Russian Journal of General Chemistry, Vol. 71, No. 3, 2001, pp. 437–442. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 3, 2001, pp. 473–478.

Reactions of *N*,*N*'-Dialkylcyclohexane-1,2-diimines with Trivalent Phosphorus Acid Chlorides

V. G. Lodochnikov, T. V. Gryaznova, P. I. Gryaznov, R. Z. Musin, and A. M. Kibardin

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

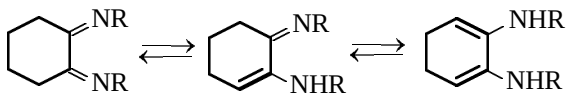
Received December 28, 1999

Abstract — *N*,*N*'-Dialkylcyclohexane-1,2-diimines react with trivalent phosphorus acid chlorides to give, depending on the structure of the organophosphorus reagent and reaction conditions, either 1,3,2-diazaphospholanes (three-coordinate phosphorus) containing the cyclohexadiene fragment in positions 4 and 5, or 1,3,2-diazaphospholines (four-coordinate phosphorus).

Previously we have demonstrated the feasibility of preparing P,N-containing heterocycles by reactions of acyclic α-diimines with electrophilic phosphorus compounds [1–4]. We suggested that the reaction of α-diimines with trivalent phosphorus acid chlorides follows the pattern [1+4]-cycloaddition, with diimine as the diene component. Therefore, it seemed interesting to perform such reactions with α-diimines having a rigid *s-cis* arrangement of the C=N bonds. However, the reactions of diimines containing endocyclic C=N bonds (5,6-dihydropyrazines) with both three- and four-coordinate phosphorus acid chlorides involved only one of the two C=N bonds and yielded the corresponding *N*-phosphorylated tetrahydropyrazines [5].

Alternative objects with such a feature are *N*,*N*'-dialkylcyclohexane-1,2-diimines with exocyclic location of the C=N bonds. The "cisoid" arrangement of the C=N bonds gives strong grounds to believe that this compounds will actively participate in [1+4]-cycloaddition reactions with trivalent phosphorus derivatives, yielding new P,N-containing heterocycles.

N,*N*'-Dialkylcyclohexane-1,2-diimines **I** and **II** theoretically can exist as tautomers **A**–**C**. According to the ^{1}H and ^{13}C NMR and IR data, tautomer **B** prevails, although the presence of minor amounts of tautomers **A** and **C** cannot be ruled out.



A **B** **C**

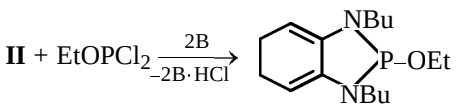
I, II

R = Me (**I**), Bu (**II**).

Here we will not discuss in detail the tautomeric transformations of cyclohexanediimines and the spectral evidences of the presence of particular isomers; it will be a subject of a separate paper. Here we report on reactions of cyclohexanediimines **I** and **II** with mono- and dichlorides of various trivalent phosphorus acids.

We have shown previously that cyclic *N*,*N*'-dibutyl-2,3-butanediimine reacts with ethyl phosphorodichloridite and diethyl phosphorochloridite exclusively by the scheme of [1+4]-cycloaddition [1]. The reaction occurs via intermediate formation of phosphoranes or phosphonium salts, which undergo dealkylation to give the final 1,3,2-diazaphospholines with the four-coordinate phosphorus atom. The reaction pathway and the structures of the final products are not affected by the presence of an organic base.

Cyclohexanediimines **I** and **II** react with both ethyl phosphorous dichloride and diethyl phosphorous chloride under mild conditions. A specific feature of such reactions is the fact that formation of one or another product depends on the presence of a base. Reaction of cyclohexanediimine **II** with ethyl phosphorous dichloride in the presence of triethylamine in a 1 : 1 : 2 ratio yields a product whose ^{31}P NMR spectrum contains a signal at δ_P 107 ppm, indicative of a trivalent phosphorus atom. The spectra of the isolated product allow its identification as 1,3-dibutyl-2-ethoxy-5,6-dihydro-1,3,2-diazaphosphindane (**III**).



