SYNTHESIS OF N'-PHOSPHINATODIAZENE N-OXIDES

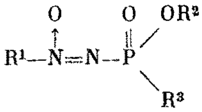
**S. G. Zlotin, M. V. Sharashkina, Yu. A. Strelenko,
and O. A. Luk'yanov**

UDC 542.91:547.231:547.241:
547.491.8:547.235.4

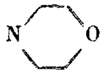
We have developed a regiospecific method for synthesis of N'-phosphinatodiazene N-oxides, a previously unknown type of azoxy compounds in which the diazene oxide fragment is directly connected with the phosphinate group. The method involves reaction of amidoesters of alkyl- and arylphosphonic acids with nitroso compounds in the presence of dibromoisocyanurate.

Keywords: *regiospecificity, N'-phosphinatodiazene N-oxides, azoxy compounds, diazene oxide fragment, phosphinate group, amidoesters of alkylarylphosphonic acids, nitroso compounds.*

Earlier we reported obtaining N'-phosphonatodiazene N-oxides (**1**) of azoxy compounds, in which the diazene oxide group is directly connected with the phosphorus atom [1, 2]. In this paper, we suggest an approach to synthesis of previously unknown structural analogs of **1**:N'-phosphinatodiazene N-oxides (**2**), compounds in which the diazene oxide fragment is connected with the phosphinate group.

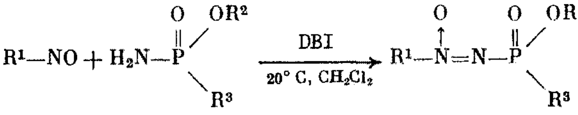


$R^1{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}P(=O)(OR^2)R^3$

R^1 = Alk, Ar, Het; R^2 = Alk, Ar; R^3 = —OAlk, —OAr,  (**1**);

R^3 = Alk, Ar (**2**).

For the first time we have shown that amidoesters of phosphonic acids react with nitroso compounds in the presence of dibromoisocyanurate (DBI) with formation of the desired N'-phosphinatodiazene N-oxides (**2**). For the use of DBI for synthesis of asymmetrically substituted azoxy compounds, see [1-7].



$R^1{-}NO + H_2N{-}P(=O)(OR^2)R^3 \xrightarrow[20^\circ C,\ CH_2Cl_2]{DBI} R^1{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}P(=O)(OR^2)R^3$

(**3a—i**) (**2a—v**)

This reaction involves nitroso compounds of the aliphatic, alicyclic, and aromatic series. Of the amidophosphinates, the amido derivatives of methyl- and phenylphosphonic acids **3a-i** (R^3 = CH_3, Ph)* were involved in the process. The reactions proceed easily in a medium of chlorine-containing organic solvents at ~20°C. The yields of azoxy products (**2a-v**) are 10-65% (Table 1).

---

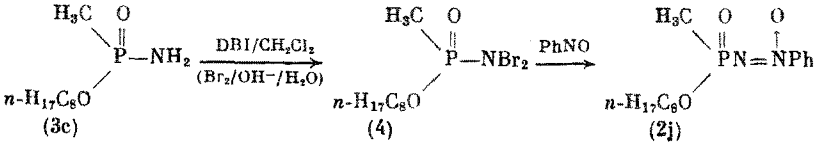
*We synthesized the amidophosphinates **3a-e**, not described previously, according to the standard scheme in [8]: treatment of the corresponding P-chloro derivatives with ammonia in ether.

N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow. Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 11, pp. 2648-2656, November, 1992. Original article submitted December 10, 1991.

N′-Phosphinatodiazene N-oxides **2a-v** are oily or crystalline materials, stable when stored at ~20°C. Chromatography of **2a-v** on Silpearl leads to partial decomposition of the products, which in our opinion explains the moderate yields of the target products isolated from the reaction mass by the indicated method. The physicochemical and spectral characteristics of **2a-v** are presented in Tables 1-3.

The synthesized compounds are pure regioisomers. The location of the oxygen atom in the azoxy group of the products was established on the basis of ^{13}C and ^{14}N NMR spectra of **2d, n**. The signal for the carbon bonded to the diazene oxide fragment in **2d, n** is appreciably broadened, which may be due only to spin–spin coupling through one $^{13}C-^{14}N$ bond with the oxide nitrogen atom of the diazene oxide group. In fact, the observed broadening disappears upon suppression of the rather narrow ($\Delta\nu_{1/2}$ = 80-250 Hz) signal of the latter at the ^{14}N frequency [9], which allows us to unambiguously assign the structure of N′-phosphinatodiazene N-oxides to the studied compounds **2a-v**.

