Heteroatom Chemistry
Volume 9, Number 2, 1998

Chlorotropy in the Phosphorus–Carbon Diad

Oleg I. Kolodiazhnyi* and Vladimir E. Grishkun

Institute of Bioorganic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Street, 1, Kiev, 253094, Ukraine

Received 15 April 1997; revised 7 July 1997

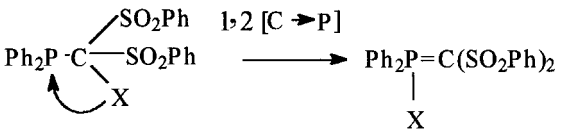
ABSTRACT

Chlorotropy in the phosphorus–carbon diad, proceeding with interconversion of α-chloroalkylphosphines and P-chloroylides, $R_2PC(Cl)R'_2$ $R_2P(Cl)=CR'_2$, was studied with regard to substituents, nature of solvents, and temperature. Kinetic measurement of 1.2-[C→P]- and 1.2-[P→C]-chlorotropic rearrangements were performed. The reaction is monomolecular and depends strongly on the ionizing power of the solvent. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:219–228, 1998

INTRODUCTION

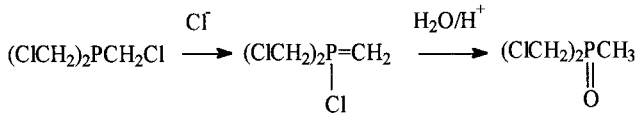
Tervalent phosphorus compounds containing a halogenomethyl group possess interesting chemical properties, in particular, phosphorus–carbon halogenotropy, which proceeds with interconversion of P-halogenoylides and α-halogenoalkylphosphines [1–3].

For the first time, phosphorus–carbon diad halogenotropy has been shown by the example of the rearrangement of diphenyl-bis(phenylsulphonyl)halogenomethylphosphines into the corresponding P-halogenoylides [4].

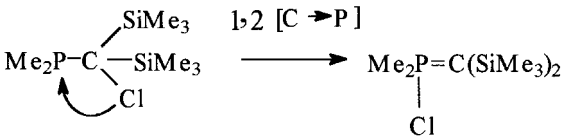


X=Cl, Br

Chlorotropic mobility in the phosphorus–carbon diad has been employed in explanations of mechanisms of certain reactions, in particular, of the hydrolysis and the rearrangement of tris(chloromethyl)phosphine into methyl-bis(chloromethyl)phosphine oxide [5].



Appel et al. [6] and Fritz et al. [7] used the 1.2-[C→P]-chlorotropic shift of silylated chloromethylphosphines for the preparation of P-chloroylides.

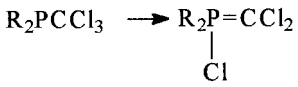


Interesting examples of conversion of tervalent phosphorus compounds, containing the trichloromethyl group, into P-chloroylides have been described by Lutsenko [8], Pinchuk [9], and other authors [3].

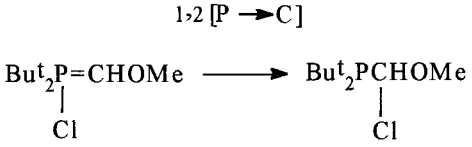
Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

 CCC 1042-7163/98/020219-10



The reverse 1,2[P→C]-halogenotropic shift of P-halogenoylides into α-halogenoalkylphosphines, proceeding with decreasing coordination number of the phosphorus atom, is also possible. Different examples of such rearrangements have been described by us [10–12].



It is seen then that phosphorus–carbon chlorotropy is an interesting example of unusual anionotropic transformations. This reaction is also interesting from the synthetic point of view and can be used for preparations of organophosphorus compounds accessible only with difficulty by other methods. Therefore, further studies of diad phosphorus–carbon chlorotropy deserve to be continued.

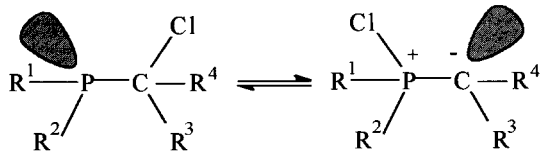
In this work, we describe new results concerning the influence of various factors on the phosphorus–carbon chlorotropy:

1. Influence of substituents at the phosphorus and carbon atoms.
2. Influence of solvent.
3. Influence of temperature.
4. Kinetic studies and discussion of mechanism.

RESULTS AND DISCUSSION

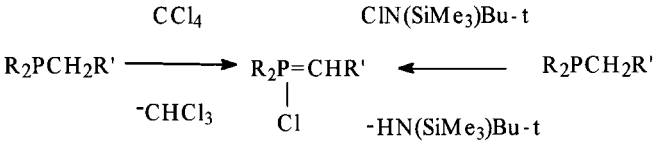
Synthesis of Ylidic and Phosphinic Chlorotropic Isomers

The interconversion of P-chloroylides and α-chloroalkylphosphines is accompanied by the migration of chlorine and a free electron pair between phosphorus and carbon atoms and by change of the coordination numbers of these atoms. It is known that ylides are essentially carbanions connected directly to a phosphorus carrying a substantial degree of positive charge [3]. Energetic advantages and disadvantages of such coordination transformations of tri- and tetracoordinated phosphorus and carbon atoms evidently must be approximately equal and must depend on the substituents connected to these atoms.



To define the influence of substituents at the phosphorus and carbon atoms on the chlorotropic rearrangements, we have studied a number of P-chloroylides and α-chloroalkylphosphines containing various substituents R and R′ (Table 1).

P-Chloroylides, containing different substituents R and R′, were obtained by reaction of tertiary phosphines with carbon tetrachloride or with sterically hindered N-chloro-*tert*-butyl(trimethylsilyl)amide [13].

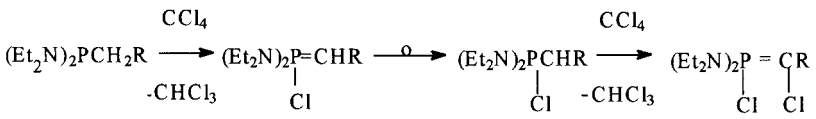


The reaction of tertiary phosphines with N-chloro-*tert*-butyl(trimethylsilyl)amide is more selective than the reaction with carbon tetrachloride, which affords chloroform, catalyzing the rearrangement of P-chloroylides into α-chloroalkylphosphines. Therefore, the reaction of bis(diethylamino)-isobutylphosphine **1** or neopentylphosphine **2** with carbon tetrachloride does not give P-chloroylides **3,4** but leads to the formation of P-chloro α-chloroalkylides **7,8,** which have been isolated in good yields as yellow liquids smoking in the air.