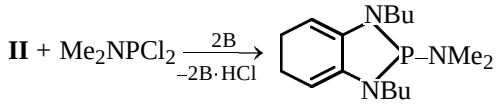
III

1070-3632/01/7103-0437 $25.00

The ^{1}H NMR spectrum of **III** contains two triplets at δ 0.82 and 1.03 ppm due to methyl protons of the butyl groups and ethoxy substituent at the phosphorus atom. The β,γ-methylene protons of the butyl group give a multiplet at δ 1.25–1.65 ppm, and the methylene protons of the cyclohexyl substituent give a narrow multiplet centered at δ 2.24 ppm. The spectrum also contains a doublet of triplets from α-methylene protons of the butyl groups and a doublet of quartets from the methylene protons of the ethoxy group. A broadened singlet at δ 4.43 ppm belongs to the methine protons of the cyclohexadiene ring. The IR spectrum of **III** contains the bands of the P–O–C bonds (1030 cm^{-1}), C=C bonds of the cyclohexadiene ring (1615 s and 1670 w, cm^{-1}), and C–H bonds at the sp^2-hybridized carbon atom (3040 cm^{-1}).

The structure and composition of the resulting diazaphospholane **III** were confirmed by high-resolution mass spectrometry. The spectrum contains a peak at *m/z* 296 assignable to the molecular ion $[M]^+$ of **III**. The accurately measured weight of this ion, 296.2016, is nicely consistent with the calculated weight of the molecule $C_{16}H_{29}N_2OP$, 296.2017. The main fragmentation pathway of $[M]^+$ involves the loss of olefin molecules C_2H_4 and C_4H_8 and of radicals $^{\cdot}OC_2H_5$, $^{\cdot}C_2H_5$, and $^{\cdot}C_4H_9$ from substituents at N and P. Further fragmentation involves the loss of the C_4H_8 or C_4H_9 group from the other nitrogen atom. The sequence of losses can also be inverse. The base peak, *m/z* 179, is due to the ion $[C_6H_5N(C_4H_9)P]^+$ originating probably from cleavage of the C–N and P–N bonds in the ion $[M - OC_2H_5]$. For all the fragment ions mentioned above, the experimental *m/z* values agree with the values calculated from the elemental composition. The fragmentation pattern under electron impact is also consistent with the proposed structure.

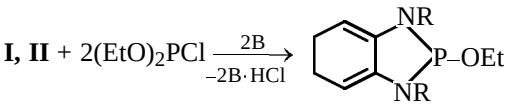
The reaction of cyclohexanediimine **II** with dimethylamidophosphorous dichloride in the presence of a base at the reactant ratio of 1 : 1 : 2 occurs similarly. Its product, 1,3-dibutyl-2-dimethylamino-5,6-dihydro-1,3,2-diazaphosphindane **IV**, was isolated and characterized.



IV

The ^{31}P NMR spectrum of **IV** consists of a single signal at δ_P 107 ppm. The ^{1}H and IR spectra confirm the structure of the product. The ^{1}H NMR spectrum, along with the signals from butyl protons, contains a narrow multiplet centered at δ 2.29 ppm, belonging to the methylene protons of the cyclohexadiene ring, a doublet at 2.42 ppm ($^3J_{PH}$ 8 Hz) from *N*-methyl protons, and a broadened singlet at δ 4.38 ppm from methine protons. The IR spectrum contains characteristic absorption bands of the diene system of the cyclohexadiene substituent.

Cyclohexanediimines **I** and **II** react with phosphorous monochlorides in the presence of a base at a molar ratio of the reactants of 1 : 2 : 2. With diethyl phosphorochloridite as the second reactant, we isolated and characterized 2-ethoxy-1,3,2-diazaphospholanes **III** and **V** and triethyl phosphite.

