskaya, I.P., Dolgina, T.M., and Goulioukina, N.S., Abstracts of Papess, *International Memorial I. Postovsky Conference on Organic Chemistry, Ekaterinburg*, 1998, p. 47.
38. Truel, I., Mohamed-Hachi, A., About-Jaudet, E., and Collignon, N., *Synth. Commun.*, 1997, vol. 27, p. 297.
39. Kazankova, M.A., Efimova, I.V., Kochetkov, A.N., Afanas'ev, V.V., Beletskaya, I.P., and Dixneuf, P.H., *Synlett.*, 2001, p. 497.
40. Sainz-Diaz, C.I., Galvez-Ruano, E., Hernandez-Laguna, A., and Bellanato, J., *J. Org. Chem.*, 1995, vol. 60, p. 74.
41. Lin-Vien, D., Colthup, N.B., Fateley, W.G., and Grasselli, J.G., *Infrared and Raman Characteristic Frequencies of Organic Molecules*, San Diego: Acad. Press, 1991, p. 263.
42. Ogawa, T., Usuki, N., and Ono, N., *J. Chem. Soc., Perkin Trans. II*, 1998, vol. 17, p. 2953.
43. Han, L.-B., Mirzaei, F., Zhao, C.-Q., and Tanaka, M., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 5407.
44. Zhao, C.-Q., Han, L.-B., Goto, M., and Tanaka, M., *Angew. Chem., Int. Ed.*, 2001, vol. 40, p. 1929.
45. Costa, E., Pringle, P.G., Smith, M.B., and Worboys, K., *J. Chem. Soc., Dalton Trans.*, 1997, p. 4277.
46. Wicht, D.K., Kourkine, I.V., Kovacik, I., and Glueck, D.S., *Organometallics*, 1999, vol. 18, p. 5381.
47. Han, L.-B., Hua, R., and Tanaka, M., *Angew. Chem., Int. Ed.*, 1998, vol. 37, p. 94.
48. Kazankova, M.A., Beletskaya, I.P., Afanas,ev, V.V., Shulupin, M.O., and Efimova, I.V., Abstracts of Papers, *XXth International Conference on Organo metallic Chemistry* Corfu, 2002, p. 185.
49. Allen, Jr. A., Manke, D.R., and Lin, W., *Tetrahedron Lett.*, 2000, vol. 41, p. 151.
50. Smissman, E.E., Johnson, R.H., Carlson, A.W., and Aycock, B.F., *J. Am. Chem. Soc.*, 1956, 78, 3395; Johnson, J.R., McEewen, W.L., *J. Am. Chem. Soc.*, 1926, vol. 48, p. 469.
51. Hiyama, T., Wakasa, N., Ueda, T., and Kusumoto, T., *Bull. Chem. Soc. Jpn.*, 1990, vol. 63, p. 640.
52. Abram, T.S. and Watts, W.E., *Synthesis and Reactivity in Inorganic and Metalorganic Chemistry*, 1976, vol. 6, p. 31.
53. Sakamoto, T., Shiraiwa, M., Kondo, Y., and Yamanaka, H., *Synthesis.*, 1983, p. 312.
54. Bartlett, P.D. and Rosen, L.J., *J. Am. Chem. Soc.*, 1942, vol. 64, p. 543.
55. Chuchuryukin, A.V., *Cand. Sci. (Chem.) Dissertation*, Moscow, 2001, p. 62.
56. Coulson, D.R., *Inorg. Syntheses*, 1972, vol. 13, p. 121.
57. Ishii, Y., *Annals New York Academy of Sciences*, 1972, vol. 239, p. 114.
58. L'vova, S.D., Kozlov, Yu.P., and Gunar, V.I., *Zh. Obshch. Khim.*, 1977, vol. 47, p. 1251.