The first stage of the reaction gives P-chloroylides **3,4** and chloroform, catalyzing a rearrangement of P-chloroylides **3,4** into α-chloroalkylphosphines **5,6,** which react then with the excess of carbon tetrachloride to yield P-chloro-α-chloroalkylides **7,8.** We detected P-chloroylides **3,4** and α-chloroalkylphosphines **5,6** in a reaction mixture by ^{31}P NMR spectroscopy; however, they could not be isolated in pure form, because the deficiency of carbon tetrachloride led to a mixture of compounds.

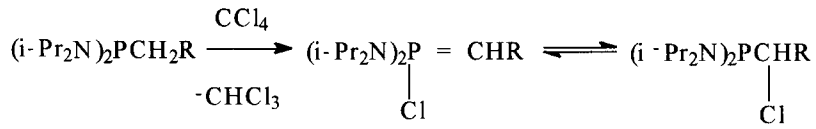
Sterically hindered bis(diisopropylamino)-phosphines **9–13** react with carbon tetrachloride at temperatures below 0°C, quantitatively being converted into P-chloroylides **14–20,** which, depending on the substituents R, can exist as ylides, can rearrange into α-chloroalkylphosphines, or can give a mixture of ylide and phosphine chlorotropic tautomers.

Thus, bis-diisopropylaminoalkylphosphines **9–12,** containing a hydrogen atom and alkyl groups at the α-carbon atom (R = H, Pr, *i*-Pr, *t*-Bu), react with



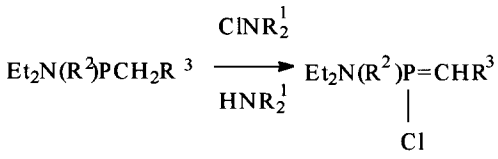
1,2 **3,4** **5,6** **7,8**

R=i-Pr (**1,3,5,7**), t-Bu (**2,4,6,8**)



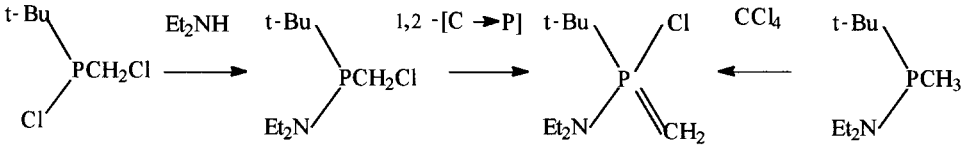
9-13 **14-20** **21-25**

R=H (**9,14,21**), n-Pr (**10,15,22**), i-Pr (**11,16,23**), t-Bu (**12,17,24**), Ph (**13,18**), $SiMe_3$ (**19**), Cl (**20,25**)



1,2,26,27 **3,4,28,29**

$R^1{}_2N$=t-Bu(Me_3Si)N; R^2=t-Bu, R^3=i-Pr (**26,28**); R^2=t-Bu, R^3=H (**27,29**)



30 **29** **27**

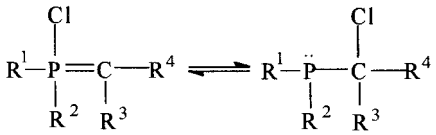
carbon tetrachloride to form P-chloroylides **14–17,24,** which are stable in the solution below 0°C and can be detected by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Above 0°C, these ylides are converted quantitatively into α-chloroalkylphosphines **21–25.** P-Chloroylides **18,19** bearing at the α-carbon atom electron-accepting groups (R = Ph or Me_3Si) exist in the stable ylide form and do not rearrange into α-chloroalkylphosphines. The chemical shifts of these compounds, δ_P 54 and 61, are characteristic for P-chloroylides, containing two NR_2 groups at the phosphorus atom [4]. ^{13}C NMR spectra contain signals belonging to the ylidic carbon atom, doublets at δ49, $^1J_{CP}$ 192 (**19**) and at 21, $^1J_{CP}$ 142 Hz (**20**) [10].

The replacement of the carbon tetrachloride by N-chloro-*tert*-butyl(trimethylsilyl)amide gives P-chloroylides, which, in the absence of chloroform, are more stable. Thus, the reaction of phosphines, **1,2,26,27,** R = *i*-Pr, *t*-Bu, with the sterically hindered N-chloro(*tert*-butyl) trimethylsilylamine readily occurs in diethyl ether or benzene at 0°–+20°C to give P-chloroylides **3.4,28,29** in very high yields. The ylides **3,4** are stable in solution during several hours. The addition of chloroform to the ether solution of the ylides **3,4** catalyzes their fast rearrangement into α-chloroalkylphosphines **5,6.** The treatment of these ylides with excess carbon tetrachloride leads to the formation of P-chloro-α-chloroalkylides **7,8.**

Chlorotropic Rearrangements

P-chloroylides, containing H or alkyl at the α-carbon atom rearranged easily into α-chloroalkylphos-

TABLE 1 Influence of the Substituents at the Phosphorus and Carbon Atoms on the Diad Phosphorus–Carbon Chlorotropic Rearrangements



a **b**

Compound	R^1	R^2	R^3	R^4	δ_P (**a**) *ppm*	δ_P (**b**) *ppm*	*Ratio*[a] **a:b**
3, 5	Et_2N	Et_2-N	Pr-*i*	H	62	87.8	4:1
4, 6	Et_2N	Et_2N	Bu-*t*	H	63.91	85	4:1
7	Et_2N	Et_2N	Pr-*i*	Cl	58.50	—	100:0
8	Et_2N	Et_2N	Bu-*t*	Cl	52.03	—	100:0
14, 21	*i*-Pr_2N	*i*-Pr_2N	H	H	61	46	0:100
15, 22	*i*-Pr_2N	*i*-Pr_2N	Pr	H	—	53.6	0:100
16, 23	*i*-Pr_2N	*i*-Pr_2N	Pr-*i*	H	—	50.45	0:100
17, 24	*i*-Pr_2N	*i*-Pr_2N	Bu-*t*	H	63	52.03	0:100
18	*i*-Pr_2N	*i*-Pr_2N	Ph	H	54.08	—	100:0
19	*i*-Pr_2N	*i*-Pr_2N	$SiMe_3$	H	61	—	100:0
20, 25	*i*-Pr_2N	*i*-Pr_2N	H	Cl	64	46	1:12
28	Et_2N	*t*-Bu	Pr-*i*	H	94.45	—	100:0
29, 30	Et_2N	*t*-Bu	H	H	107	76	95:5