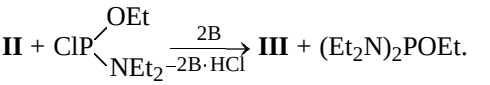


III, V

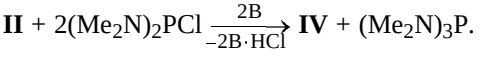
$$+ (EtO)_3P,$$

R = Bu (**III**), Me (**V**).

The reaction of **II** with ethyl diethylamidophosphorous chloride in the presence of a base occurs similarly, yielding exclusively 2-ethoxydiazaphospholane **III** and ethyl ethyl phosphorous tetraethyldiamide.

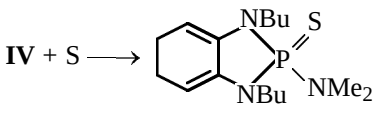


The above-described amidodiazaphospholane **IV** was also prepared by reaction of diimine **II** with tetramethylphosphorodiamidous chloride in the presence of triethylamine.



The reaction occurs under mild conditions (benzene, room temperature), as in the case of alkyl phosphorochloridites. It should be noted that the previously studied reactions of acyclic *N*,*N*'-dibutyl-2,3-butanediimine with phosphorodiamidous chlorides in the presence of a base are complete in 30 days, or in 14 h under refluxing in benzene [6].

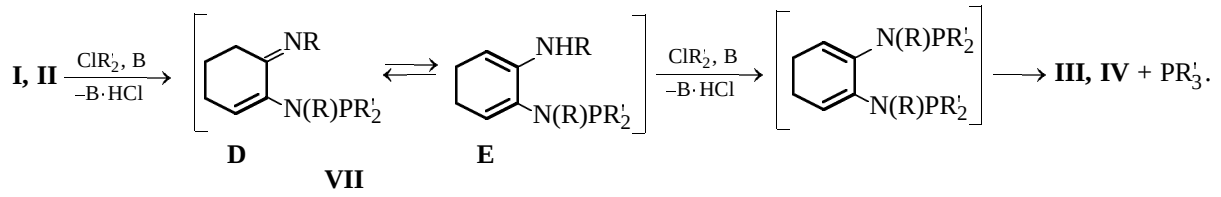
2-Aminophospholane **IV** readily takes up sulfur to give 1,3-dibutyl-2-dimethylamino-5,6-dihydro-1,3,2-diazaphosphindane 2-sulfide **VI**.



VI

Our results suggest that reactions of cyclohexanediimines with trivalent phosphorus acid chlorides

occur in steps. First, apparently, nucleophilic substitution at phosphorus yields monophosphorylation product **VII**, enamino imine **D** occurring in equilibrium with diamine **E**, which subsequently reacts with the second molecule of phosphorous chloride to give *N*,*N*'-diphosphorylated cyclohexadienediamine **VIII**. The latter undergoes cyclization to give the final products, 1,3,2-diazaphospholanes **III** and **IV**.



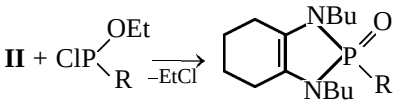
D **VII** **E**

With phosphorous dichlorides, the cyclization can occur in the stage of formation of monophosphorylated diamine **VII** of type **D**.

Since cyclohexanediimines **I** and **II** exist mainly in the form of tautomer **B**, we suggested that they would react with phosphorous triamides similarly to secondary amines [7]. We found, however, that diimine **II** does not react with hexamethylphosphorous triamide even on heating to 150°C in a sealed ampule.