The reaction mechanism is probably analogous to the mechanism for the process of formation of the diazene oxide group from amidophosphonates and nitroso compounds in the presence of DBI [2], and probably includes introduction of two bromine atoms into the molecules of the starting amido derivatives and reaction of the N,N-dibromoamides formed with the nitroso compounds present in the system, according to the scheme suggested in [10]. This hypothesis is confirmed by isolation of the low-stability P-(N,N-dibromoamido)-O-octyl-P-methylphosphinate (**4**) upon treatment of the corresponding amidophosphinate with DBI in an inert organic solvent (or with bromine in an alkaline aqueous solution) and synthesis of **2j** from **4** and nitrosobenzene under the conditions of the reaction under study.



EXPERIMENTAL

The IR spectra of the liquid compounds were taken in a thin layer and the IR spectra of the solid compounds were taken in a KBr disk on the Specord IR-75 spectrometer. The NMR spectra for the ^{1}H, ^{13}C, ^{14}N, and ^{31}P nuclei were obtained in acetone-d_6 on the Bruker AM-300 spectrometer at frequencies 300.13 (^{1}H), 75.5 (^{13}C), 21.7 (^{14}N), and 121.5 MHz (^{31}P). The chemical shifts of the ^{1}H and ^{13}C signals were measured relative to acetone-d_6 (δ 30.0 ppm); for ^{14}N, relative to nitromethane (external standard, δ 0.0 ppm); for ^{31}P, relative to the external standard H_3PO_4 (δ 0.0 ppm).

Dibromoisocyanurate [11], 2-nitro-2-nitrosopropane [12], 1-nitro-1-nitrosocyclopentane [13], 1-nitro-1-nitrosocyclohexane [13], amidophosphinates **3f-i** [8] were obtained according to literature techniques.

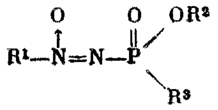
O-Alkyl-P-methyl and O-Cycloalkyl-P-phenyl-P-amidophosphinates (3a-e). Dry NH_3 was passed through a solution of 10 mmoles of the corresponding P-chlorophosphinate in 10 ml absolute ether at −50°C until precipitation stopped (~40 min). The precipitated NH_4Cl was filtered and washed with ether, and the solvent was removed. The products were crystallized from hexane. The yield and properties of **3a-e** are presented in Table 4.

N′-Phosphinatodiazene N-Oxides (2a-v). A mixture of 10 mmoles of the nitroso compound, 10 mmoles amidophosphinate, and 20 mmoles dibromoisocyanurate in 10 ml CH_2Cl_2 was stirred for 12-24 h at 20°C. The excess DBI and cyanuric acid were filtered off, washed with CH_2Cl_2 (2 × 5 ml). The filtrate was evaporated under vacuum. The products **2a-v** were isolated using TLC (Silpearl, ether as eluting agent). Compounds **2k, p, r, u** were crystallized additionally from hexane. The yields and properties of **2a-v** are presented in Table 1.

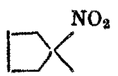
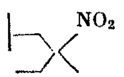
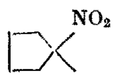
P-(N,N-Dibromoamido)-O-octyl-P-methylphosphinate (4). *A*. A mixture of 1.0 g (5 mmoles) O-octyl-P-methylamidophosphinate and 2.87 g (10 mmoles) dibromisocyanurate in 5 ml CH_2Cl_2 was stirred for 12 h at 20°C. The excess DBI and cyanuric acid were filtered off and washed with CH_2Cl_2 (2 × 3 ml). The filtrate was evaporated under vacuum. Obtained: 1.65 g (94%) **4** in the form of a transparent yellow oil. IR spectrum (ν, cm^{-1}): 1050 (P−O−C), 1260 (P=O). PMR spectrum (δ, ppm): 1.0 m (15H, C_8H_{17}); 1.79 d (3H, PCH_3); 4.05 m (2H, C_8H_{17}). Found, %: P 8.49; Br 43.80. $C_9H_{20}PO_2NBr_2$. Calculated, %: P 8.55; Br 39.02.