[a]Ratio of chlorotropic isomers in an equilibrium state.

phines, which were isolated in crystalline form. The course of rearrangement can be observed by ^{31}P NMR spectroscopy. Thus, the reaction of bis(diisopropylamino)methylphosphine with carbon tetrachloride leads quantitatively to P-chloroylide **14.** The ^{31}P NMR spectrum of ylide **14** contains only one signal at δ_P 61 corresponding to the P-chloroylide. The ^{13}C NMR spectrum reveals the doublet of an ylidic carbon atom at δ_P 33.3, $^1J_{CP}$ 146 Hz. The increase of the temperature to +20°C results in the complete rearrangement of the ylide **14** into α-chloroalkylphosphine **15.** In the ^{31}P NMR spectrum, one can observe disappearance of the signal at δ_P 61 (ylide **14**) and creation of signal δ_P 46 (phosphine **15**). The rate of the rearrangement depends on the nature of the solvents and temperature. The rearrangement of P-chloroylides **14** into α-chloroalkylphosphines **15** proceeds slowly in nonpolar solvents (hexane and benzene) and is accelerated strongly in the presence of polar solvents (acetonitrile, chloroform, and methylene chloride).

1.2-[(C → P]-Chlorotropic rearrangement of α-chloroalkylphosphines into P-chloroylides was studied with the example of diethylamino(*tert*-butyl)chloromethylphosphine **30.** This compound was obtained by reaction of *tert*-butyl(chloromethyl)-chlorophosphine with diethylamine. The chloromethylphosphine **31** is stable during several hours at room temperature and can be kept in a freezer.

However, the α-chloromethylphosphine **30** rearranges readily into P-chloroylide **29** in ionizing solvents (acetonitrile, chloroform, methylene chloride, and tetrachloroethane).

One can observe the course of rearrangement by ^{31}P NMR spectroscopy, following the change of integral intensity of signals δ_P 76(phosphine) and 107 (ylide). The chemical shift of the ylide **29** is characteristic for P-chloroylides containing alkyl and dialkylamino groups at the phosphorus atom. NMR spectroscopy shows that the rearrangement proceeds to result in complete conversion of phosphine into ylide. The same P-chloroylide **29** has been obtained by reaction of diethylamino(*tert*-butyl)methylphosphine **27** with carbon tetrachloride [14]. The structure of the P-chloroylide was also confirmed by chemical transformations.

The reaction of bis(diethylamino)isobutylphosphine **1** with N-chlorotrimethylsilyl(*tert*-butyl)amine proceeds in ether or benzene at 0 to +20°C to form highly reactive P-chloroylide **3** that is stable for several hours in solution. On heating or distillation in vacuum, it easily rearranges into the α-chloroalkylphosphine **5** to result in a tautomeric mixture of two chlorotropic isomers **3** ⇌ **5** in the ratio 4:1.

The chlorotropic isomers were detected by NMR spectroscopy where the signals at δp 62 (ylide **3**) and 87.8 (phosphine **5**) were found. The ^{1}H NMR spectrum shows the signal δ 4.07, a double doublet with J_{HH} 2.0 Hz and J_{HP} 3.4 Hz (CHCl group). The ylide **3** adds methyl alcohol to form the bis(diethylamino)-isobutylmethoxyphosphonium chloride, which was detected by its ^{31}P NMR spectrum (δ_P 61) and then converted into stable bis(diethylamino)isobutylmethoxyphosphonium perchlorate **31.** The bis-(diethylamino)isobutylmethoxyphosphonium chloride is converted into bis(diethylamino)isobutylphosphonate **32** in accordance with the Arbuzov reaction.

Therefore, the analysis of the data collected in Table 1 shows that electron-accepting groups Ph, $SiMe_3$, Cl at the α-carbon atom stabilize the ylide form **a** (compounds **7,8,18,19**). At the same time, the hydrogen atom and alkyl groups at the α-carbon atom, R^3, R^4 = H, Pr, *i*-Pr, *t*-Bu, stabilize form **b.** Thus, P-chloroylides **14–17** rearrange into α-chloroalkylphosphines **b.** Bulky *tert*-butyl groups at the phosphorus atom stabilize the ylide form (compounds **28,29**) and shift the equilibrium ***a*** $\rightleftharpoons$ ***b*** toward the form ***a.*** For example, α-chloromethylphosphine **30** rearranges into P-chloroylide **29.** However, sterically bulky isopropyl groups more effectively stabilize phosphine form **b,** then, with diethylamino groups present, the equilibrium ***a*** $\rightleftharpoons$ ***b*** is shifted toward this form (compounds **3,4** and **16,17**).

Influence of Temperature, Concentration and Solvent. Kinetic Measurements

1.2-[P → C]- and 1.2-[C → P]-chlorotropic rearrangements have been studied by kinetics methods. Kinetic studies of the 1.2-[P → C]-chlorotropic rearrangement were performed with the example of bis(diisopropylamino)chlorophosphonium methylide **14.** We followed the course of the reaction by ^{31}P NMR spectroscopy, observing the change of the integral intensity of signals δ_P 61 (ylide **14**) and 46 (phosphine **21**).

Kinetic tests at different initial concentrations of P-chloroylide **14** (C 0.05–0.5 mol/L), at various temperatures (−20 to +25°C), in different solvents showed that the reaction follows a first-order rate equation until 90% conversion [25]. The calculation performed by the graphic method showed the linear dependence of semi-logarithmic anamorphoses on the time in accordance with the rate equation of the first order. The first order of reaction was confirmed as well by the constant values of semi-conversions at different initial concentrations of P-chloroylide. The rate constants do not depend on the initial concentration of P-chloroylide but depend strongly on the solvent polarity. In the presence of such polar solvents as CH_3CN, $CHCl_3$, and CH_2Cl_2, the rate of rearrangement increases significantly. The increase of chloroform content in diethyl ether leads to a proportional increase of the rate constants (Table 2). The influence of the solvents on the rate constant corresponds to the increase of their ionizing power in the following sequence:

$$CH_3CN > CHCl_3 > CH_2Cl_2 > C_6H_6 > Et_2O > C_6H_{14}$$

The thermodynamic parameters were determined from temperature dependence of the rate constants: E_a 47,700 J/mol and $\Delta S^{\neq}$ −102 J/(K)mol (in diethyl ether, containing 5% of $CHCl_3$).