We expected that the reactions of cyclohexanediimines of phosphorus acid chlorides in the absence of a base would yield diazaphospholines with four-coordinate phosphorus, similar to reactions of acyclic *N*,*N*'-dibutyl-2,3-butanediimine with phosphorous chlorides [1]. However, the ^{31}P NMR spectrum of the reaction mixture of cyclohexanediimine **II** with alkyl dialkylamidophosphorous chloride contains a single signal at δ_P 106.8 ppm. Based on the spectroscopic data, physicochemical constants, and previous results, we ascribed to the product the structure of **III**. Along with diazaphospholane **III**, we isolated a crystalline compound identified by analysis as diethylamine hydrochloride. Apparently, similar to all the above-described reaction systems, the reaction starts with the nucleophilic attack of the diimine nitrogen atom at the phosphorus atom of the amidophosphorous chloride, yielding the monophosphorylated enamino imine or its tautomer **IX** occurring in the form of hydrochloride as the reaction mixture contains no organic base. The subsequent elimination of diethylamine hydrochloride and intramolecular cyclization ultimately yield 1,3,2-diazaphospholane **III**.

Reaction of cyclohexanediimine **II** with ethyl phosphorous dichloride or diethyl phosphorous chloride in a 1 : 1 ratio in the absence of triethylamine, in contrast to the process described above, yields the four-coordinate phosphorus compounds. The IR spectra of the reaction products contain no bands characteristic of the cyclohexadiene moiety but contain a weak band at 1680 cm^{-1}. The ^{1}H NMR spectra contain no signals assignable to the methine proton of the cyclohexadiene moiety. Therefore, we suggested that these reactions yielded 2-R-1,3-dibutyl-4,5,6,7-tetrahydro-1,3,2-diazaphosphindane 2-oxides **X** and **XI**, similar to the reactions of acyclic *N*,*N*'-dibutylbutanediimine with phosphorus acid chlorides [1].



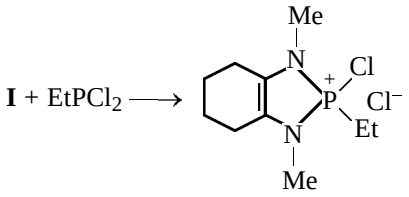
X, XI

R = OEt (**X**), Cl (**XI**).

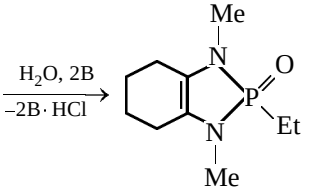
The poor yield of **X** and **XI** is probably due to the fact that in the absence of organic base both [1+4]-cycloaddition and nucleophilic substitution at phosphorus are possible. In the latter case the reaction mixture will contain, along with trivalent phosphorus compounds, also HCl and C_2H_5OH molecules, which will induce cleavage of the endocyclic P–N bond in the forming diazaphospholanes [8]. Therefore, it is feasible to isolate only diazaphospholines **X** and **XI** with a four-coordinate phosphorus atom, since they are more resistant to HCl and C_2H_5OH.

Cyclohexanediimine **I** reacts with ethyldichlorophosphine in the absence of triethylamine under mild conditions exclusively by the [1+4]-cycloaddition scheme to give phosphonium salt **XII** which was isolated and characterized. Hydrolysis of salt **XII** yields 1,3-dimethyl-2-ethyl-4,5,6,7-tetrahydro-1,3,2-diazaphosphindane 2-oxide **XIII** identified by elemental analysis and spectroscopy.

Thus, reactions of cyclohexanediimines with trivalent phosphorus acid chlorides can yield two differ-



XII



XIII

ent types of products depending on the presence of a base (HCl acceptor) in the reaction mixture. In the presence of a base, the reaction yields 1,3,2-diazaphospholanes containing a cyclohexadiene moiety, and in the absence of a base, bicyclic 1,3,2-diazaphospholenes containing a four-coordinate phosphorus atom are formed.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer in the 400–3600 cm^{-1} range from thin films of substances on KBr and NaCl supports; the wave numbers were determined to within ±2 cm^{-1}.

The NMR spectra of solutions and reaction mixtures were recorded on a Bruker WM-250 NMR Fourier spectrometer (working frequency 101.3 MHz, internal reference deuterium signal of deuterated solvent, pulse length 7 μs). The spectra of a number of pure substances were measured on a KGU-4 custom-made NMR spectrometer (working frequency 10.2 MHz) with broad-band $^{31}P–\{^1H\}$ decoupling (external reference 85% H_3PO_4). The ^1H NMR spectra were measured on a Varian T-60 spectrometer (working frequency 60.0 MHz) in calibrated ampules; samples were prepared as 10 vol % solutions, with TMS as internal reference.