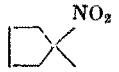
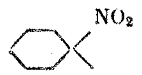
B. 1.5 g (10 mmoles) bromine was added dropwise to a solution of 1.0 g (5 mmoles) O-octyl-P-methylamidophosphinate and 0.7 g (5.3 mmoles) K_2CO_3 in 5 ml water at 0°C with stirring. The mixture was stirred for 30 min at 0°C and then for 1 h at 20°C. CH_2Cl_2 (15 ml) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 ×

TABLE 1. Yields and Some Physicochemical and Spectral Characteristics of N′-Phosphinatodiazene N-Oxides*



$R^1{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}\overset{\overset{O}{\|}}{P}(OR^2)R^3$

Compound	R^1	R^2	R^3	Yield, %	IR spectrum (ν, cm^{-1})				PMR spectrum (δ, ppm; J, Hz)†		Found/Calculated, %			
					$\overset{O}{\uparrow}$ N=N	P=O	P–O–C P–O–N	other characteristic absorption bands	R^1	R^2, R^3	C	H	N	P
2a	–Ph	Me	Me	13	1490	1220	1040	–	7.36 m (3H, Ph); 8.15 m (2H, Ph)	1.73 d (3H, CH_3, J=8); 3.90 d (3H, OCH_3, J=10)	45.21 44.86	5.03 5.14	12.79 13.08	13.95 14.48
2b	–$C(CH_3)_2NO_2$	Et	Me	10	1515	1230	1040	1575 (NO_2)	2.07 s (6H, CH_3)	1.27 t (3H, CH_3, J=7); 1.67 d (3H, CH_3, J=8); 4.20 m (2H, CH_2)	29.77 30.12	5.91 5.86	17.36 17.57	12.13 12.97
2c		Et	Me	18	1510	1220	1040	1570 (NO_2)	1.91 m (4H, CH_2); 2.77 m (4H, CH_2)	1.30 t (3H, CH_3, J=7); 1.73 d (3H, CH_3, J=8); 4.23 m (2H, CH_2O)	35.86 36.23	6.15 6.04	15.61 15.85	11.49 11,78
2d	–Ph	Et	Me	23	1490	1230	1040	–	7.57 m (3H, Ph); 8.17 m (2H, Ph)	1.33 t (3H, CH_3, J=7); 1.77 d (3H, CH_3, J=8); 4.30 m (2H, CH_2)	46.42 47.36	5.45 5.70	11.56 12.28	13.09 13.60
2e	–$C(CH_3)_2NO_2$	C_6H_{11}-c	Me	22	1520	1240	1020	1575 (NO_2)	2.08 s (6H, CH_3)	1.75 d (3H, CH_3, J=8); 4.60 m (1H, CH); 1.80 m (10H, $(CH_2)_5$)	40.84 40.93	6.93 6.82	13.51 14.32	10.26 10.57
2f		C_6H_{11}-c	Me	20	1520	1250	1010	1570 (NO_2)	1.92 m (4H, CH_2); 2.76 m (4H, CH_2)	1.70 d (3H, CH_3, J=8); 4.65 m (1H, CH); 1.65 m (10H, $(CH_2)_5$)	45.38 45.14	6.95 6.90	12.97 13.17	9.50 9.72
2g	–Ph	C_6H_{11}-c	Me	32	1490	1240	1020	—	7.43 m (3H, Ph); 8.15 m (2H, Ph)	1.73 d (3H, CH_3, J=8); 4.63 m (1H, CH); 1.65 m (10H, $(CH_2)_5$)	55.03 55.32	6.59 6.74	9.74 9.93	11.23 10.99
2h	–$C(CH_3)_2NO_2$	C_8H_{17}-*n*	Me	25	1515	1230	1030	1575 (NO_2)	2.13 s (6H, CH_3)	1.03 m (15H, C_8H_{17}); 1.66 d (3H, CH_3, J=8); 4.15 m (2H, CH_2)	43.75 44.55	8.21 8.04	12.43 12.99	9.03 9.59
2i		C_8H_{17}-*n*	Me	37	1520	1260	1030	1575 (NO_2)	1.92 m (4H, CH_2); 2.81 m (4H, CH_2)	1.03 m (15H, C_8H_{17}); 1.68 d (3H, CH_3, J=8); 4,15 m (2H, CH_2)	47.88 48.10	8.27 8.02	11.98 12.03	8.16 8.88