Kinetic studies of 1,2[C→P]-chlorotropic rearrangement have been performed with the example of diethylamino-*tert*-butyl-chloromethylphosphine **30.** The rate measurements of the rearrangements at different concentrations of initial phosphine (C 0.05–0.5 mol/L), in various solvents, and at different temperature −20 to +50°C showed that the reaction proceeds according to the rate equation of the first order.

The activation parameters of the rearrangement were calculated from the Arrhenius equation: activation energy (*Ea*) 77,000 J/mol, and the entropy of activation $\Delta S^{\neq}$ −67 kJ/(K)mol (at 30°C in benzene-chloroform 85:15).

The reaction rate depends on the nature of the solvent. In nonpolar solvents, rearrangement pro-

TABLE 2 Kinetic Data of 1,2-[P → C]-Chlorotropic Rearrangement of P-Chloroylide **14** into α-chloromethylphosphine **21**

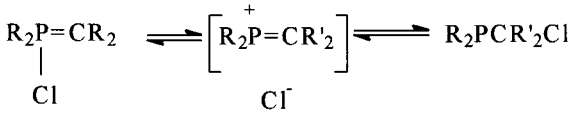
C_{ylid}, mol/L	Solvent	Temp., °C (±0.5°)	k_1 10^{-4}, s^{-1} (±5%)
0.075	Et_2O + 0.8%$CHCl_3$	25	1.2
0.26	Et_2O + 3.0%$CHCl_3$	25	4.4
0.26	Et_2O + 6.0%$CHCl_3$	25	8.25
0.26	Et_2O + 7.5%$CHCl_3$	25	12.1
0.26	Et_2O + 12.0%$CHCl_3$	25	25.6
0.26	Et_2O + 16.5%$CHCl_3$	25	30.5
0.26	Et_2O + 21.0%$CHCl_3$	25	51.2
0.26	Et_2O + 6.0%CH_3CN	25	25.6
0.26	Et_2O + 6.0%CH_2Cl_2	25	0.4
0.26	C_6H_6 + 3%$CHCl_3$	25	26
0.26	Et_2O + 7.5%$CHCl_3$	0	2.2
0.65	Et_2O + 7.5%$CHCl_3$	10	3.7
0.65	Et_2O + 7.5%$CHCl_3$	15	4.6
0.65	Et_2O + 7.5%$CHCl_3$	20	7.3
0.65	Et_2O + 7.5%$CHCl_3$	25	12.1

ceeds slowly. At the same time, in polar solvents, the rate of rearrangement increases strongly. The rate constants increase in the following solvent sequence:

$$CH_3CN > CHCl_2CHCl_2 > CHCl_3 > CH_2Cl_2 \gg C_6H_6$$

The performed studies showed that 1.2 [P → C] and 1.2 (C → P)-chlorotropic rearrangements are very similar from the kinetic point of view. They both follow the first-order rate equation and depend strongly on the solvent polarity. The kinetic characteristics and activating parameters of 1.2 (P → C)- and 1.2 (C → P)-chlorotropy are very similar and probably occur via the same intermediate. The comparatively low activation energies (E_a 77 KJ/mol and 47.7 KJ/mol) show the high thermodynamic stability of the intermediate compounds. The negative entropies of activation −67 and −102 J/(K)mol reflect changes of the transition state in chlorotropic rearrangements.

The kinetic characteristics and energy parameters allow us to conclude that 1.2[P → C]- and 1.2[C → P]-chlorotropic rearrangements proceed in accordance with a monomolecular mechanism, probably via the formation of phosphinium cation **A,** formed as a result of ionization of the P–Cl bond in a P-chloroylide, or a C–Cl bond in an α-chloroalkylphosphine, solvated by polar solvents.



A

Various types of stable phosphinium cations of tricoordinate pentavalent phosphorus are well known [15]. Moreover, we have previously described the conversion of P-chloroylides containing dialkylamino group at the α-carbon atom into stable phosphinium cations, which were isolated and studied by X-ray analysis [2,3,16], this to a certain degree confirming the formation of the intermediate **A.** We plan to continue our studies of phosphorus–carbon diad chlorotropy, in particular to define the influence of substituents at the phosphorus and carbon atom of the PC diad on the position of chlorotropic equilibrium, and to investigate as well the nature and properties of the phosphinium intermediate.

EXPERIMENTAL

Melting points were uncorrected. The NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 (^{1}H) and 121.8 MHz (^{31}P). Reaction rate measurements were performed in NMR tubes at constant temperatures (−20 ± 0.5°C)–(+60 ± 0.5°C) All chemical shifts are expressed in δ. Chemical shifts of ^{1}H and ^{13}C are expressed relative to Me_4Si as an internal standard. ^{31}P NMR spectra are referenced to external 85% H_3PO_4. All manipulations were carried out under argon. Solvents were also distilled under an inert atmosphere from appropriate drying agents: diethyl ether, pentane, hexane, benzene, toluene, chloroform, carbon tetrachloride, methylene chloride (P_2O_5); methanol, triethylamine (sodium).

Bis(diethylamino)neopentylphosphonite (**2**)

To 5.0 g (0.21 mol) of magnesium activated by bromine, a solution of 24 g (0.157 mol) of neopentyl bromide in 100 mL of ether was added. Then the solution was refluxed for 1.5 hours resulting in a solution of neopentylmagnesium bromide (1.5 mol/L).

To a solution of 0.1 mol of bis(diethylamine)chlorophosphine in 50 mL of ether, a solution of 0.11 mol of neopentylmagnesium bromide in ether was added dropwise with stirring and cooling to 0°C. Then the mixture was stirred for 30 minutes. The solution was filtered and the residue was washed with ether; the solvent was evaporated and the residue was distilled under vacuum. Yield 85%. Bp 74–76°C/0.04 mm Hg. ^{31}P NMR spectrum (δ; $CDCl_3$): δ_P 85.87. Calculated for the $C_{13}H_{31}N_2P$: P, 12.58. Found: P, 12.35.