The mass spectra were taken on an MKh-1310 spectrometer at the ionizing electron energy of 70 eV and electron collector current of 30 μA. The samples were introduced with an SVP-5 direct inlet system at the vaporizer temperature of 120°C. The accurate weights were determined by off-line processing of the mass spectra with an SM-4 computer using reference peaks of perfluorokerosene. The *m/z* values were determined to within 5×10^{-6} amu.

All experiments were performed under argon with absolute solvents and freshly distilled chemicals.

1,3-Dibutyl-2-ethoxy-5,6-dihydro-1,3,2-diazaphosphindane III. *a*. A solution of 3.67 g of ethyl phosphorous dichloride in 50 ml of benzene was added dropwise with stirring to a solution of 5.55 g of diimine **II** and 5.05 g of triethylamine in 150 ml of benzene, cooled to ~10°C. The mixture was left overnight, after which the precipitate of triethylamine hydrochloride was filtered off; yield 6.3 g (92%). The solvent was removed in vacuo, and the residue was distilled; 3.71 g (50%) of diazaphospholane **III** was obtained, bp 140°C (0.06 mm), d_4^{20} 1.01336. n_D^{20} 1.5158. ^{31}P NMR spectrum: δ_P 107 ppm. Mass spectrum, *m/z* (I_{rel}, %): 297 (9.3), 296 (37), M^+ $[C_{16}H_{29}N_2OP]^+$, 296 (14) $[M – C_2H_4]^+$, 267 (29) $[M – C_2H_5]^+$, 251 (21) $[M – OC_2H_5]^+$, 240 (13) $[M – C_4H_8]^+$, 239 (36) $[M – C_4H_9]^+$, 212 (14) $[M – C_2H_4 – C_2H_8]^+$, 211 (21) $[M – C_2H_4 – C_7H_9]^+$, 210 (3.8) $[M – OC_2H_5 – C_4H_9]^+$, 195 (1.5) $[M – OC_2H_5 – C_4H_8]^+$, 194 (5.9) $[M – OC_2H_5 – C_4H_9]^+$, 180 (15), 179 (100) $[C_6H_5N(C_4H_9)P]^+$, 156 (2.6) $[M – C_2H_4 – (C_4H_8)_2]^+$, 154 (7.5) $[M – C_2H_4 – (C_4H_9)_2]^+$, 153 (5.5) $[M – C_2H_5 – (C_4H_9)_2]^+$, 139 (7.7) $[M – OC_2H_5 – (C_4H_8)_2]^+$, 138 (6.6) $[M – OC_2H_5 – C_4H_8 – C_4H_9]^+$, 137 (11) $[M – OC_2H_5 – (C_4H_9)_2]^+$.

b. A solution of 7.82 g of diethyl phosphorous chloride in 25 ml of benzene was added dropwise with stirring to a solution of 5.55 g of diimine **II** and 5.05 g of triethylamine in 150 ml of benzene, cooled to 10–15°C. The mixture was left overnight, after which the precipitate of triethylamine hydrochloride was filtered off; yield 5.4 g (79%). The solvent was removed in vacuo, and the residue was distilled. Triethyl phosphite and diazaphospholane **III** were isolated. Triethyl phosphite: yield 2.01 g (48%), bp 42–43°C (10 mm), n_D^{20} 1.4108. ^{31}P NMR spectrum: δ_P 139 ppm. Compound **III**: yield 3.1 g (42%), bp 138–139°C (0.06 mm Hg), n_D^{20} 1.5157. IR spectrum, ν, cm^{-1}: 1030 (POC), 1620 s, 1675 w (=C–C=), 3040 (HC=). ^1H NMR spectrum (C_6D_6), δ, ppm: 0.82 t (6H, $CH_3CH_2CH_2CH_2$, $^3J_{HH}$ 6 Hz), 1.05 t (3H, CH_3CH_2O, $^3J_{HH}$ 7 Hz), 1.18–1.65 m (8H, $CH_3CH_2CH_2CH_2$), 2.22 m (4H, *cyclo*-CH_2–CH_2), 3.03 d.t (4H, $CH_3CH_2 \cdot CH_2CH_2$, $^3J_{HH}$ 6.5, $^3J_{PH}$ 13 Hz), 3.17 d.q (2H, CH_3CH_2O, $^3J_{HH}$ 7, $^3J_{PH}$ 14 Hz), 4.38 br.s (2H, CH). ^{31}P NMR spectrum: δ_P 107 ppm. Found P, %: 10.13. $C_{16}H_{29}N_2OP$. Calculated P, %: 10.47.