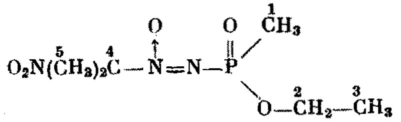
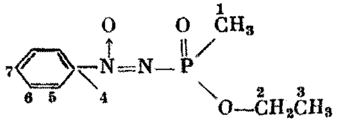
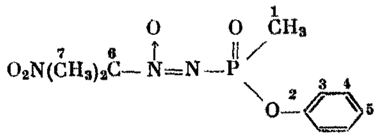
2j	–Ph	C_8H_{17}-*n*	Me	33	1490	1250	1020		7.42 m (3H, Ph); 8.10 m (2H, Ph)	1.02 m (15H, C_8H_{17}); 1.73 d (3H, CH_3, $J=8$); 4.20 m (2H, C_8H_{17})	58.03 57.69	8.14 8.01	8.69 8.97	9.71 9.93
2k	$-C(CH_3)_2NO_2$	Ph	Me	36	1500	1240	950	1570 (NO_2)	2.08 s (6H, CH_3)	1.85 d (3H, CH_3, $J=8$) 7.20 br.s (5H, OPh)	42.19 41.81	5.01 4.88	14.35 14.63	10.53 10.80
2l		Ph	Me	62	1510	1230	1030	1570 (NO_2)	1.87 m (4H, CH_2); 2.83 m (4H, CH_2)	1.83 d (3H, CH_3, $J=8$); 7.10 br.s (5H, OPh)	45.62 46.01	5.11 5.10	13.15 13.42	9.97 9.90
2m		Ph	Me	65	1520	1220	1020	1580 (NO_2)	1.50 m (6H, CH_2); 2.46 m (4H, CH_2)	1.87 d (3H, CH_3, $J=8$); 7.13 br.s (5H, OPh)	47.53 47.70	5.40 5.50	11.71 12.80	9.03 9.50
2n	–Ph	Ph	Me	52	1490	1250	950	–	7.42 m (3H, Ph); 8.12 m (2H, Ph)	1.92 d (3H, CH_3, $J=8$); 7.22 br.s (5H, OPh)	55.81 56.52	4.51 4.71	9.47 10.14	10.09 11.23
2o	$-C_6H_4-o-NO_2$	Ph	Me	41	1490	1250	950	1540 (NO_2)	7.65 s (4H, C_6H_4)	1.92 d (3H, CH_3, $J=8$); 7.15 br.s (5H, OPh)	48.72 48.59	3.92 3.74	12.89 13.08	9.92 9.66
2p	$-C(CH_3)_2NO_2$	Me	Ph	24	1510	1255	1040	1570 (NO_2)	2.05 d (6H, CH_3, $J=6$)	3.88 d (3H, CH, $J=8$); 7.56 m (5H, Ph)	41.31 41.81	4.99 4.88	14.27 14.63	11.4 10.80
2q	–Ph	Me	Ph	47	1490	1240	1040	–	7.38 m (5H, Ph)	3.96 d (3H, CH_3, $J=8$); 8.08 m (5H, Ph)	56.02 56.52	4.70 4.71	9.85 10.14	11.54 11.23
2r	$-C(CH_3)_2NO_2$	Et	Ph	48	1510	1270	1040	1575	2.02 d (6H, CH_3, $J=6$)	1.35 t (3H, CH_3, $J=7$); 4.25 m (2H, CH_2); 7.65 m (5H, Ph)	43.63 43.85	5.69 5.32	13.90 13.95	10.30 10.79
2s	$-C(CH_3)_2NO_2$	Bu-*n*	Ph	30	1520	1255	1040	1570	2.05 d (6H, CH_3, $J=6$)	1.26 m (7H, C_3H_7); 4.25 m (2H, CH_2); 7.63 m (5H, Ph)	47.10 47.40	6.13 6.08	12.68 12.76	9.08 9.42
2t		Bu-*n*	Ph	38	1505	1255	1045	1570	1.63 m (6H, CH_2-c); 2.50 m (4H, CH_2-c)	1.05 m (7H, C_3H_7); 4.23 m (2H, CH_2); 7.60 m (5H, Ph)	51.81 52.05	6.34 6.50	11.40 11.58	8.12 8.40
2u	–Ph	Bu-*n*	Ph	37	1490	1250	1020	–	7.31 m (5H, Ph)	1.35 m (7H, C_3H_7); 4.30 m (2H, CH_2); 8.01 m (5H, Ph)	60.05 60.36	5.79 5.97	8.83 8.80	9.20 9.74
2v	$-C(CH_3)_2NO_2$	C_6H_{11}-c	Ph	48	1510	1260	990	1570 (NO_2)	2.03 d (6H, CH_3, $J=6$)	1.8 m ($(CH_2)_5$); 4.65 m (1H, CH); 7.70 m (5H, Ph)	50.65 50.70	5.88 6.20	11.71 11.80	8.88 8.73