Bis(diethylamino)chlorophosphonium Isobutylide (**3**)

A solution of 5.37 g (0.03 mol) of N-chloro-*tert*-butyl(trimethylsilyl)amine was added dropwise to a solution of 4.6 g (0.025 mol) of bis(diethylamino)-isobutylphosphonite in 15 mL of diethyl ether at −70°C with stirring. Then the temperature was raised to +20°C and the reaction mixture was left for 30 minutes. The NMR spectrum showed a quantitative yield of the ylide **3.** The ylide **3** is stable in the solution. After the evaporation of solvent in a vacuum, P-chloroylide **3** was obtained as a colorless liquid. NMR spectra (δ, *J*, Hz; C_6D_6): δ_H 0.933, t, J_{HH} 7 ($C\underline{H}_3CH_2$); the signal of P=CH coincides with this one of $C\underline{H}_3CH_2$; 1.25, dd, *J* 6.6, *J* 2 [$(C\underline{H}_3)_2C$]; 1.45 m [$(CH_3)_2C\underline{H}$]; 2.97 dq J_{HH} 7, J_{HP} 12.3 (CH_2N). δ_P 62.

During one day at ambient temperature or after distillation under vacuum, the mixture of two chlorotropic tautomers **3** and **5** was obtained. The solution of the bis(diethylamino)chloro-phosphoniumisobutylide **3** was evaporated, and the residue was distilled under reduced pressure. Yield 70%. Bp 85°C (0.05 mm Hg). Colorless liquid. NMR spectra (d,

ppm; *J,* Hz; $CDCl_3$): δ_H 0.78 t, J_{HH} 7.2, $C\underline{H}_3CH_2'$; 0.91 t, J_{HH} 7.2, $C\underline{H}_3CH_2''$; 1.18 d, J_{HH} 6.5 $(C\underline{H}_3)_2CH'$; 1.05 d, J_{HH} 6.5 $(C\underline{H}_3)_2CH'$; 2.02 m $(CH_3)_2C\underline{H}$; 2.70 m, CH_2N'; 2.90, m, CH_2N''; 4.07, dd, J_{HH} 2.0, J_{HP} 3.4, CHCl. δ_P 62 (ylide **3**) and 87.79 (phosphonite **5**) (ratio is 4:1). Calcd. for $C_{12}H_{28}ClN_2P$: Cl, 13.29; P, 11.61. Found: Cl, 12.98; P, 11.28.

Bis(*diethylamino*)*chlorophosphonium Neopentylide* (**4**).

The ylide **4** was obtained analogously to the procedure for the preparation of bis(diethylamino)chlorophosphonium isobutylide **3.** The NMR spectrum showed a quantitative yield of the ylide **4.** The ylide **4** was stable in the solution. After the evaporation of solvent in a vacuum, P-chloroylide **4** was obtained as a colorless liquid. NMR spectra (*δ; J,* Hz; C_6D_6): δ_H 0.818, t, J_{HH} 7 $(C\underline{H}_3CH_2)$; 1.34, d, *J* 8.0 $[(C\underline{H}_3)_3C]$; 2.9 m (CH_2N). δ_P 63.91 ppm. Calcd for $C_{12}H_{28}ClN_2P$: Cl, 13.10. Found: Cl, 13.30.

Bis(*diethylamino*)*chlorophosphonium 1-chloro-2-methylpropylide* (**7**)

Method A. To a solution of the bis(diethylamino)-chlorophosphonium isobutylide **3,** prepared as previously described, was added dropwise 0.05 mole of carbon tetrachloride with stirring at −20°C. Then the mixture was stirred at ambient temperature for 20 minutes, and the solvent was evaporated under reduced pressure. To the residue was added 15 mL of pentane with stirring. The resultant dark oil was separated, and the solvent was evaporated under reduced pressure. The residue was distilled in a vacuum. Yield 50%, bp 105°C (0.012 mm Hg). NMR spectra (*δ; J,* Hz; C_6D_6): δ_H 0.88, t J_{HH} 7 (CH_3C); 1.18 dd J_{HH} 7, J_{HP} 1 $[(C\underline{H}_3)_2CH]$; 2.64 m $[C\underline{H}(CH_3)_2]$; 2.9 dq J_{HH} 7, J_{HP} 12.5 $(C\underline{H}_2N)$; δ_C 13.60 s $(\underline{C}CN)$; 23.20 d J_{CP} 16 $(PCC\underline{C})$; 30.20 d, J_{CP} 16 $(PC\underline{C})$; 40.7 d, J_{CP} 4 (CN); 66.70 d, J_{CP} 200 (P=C); δ_P 58.50. Calcd for $C_{12}H_{27}Cl_2N_2P$: Cl, 23.62; P, 10.32. Found: Cl, 23.28; P, 10.22.

Bis(*diethylamino*)*chlorophosphonium 1-chloro-2,2-dimethylpropylide* (**8***)*

To a solution of the bis(diethylamino)chlorophosphonium neopentylide **4** (prepared from 0.03 mol of bis(diethylamino)neopentylphosphine as described earlier) was added dropwise 0.05 mol of carbon tetrachloride with stirring at −20°C. Then the mixture was stirred at ambient temperature for 20 minutes, and the solvent was evaporated under reduced pressure. To the residue was added 15 mL of pentane with stirring. A dark oil was separated, and the solvent was evaporated under reduced pressure. The residue was distilled in a vacuum. Yield 60%, bp 130°C (0.02 mm Hg). NMR spectra (*δ; J,* Hz; C_6D_6): δ_H 0.9, t, *J* 7 $(C\underline{H}_3CH_2)$; 1.3 s $[(CH_3)_3C]$; 3.0 m (CH_2N); δ_P 52.03. Calcd for $C_{13}H_{29}Cl_2N_2P$: Cl, 23.30; P, 10.32. Found: Cl, 23.28; P, 10.22.

Bis(*diisopropylamino*)*neopentylphosphonite* (**12**)

To a solution of 0.1 mol of bis(diisopropylamino)-chlorophosphine in 50 mL of ether, a solution of 0.11 mol of neopentylmagnesium bromide was added dropwise, with stirring and cooling to 0°C. Then the mixture was left for 60 minutes. The precipitate of $MgCl_2$ was filtered off, and the solvent was evaporated. The residue was again dissolved in hexane and filtered, and the filtrate was placed in a freezer. A crystalline product (needles) was obtained. A product suitable for further chemical transformations can be obtained as well after evaporation of solvent under vacuum in 80% yield. NMR spectra (*δ; J,* Hz; $CDCl_3$): δ_H 0.96 d, J_{HP} 1 $(C\underline{H}_3)_3CCP$; 1.05, d J_{HP} 6.8 $[(C\underline{H}_3)_2CH]$; 1.32 d, J_{HP} 6.8 $[(C\underline{H}_3)_2CH]$; 1.63 d, J_{HP} 3.0 $(PC\underline{H}_2)$; 3.35 m (CHN), δ_P: 47.25. Calcd for $C_{17}H_{39}N_2P$: P, 10.24. Found: P, 10.11.