c. A solution of 3.75 g of ethyl diethylamidophosphorous chloride in 20 ml of benzene was added dropwise with stirring to a solution of 2.27 g of diimine **II** and 2.07 g of triethylamine in 100 ml of benzene, cooled to 10–15°C. The precipitate of triethylamine hydrochloride was filtered off; yield 2.7 g (96%). The solvent was removed in vacuo, and the residue was distilled. Ethyl tetraethylamidophosphite and

diasaphospholane **III** were isolated. Ethyl tetraethylamidophosphite: yield 1.31 g (58%), bp 92–95°C (10 mm). ^{31}P NMR spectrum: δ_P 130 ppm. Compound **III**: yield 1.85 g (61%), bp 138–140°C (0.06 mm Hg), d_4^{20} 1.0135, n_D^{20} 1.5150. ^{31}P NMR spectrum: δ_P 107 ppm.

d. A solution of 2.05 g of ethyl diethylamidophosphorous chloride in 25 ml of benzene was added dropwise with stirring to a solution of 2.48 g of **II** in 50 ml of benzene, cooled to 10–15°C. The mixture was left for 12 h, after which the precipitate of diethylamine hydrochloride was filtered off; yield 1 g (82%), mp 230°C. ^{1}H NMR spectrum, δ, ppm: 1.84 t (6H, C*H*$_3$CH$_2$, $^3J_{HH}$ 7 Hz), 2.97 q (4H, CH$_3$C*H*$_2$, $^3J_{HH}$ 7 Hz), 7.95 br.s (2H, NH_2^+). The solvent was removed in vacuo, and the residue was distilled. Diazaphospholane **III** (1.52 g, 46%) was obtained; bp 136–138°C (0.06 mm), n_D^{20} 1.5154. IR spectrum, ν, cm^{-1}: 1030 (POC), 1615 s, 1670 w (=C–C=), 3040 (HC=). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.82 t (6H, C*H*$_3$CH$_2$CH$_2$CH$_2$, $^3J_{HH}$ 6 Hz), 1.1 t (3H, C*H*$_3$CH$_2$O, $^3J_{HH}$ 7 Hz), 1.13–1.60 m (8H, CH$_3$C*H*$_2$C*H*$_2$CH$_2$), 2.27 m (4H, *cyclo*-CH$_2$CH$_2$), 3.07 d.t (4H, CH$_3$CH$_2$·CH$_2$C*H*$_2$, $^3J_{HH}$ 6.5, $^3J_{PH}$ 13 Hz), 3.15 d.q (2H, CH$_3$C*H*$_2$O, $^3J_{HH}$ 7, $^3J_{PH}$ 14 Hz), 4.33 br.s (2H, CH). ^{31}P NMR spectrum: δ_P 106.8 ppm.