---

*The synthesized compounds have the following T_{mp}, °C: **2k**, 84-86 (hexane); **2p**, 73-75 (hexane); **2h**, 65-67 (hexane), **2u**, 42-45 (hexane). The products **2a-j**, **o-k**, **g**, **s-t**, **v** were isolated in the form of an oil.

†Relative to HMDS.

TABLE 2. Chemical Shifts of ^{13}C NMR Signals (δ, ppm) and $^{13}C-^{31}P$ Spin–Spin Coupling Constants for N′-Phosphinatodiazene N-Oxides **2b, d, k-n**

Compound	Structural formula	^{13}C NMR, δ, ppm							$^{13}C-^{31}P$ (ν, Hz)			
		C^1	C^2	C^3	C^4	C^5	C^6	other ^{13}C signals	$^1J_{C^1-P}$	$^2J_{C^2-P}$	$^3J_{C^3-P}$	other constants $J_{^{13}C-^{31}P}$
2b		12.3	63.3	16.8	115.8	25.0	–	–	122.2	7.19	5.47	$^4J_{C^5-P} = 11.9$
2d		13.0	62.9	16.8	148.9	123.7	130.4	134.8 (C^7)	121.9	6.7	5.9	$^3J_{C^4-P} = 10.1$
2k		12.2	151.5	121.6	130.7	126.3	116.1	25.0 (C^7)	118.6	9.2	4.4	$^3J_{C^4-P} = 8.6$ $^3J_{C^7-P} = 14.4$

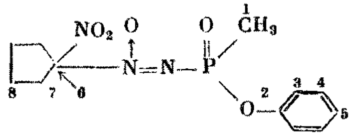
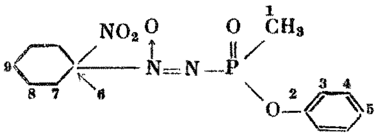
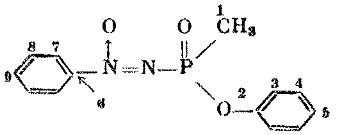
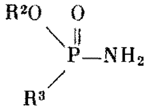
2l		12.2	151.3	121.7	130.7	126.3		38.2 (C^7) 25.0 (C^8)	118.2	9.2	4.3	$^{4}J_{C^{7}-P} = 16.6$
2m		12.2	151.4	121.7	130.5	126.2	118.5	33.8 (C^7) 23.2 (C^8) 24.1 (C^9)	118.4	9.4	4.5	$^{3}J_{C^{6}-P} = 8.4$ $^{4}J_{C^{7}-P} = 10.3$
2n		13.0	151.7	121.8	130.6	125.9	148.4	123.6 (C^7) 130.2 (C^8)	118.1	9.0	4.5	$^{3}J_{C^{6}-P} = 10.7$

TABLE 3. Chemical Shifts (δ, ppm) and Width of ^{14}N signals ($\Delta\nu_{1/2}$, Hz) and Chemical Shifts of ^{31}P Signals (δ, ppm) for N'-Phosphinatodiazene N-Oxides **2b, d, k-n**

Compound	$-^{14}N(O)=$		$^{14}NO_2$		^{31}P
	δ	$\Delta\nu_{1/2}$	δ	$\Delta\nu_{1/2}$	δ
2b	−30.6	84	0.1	66	30.9
2d	−36.0	135	–	–	31.5
2k	−28.5	100	−0.2	70	28.3
2l	−29.6	144	−1.0	117	28.7
2m	−30.3	168	−1.2	126	28.7
2n	−33.8	248	–	–	29.8

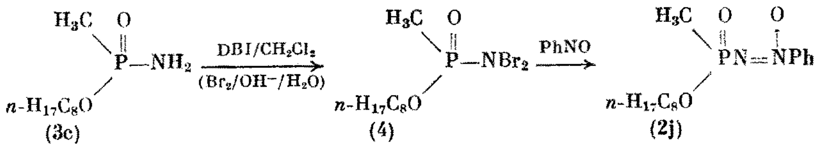
TABLE 4. Yields, Physicochemical and Spectral Characteristics of Amides of Methylphosphonic and Phenylphosphonic Acids **3a-e**