Bis(*diisopropylamino*)*chlorophosphonium Methylide* (**14**)

(a) To a solution of 0.05 mol of bis(diisopropylamino)methylphosphine in 10 mL of toluene-D_8 was added 0.05 mL of carbon tetrachloride, dropwise with cooling to −70°C. Then the temperature of the mixture was raised slowly to +10°C and then lowered to −20°C. ^{13}C and ^{31}P spectra were recorded.

(b) To a solution of 0.05 mol of bis(diisopropylamino)methylphosphine in 10 mL of ether was added 0.05 mol of a solution of 0.05 mol of N-chloro(trimethylsilyl)*tert*-butylamine dropwise with stirring and cooling to −20°C. Then the temperature of the mixture was raised slowly to +10°C, and the reaction mixture was left for 30 minutes. The solvent was evaporated under a vacuum (10 mm and 0.01 mm Hg). ^{13}C and ^{31}P spectra were recorded. NMR spectra (*δ; J,* Hz; C_6D_8): δ_C 23.1 d, $^3J_{CP}$ 40 $(\underline{C}H_3C)$; 44.8 d, $^2J_{CP}$ 4.5 (CN); 33.3 d, $^1J_{CP}$ 146 (P=C); δ_P 61.

Bis(*diisopropylamino*)*chlorophosphonium Benzylide* (**18**)

With stirring, a solution of 3.6 g (0.03 mol) of carbon tetrachloride in 5 mL of diethyl ether was added dropwise to a solution of 6.4 g (0.02 mol) of

bis(diethylamino)benzylphosphonite in 10 mL of ether at 0°C. The reaction mixture was allowed to stand for 1 hour at ambient temperature, then the solvent was evaporated. Yield 95%. The ylide was obtained in spectroscopically pure form, without special purification, as a yellow liquid. NMR spectra (*δ; J,* Hz; C_6D_6): δ_C 22.62 d, J_{CP} 24.4 (CCN); 47.46 d J_{CP} 5 (CN); 49.01 d J_{CP} 192 (P=C); 117.65; 122.41 d, J_{CP} 19.5; 126.7 d, J_{CP} 24; 142 d J_{CP} 5 (C_6H_5). δ_P 54.08.

Bis(*diisopropylamino*)*chloromethylphosphine* (**21**)

(a) To a solution of 0.05 mol of bis(diisopropylamino)methylphosphine **9** in 10 mL of toluene-D_8 was added 0.05 mol of carbon tetrachloride dropwise with cooling to −70°C. The temperature of the reaction mixture was raised slowly to +10°C and then lowered quickly to −20°C. ^{13}C and ^{31}P spectra were recorded.

(b) To an ether solution of bis(diisopropylamino)chlorophosphonium methylide **14** was added 0.5 mL of chloroform, and the solution was left for 40 minutes at room temperature. Then the solvent was evaporated in a vacuum and the residue was crystallized from pentane. Yield 80%, mp 29–31°C. NMR spectra (*δ; J,* Hz; C_6D_6): δ_H 0.98 d J_{HH} 6.6; 1.02 d J_{HH} 6.6 ($C\underline{H}_3C$); 3.06 m (CHN); 3.40 d J_{HP} 9.96 (CHCl). δ_C 22.04 d, $^3J_{CP}$ 7 ($\underline{C}H_3C$); 22.4 d, $^3J_{CP}$ 8 ($\underline{C}H_3C$); 40.33 d, $^1J_{CP}$ 19 (PC); 44.8 d, $^2J_{CP}$ 8 (CN); δ_P 46. Calcd for $C_{13}H_{30}ClN_2P$: Cl, 12.62; P, 11.03. Found: Cl, 12.61; P, 11.05.

Bis(*diisopropylamino*) *1-Chlorobutylphosphonite* (**22**)

To a solution of 0.05 mol of bis(diisopropylamino)butylphosphine in 10 mL of toluene at −70°C was added 0.075 mol of carbon tetrachloride. Then the temperature was raised to 20°C. The solvent was removed under a vacuum, and the residue was crystallized from hexane. Yield 70%, Mp 44–47°C. NMR spectra (*δ; J,* Hz; C_6D_6): δ_C 11.75, 19.14, 19.38 (C_3H_7); 22.20 d; 22.30 d, J_{CP} 5 (NCC); 22.78 d; 22.74 d, J_{CP} 6.5 (NCC); 46.67 d, J_{CP} 11.5 (NC); 45.85 d, J_{CP} 10.5 (NC); 57 d, J_{CP} 17 (PCCl); δ_P 53.6. Calcd for $C_{16}H_{36}ClN_2P$: Cl, 10.98; P, 9.59. Found: Cl, 10.85; P, 9.68.

Bis(*diisopropylamino*) *1-Chloro-2-methylpropylphosphonite* (**23**)

To a solution of 0.01 mol bis(diisopropylamino)isobutylphosphine in 10 mL of toluene at −70°C was added 0.025 mol of carbon tetrachloride. Then the temperature was raised to 20°C. The solvent was removed under a vacuum, and the residue was crystallized from hexane.

Yield 70%, mp 81–83°C. NMR spectra (*δ; J,* Hz; C_6D_6): δ_H 0.868 d, J_{HH} 6.5 Hz, [$C\underline{H}_3CC$]; 1.06 dd, J_{HH} 6.5 ($C\underline{H}_3CN$); 1.18 dd, J_{HH} 6.5 ($C\underline{H}_3CN'$); 2.22 m (PCCH); 3.07 m (CHN); 3.19 m (CHN); 4.115 dd $^3J_{HH}$ 1.5, $^2J_{HH}$ 2.5 (CHCl). d_c: 17.6 d, *J* 14 (PCCC[a]); 22.55 d, *J* 5 (PCC$\underline{C}$[b]); 24.33 d; 24.48 d, *J* 8 (NC$\underline{C}$[a]); 25.23 d; 25.38 d, *J* 8 (NCC[b]); 30.13 d, *J* 21 (P$\underline{C}$); 46.0 d, *J* 11 (Nc[a]); 48.11 d, *J* 13 (NC[b]); 64.8 d, *J* 19 (P$\underline{C}$Cl); δ_P 50.45. Calcd for $C_{16}H_{36}ClN_2P$: Cl, 10.98; P, 9.59. Found: Cl, 10.87; P, 9.65.

Bis(*diisopropylamino*)*dichloromethylphosphine* (**25**)

To a solution of 0.01 mol of bis(diisopropylamino)-chloromethylphosphine **21** in 10 mL of ether was added 0.05 mol of carbon tetrachloride, and the solution was left for 40 minutes at room temperature. Then the solvent was evaporated in vacuum, and the residue was crystallized from pentane. Yield 70%, mp 98.8–99.5°C. NMR spectra (*δ; J,* Hz; C_6D_8): δ_H 0.98 d, J_{HH} 6.5; 1.05 d, J_{HH} 6.8 (CH_3C); 3.05 d.spt [J_{HH} 6.5, J_{HP} 5 (CHN)]; 5.67 d J_{HP} 1.8, ($CHCl_2$). δ_C 22.05 d, $^3J_{CP}$ 5.4 ($\underline{C}H_3C$); 22.56 d, $^3J_{CP}$ 6.8 [($\underline{C}H_3)_2C$]; 45.92 d, $^2J_{CP}$ 12.2 (CN); 68.5 d, $^1J_{CP}$ 38.0 (PC). δ_P ($CDCl_3$): 58 and 63.6 ppm (12:1). Calcd for $C_{13}H_{29}Cl_2N_2P$: Cl, 22.01; P, 10.18. Found: Cl, 22.49; P, 9.82.

Diethylamino-tert-butyl-chlorophosphonium Isobutylide (**28**)

To a solution of 4.6 g (0.025 mol) of bis(diethylamino)isobutylphosphine **1** in 15 mL of diethyl ether, an ether solution of 5.37 g (0.03 mol) of N-chloro(*tert*-butyl)trimethylsilylamine was added dropwise at −70°C with stirring. Then the temperature was raised to +20°C, and the reaction mixture was left for 30 minutes. The NMR spectrum (C_6D_6) showed a quantitative yield of the ylide **28,** δ_P 94.45. The spectral data are identical with those reported in the literature. The solvent was evaporated under reduced pressure to give a colorless liquid, smoking in the air. Yield 95%. Calcd for $C_{12}H_{27}ClNP$: Cl, 14.08. Found: Cl, 13.70.

Diethylamino-tert-butyl-chlorophosphonium Methylide (**29**)

To a solution of 0.05 mol of diethylamino *tert*-butyl(chloromethyl)phosphine **30** in 20 mL of C_6D_6 was added 0.05 mol of chloroform, and the mixture was left for 20–30 minutes. The ylide **29** was obtained in spectroscopically pure form. The ^1H, ^{13}C, and ^{31}P

NMR data correspond to ylide **29,** earlier prepared by reaction of diethylamino-*tert*-butyl-methylphosphine **27** with carbon tetrachloride [14].

Diethylamino tert-Butyl(chloromethyl)phosphine (**30**)

To 0.1 mol of chloromethyl-*tert*-butyl-chlorophosphine in 50 mL of pentane was added dropwise with stirring at −50°C 0.2 mol of diethylamine in 60 mL of pentane. Then the temperature was raised to ambient, the precipitate was filtered off, and the solvent was evaporated under vacuum. The residue was obtained in a spectroscopically pure form. NMR spectra (*δ; J,* Hz; C_6D_6): δ_H 0.9 d, J_{HP} 3.4 (CH_3CP); 1.05 t *J* 7.0 ($C\underline{H}_3CH_2$); 1.2 m, 1.4 m ($CH_3C\underline{H}_2$); 2.8 m (NCH_2); 3.84 s (CH_2Cl); δ_P 76.

Bis(diethylamino)isobutylmethoxyphosphonium Perchlorate (**31**)

To an ether solution of bis(diethylamino)chlorophosphonium isobutylide **3** (0.025 mol), prepared as described earlier, was added with stirring 1 g (0.031 mol) of methyl alcohol. The temperature was raised to 0°C, and 5 mL of water was added with stirring, the aqueous layer then being separated. The ^{31}P NMR spectrum showed a single signal, δ_P 60, of the bis(diethylamino)isobutylmethoxy phosphonium chloride.

Then the aqueous solution was cooled to +5°C, and a solution of 1 g of $NaClO_4$ in 2–3 mL of water was added. The precipitate was filtered off and recrystallized from ethanol-ether giving a colorless crystalline solid. Mp 165–168°C, 95% yield. NMR spectra (*δ*; *J,* Hz; $CDCl_3$): 1.07 dd, J_{HH} 6.6, J_{HP} 6.6, $(CH_3)_2CH$]; 1.55 t (J_{HH} 7.0, $C\underline{H}_3CH_2$); 1.42 m (CHN) 2.3 dd (J_{HH} 6.6, J_{HP} 13.0, PCH_2]; 3.13 dq (J_{HH} 7.0, J_{HP} 11.4, CH_2N), 3.85 d (J_{HP} 13.0, OCH_3); δ_P 60.3. Calcd for $Cl_3H_{32}ClN_2O_5P$: N, 7.72; P, 8.54. Found: N, 7.64; P, 8.46.

Bis(diethylamino)isobutylphosphonate (**32**)

To an ether solution of the bis(diethylamino)chlorophosphonium isobutylide **3** (0.025 mol), prepared as described earlier, was added dropwise 1 g (0.031 mol) of methyl alcohol with stirring at 0°C. Then the solvent was evaporated, and the residue was distilled under reduced pressure. Yield 90%, bp 105°C (0.06 mm Hg). Colorless liquid. NMR spectra (*δ*; *J*, Hz; $CDCl_3$): NMR spectra (*δ,* ppm; *J*, Hz; C_6D_6): δ_H: 1.0 d, *J* 7.0 $(C\underline{H}_3)_2CH$]; 1.022 t [J_{HH} 7.0 $(C\underline{H}_3CH_2$]; 1.54 dd (J_{HH} 6.5, J_{HP} 13.5 PCH_2); 1.93 spt, *J* 6.0 [$(CH_3)_2C\underline{H}$]; 3.0 dq (J_{HH} 7.0, J_{HP} 10.0, CH_2N); δ_P 36.8. Calcd. for $C_{12}H_{29}N_2OP$: N, 11.28; P, 12.47. Found: N, 11.17; P, 12.35.