Compound	R²	R³	Yield, %	T_{mp}, °C	IR spectrum (ν, cm^{-1})			PMR spectrum (δ, ppm, J, Hz)
					P—O—C	P=O	NH_2	
3a	Me	Me	31	53–55	1050	1210	3100–3450	1.43 d (3H, CH_3P, J=17); 3.56 d (3H, CH_3O, J=11); 3.70 br.s (2H, NH_2)
3b	Et	Me	30	35–37	1040	1210	3100–3400	1.28 t (3H, CCH_3, J=7); 1.55 d (3H, CH_3P, J=17); 3.95 m (4H, CH_2, NH_2)
3c	C_8H_{17}-c	Me	99	20	1030	1200	3100–3400	1.38 d (3H, CH_3P, J=17); 0.68–1.67 m (15H, C_7H_{15}); 3.78m (4H, CH_2, NH_2)
3d	C_6H_{11}-c	Me	31	72–74	1050	1205	3150–3350	1.45 d (3H, CH_3P, J=17); 1.15–2.00 m (6H, $(CH_2)_5$); 3.15 br.s (2H, NH_2); 4.32 m (1H, CH)
3e	C_6H_{11}-c	Ph	45	108–115	1020	1210	3150–3350	0.90–2.00 m (C_6H_{10}); 4.30 m (1H, CH); 7.33m (5H, C_6H_5)

---

*In acetone-d_6 relative to HMDS [sic].



5 ml). The combined organic layer was washed with cold water (2 × 5 ml) and dried. The solvent was removed under vacuum. Obtained: 1.2 g (68%) **4** in the form of a transparent oil, according to IR and PMR spectra identical to the product obtained according to method A.

N-Phenyl-N'(O-octyl-P-methylphosphinato)diazene N-oxide (2j). A mixture of 1.0 g (3 mmoles) **4** and 0.35 g (3.3 mmoles) nitrosobenzene in 10 ml CH_2Cl_2 was stirred for 12 h at 20°C. The solvent was removed under vacuum and the residue was chromatographed on silica gel (eluting agent, ether). Obtained: 0.15 g (17%) **2j**, according to IR and PMR spectra identical to the product synthesized from nitrosobenzene and O-octyl-P-methylamidophosphinate in the presence of DBI.

REFERENCES

1. S. Zlotin, M. Sharashkina, Yu. Strelenko, and O. Luk'yanov, *Mend. Commun.*, **1**, No. 2, 49 (1991).
2. S. G. Zlotin, M. V. Sharashkina, Yu. A. Strelenko, and O. A. Luk'yanov, *Izv. Akad. Nauk, Ser. Khim.*, No. 5, 1148 (1992).
3. A. M. Churakov, E. L. Goncharova, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 953 (1990).
4. S. G. Zlotin, E. A. Vinogradova, A. I. Podgurskii, Yu. A. Strelenko, and O. A. Luk'yanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1656 (1990).
5. S. G. Zlotin, O. V. Prokshin, N. F. Karpenko, and O. A. Luk'yanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1679 (1990).
6. S. G. Zlotin, N. V. Airapetova, E. A. Vinogradova, A. I. Podgurskii, and Yu. A. Strelenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 12, 2821 (1990).
7. O. A. Luk'yanov, G. A. Smirnov, and A. M. Vasil'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2155 (1990).
8. G. M. Kosolapoff, *Organic Phosphorus Compounds*, **7**, 322 (1973).
9. Yu. A. Strelenko, V. N. Torocheshnikov, and N. M. Sergeyev, *J. Magn. Reson.*, No. 1, 123 (1990).
10. R. C. Zawalski and P. Kovacic, *J. Org. Chem.*, **44**, No. 13, 2130 (1979).
11. W. Gottardi, *Monat. Chem.*, **99**, 815 (1968).
12. N. Kornblum, D. D. Mooberry, and R. C. Blackwood, *J. Am. Chem. Soc.*, **78**, No. 7, 1504 (1956).
13. S. Nametkin, *Zh. Russk. Fiz.-Khim. Ova*, **42**, 585 (1910).