Bis(diethylamino) 1-Chloro-2-methylpropylphosphonate (**33**)

To a solution of bis(diethylamino)chlorophosphonium 1-chloro-2-methylpropylide **7** (6 g, 0.02 mol) in 15 mL of ether was added dropwise 1 g (0.031 mol) of methyl alcohol with stirring at 0°C. Then the solvent was evaporated and the residue was crystallized from pentane. Yield 80%, mp 53–55°C (pentane, at −60°C). NMR spectra (*δ*; *J,* Hz; $CDCl_3$): δ_H 1.01 d, J_{HH} 6.5 [$(C\underline{H}_3)_2CH$]; 1.07 t, J_{HH} 1.093, J_{HH} 7 ($C\underline{H}_3CH_2$); 2.49 m [$C\underline{H}(CH_3)_2$]; 3.01 m, 3.23 m (NCH_2); 3.94 dd, J_{HP} 2.5, J_{HH} 7 (PCH); δ_P 28.2. Calcd for $C_{12}H_{28}C1N_{20}P$: Cl, 12.54; P, 10.95. Found: Cl, 12.51; P, 10.83.

Bis(diethylamino)neopentylphosphonate (**34**)

To a solution of 0.03 mol of P-chloroylide **(4)** in 5 mL of ether at 0°C 0.03 mol of ethanol was added. Then the solvent was evaporated, and the residue was crystallized from hexane. Yield 70%, mp 87–89°C. NMR spectra, δ_P 32.6. Calcd. for $C_{13}H_{31}N_2OP$: N, 10.68; P, 11.81. Found %: N, 11.17; P, 12.35.

Typical Kinetic Experiments

1,2[P → C] Rearrangement. A solution of bis(diisopropylamino)chlorophosphonium methylide **14** in 3 mL of ether, prepared as described earlier, was placed in an NMR tube; the tube was then cooled to −50°C, and a polar solvent was added. The concentrations of ylide **14** and polar solvent were calculated in accordance with data of Table 2. Then the temperature was raised from −20 to 0°C, and the

TABLE 3 Kinetic Data of 1,2[C → P]-Chlorotropic Rearrangement of Diethylamino-*tert*-butyl-chloromethylphosphine **30** into P-Chloroylide **29**

Entries	*Solvent*	*Temp., °C* (±0.5°)	$k_1\ 10^{-4}$, s^{-1} (±5%)
1	C_6H_6 – 15%$CHCl_3$	20	1.23
2	C_6H_6 – 15%$CHCl_3$	22	1.54
3	C_6H_6 – 15%$CHCl_3$	32	4.42
4	C_6H_6 – 15%$CHCl_3$	40	7.85
5	C_6H_6 – 15%$CHCl_3$	51	22.15
6	C_6H_6 – 7.5%$CHCl_3$	30	1.5
7	C_6H_6 – 15%$CHCl_3$	30	3.6
8	C_6H_6 – 30%$CHCl_3$	30	6.15
9	C_6H_6 – 7.5%CH_3CN	30	6.9
10	C_6H_6 – 15%$CHCl_2CHCl_2$	30	10.95

tube was placed in the NMR spectrometer. The course of rearrangement was monitored by observation of the signals at δ_P 61 (ylide **14**) and 46 (phosphine **21**).

1,2[C → P] Rearrangement. A solution of diethylamino-*tert*-butyl-chloromethylphosphine **30** in 3 mL of benzene was placed in an NMR tube, and the tube was cooled to 0–5°C, a polar solvent being added. The concentration of ylide **30** and of the polar solvent were calculated in accordance with the data of Table 3. Then the tube was placed in the NMR spectrometer, and the course of rearrangement was monitored by observation of the signals at δ_P 107 (ylide **29**) and 74 (phosphine **30**).

REFERENCES

[1] O. I. Kolodiazhnyi, *Zh. Obshch. Khim., 56,* 1986, 2422.
[2] O. I. Kolodiazhnyi, *Z. Chem., 29,* 1989, 396.
[3] O. I. Kolodiazhnyi: *Phosphorus Ylide Chemistry,* "Naukova Dumka" Publ. Kiev, 1–560 (1994).
[4] O. I. Kolodiazhnyi, V. P. Kukhar, *Zh. Org. Khim. 14,* 1977, 275.
[5] (a) A. N. Nesmeyanov, M. I. Kabachnik, *Zh. Obshch. Khim., 25,* 1955, 41; (b) D. Purdela, R. Vilceanu: *Chemistry of Organophosphorus Compounds,* Khimia Publishing, Moscow, 150–151 (1967).
[6] R. Appel, H. Huppertz, A. Westerhaus, *Chem. Ber., 116,* 1983, 114.
[7] G. Fritz, W. Braun, W. Schick, W. Honle, H. G. von Schnering, *Z. Anorg. Allgem. Chem., 472,* 1981, 45.
[8] A. A. Prischenko, A. V. Gromov, Yu. P. Lutsenko, E. I. Lazhko, I. F. Lutsenko, *Zh. Obshch. Khim., 55,* 1985, 1194.
[9] A. P. Marchenko, G. N. Koidan, A. M. Pinchuk, *Zh. Obshch. Khim., 54,* 1984, 2691.
[10] O. I. Kolodiazhnyi, *Zh. Obshch. Khim., 59,* 1989, 2454.
[11] O. I. Kolodiazhnyi, *Zh. Obshch. Khim., 59,* 1989, 330.
[12] (a) O. I. Kolodiazhnyi, D. B. Golokhov, I. E. Boldeskul, *Tetrahedron Lett., 30,* 1989, 2445. (b) O. I. Kolodiazhnyi: in W. A. Hermann (ed): *Hermann/Brauer Synthetic Methods of Organometallic and Inorganic Chemistry,* Georg Thieme Verlag, Stuttgart-New York, vol. 3, p. 90 (1996).
[13] O. I. Kolodiazhnyi, O. R. Golovatyi, *Zh. Obshch. Khim., 65,* 1995, 341.
[14] O. I. Kolodiazhnyi, *Tetrahedron Lett., 22,* 1981, 1231.
[15] H. Grutzmacher: in W. A. Hermann (ed): *Hermann/Brauer Synthetic Methods of Organometallic and Inorganic Chemistry,* Georg Thieme Verlag, Stuttgart-New York, 1996, vol. 3, p. 85 (1996).
[16] O. I. Kolodiazhnyi, S. N. Ustenko, A. N. Chernega, *Zh. Obshch. Khim, 62,* 1992, 2671.