1,3-Dibutyl-2-dimethylamino-5,6-dihydro-1,3,2-diazaphosphindane IV. *a.* A solution of 6.96 g of tetramethylamidophosphorous chloride in 50 ml of benzene was added dropwise with stirring to a solution of 5 g of **II** and 4.55 g of triethylamine in 150 ml of benzene, cooled to ~10°C. The mixture was left overnight, after which the precipitate of triethylamine hydrochloride was filtered off; yield 5.7 g (92%). The solvent was removed in vacuo, and the residue was distilled. Phosphorous hexamethyltriamide and diazaphospholane **IV** were obtained. Phosphorous hexamethyltriamide: yield 2.71 g (74%), bp 47–48°C (10 mm Hg), n_D^{20} 1.4657. ^{31}P NMR spectrum: δ_P 120 ppm. Compound **IV**: yield 5.15 g (78%), bp 143–144°C (0.08 mm), d_4^{20} 0.9961, n_D^{20} 1.5275. IR spectrum, ν, cm^{-1}: 1620 s, 1670 w (=C–C=), 3035 (HC=). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.85 t (6H, C*H*$_3$CH$_2$CH$_2$CH$_2$, $^3J_{HH}$ 6 Hz), 1.65–1.17 m (8H, CH$_3$C*H*$_2$C*H*$_2$CH$_2$), 2.29 m (4H, *cyclo*-CH$_2$CH$_2$), 2.37 d (6H, N–CH$_3$, $^3J_{PH}$ 7 Hz), 3.5 d.t (4H, CH$_3$CH$_2$·CH$_2$C*H*$_2$, $^3J_{HH}$ 6, $^3J_{PH}$ 10 Hz), 4.38 br.s (2H, =CH). ^{31}P NMR spectrum: δ_P 106 ppm. Found P, %: 10.29. $C_{16}H_{30}N_3P$. Calculated P, %: 10.51.

b. A solution of dimethylamidophosphorous dichloride in 50 ml of benzene was added dropwise with stirring to a solution of 1.11 g of **II** and 1.01 g of triethylamine in 50 ml of benzene, cooled to 5–10°C. The mixture was left overnight, after which the precipitate of triethylamine hydrochloride was filtered off; yield 1.31 g (95%). The solvent was removed in vacuo, and the residue was distilled. Diazaphospholane **IV** was obtained; yield 0.75 g (51%), bp 140–142°C (0.06 mm), d_4^{20} 0.9969, n_D^{20} 1.5272. ^{31}P NMR spectrum: δ_P 107 ppm. Found P, %: 10.21. $C_{16}H_{30}N_3P$. Calculated P, %: 10.51.

1,3-Dimethyl-2-ethoxy-5,6-dihydro-1,3,2-diazaphosphindane V. A solution of 7.03 g of diethyl phosphorous chloride in 50 ml of diethyl ether was added dropwise with stirring to a solution of 3.1 g of diimine **I** and 4.54 g of triethylamine in 150 ml of diethyl ether, cooled to 15°C. The mixture was left for 12 h, after which the precipitate of triethylamine hydrochloride was filtered off; yield 6.1 g (99%). The solvent was removed in vacuo, and the residue was distilled. Triethyl phosphite and diazaphospholine **V** were obtained. Triethyl phosphite: yield 1.81 g (49%), bp 40–41°C (10 mm), n_D^{20} 1.4102. ^{31}P NMR spectrum: δ_P 140 ppm. Compound **V**: yield 2.84 g (60%), bp 123–124°C (0.08 mm), d_4^{20} 1.0134, n_D^{20} 1.4937. IR spectrum, ν, cm^{-1}: 1035 (POC), 1625 s, 1675 w (=C–C=), 3035 (HC=). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 1.15 t (3H, C*H*$_3$CH$_2$O, $^3J_{HH}$ 7 Hz), 2.27 m (4H, *cyclo*-CH$_2$CH$_2$), 2.64 d (6H, NCH$_3$, $^3J_{PH}$ 9 Hz), 3.95 m (2H, CH$_3$C*H*$_2$O), 4.35 br.s (2H, =CH$_2$). ^{31}P NMR spectrum: δ_P 110 ppm. Found P, %: 14.88. $C_{10}H_{17}N_2OP$. Calculated P, %: 14.62.

1,3-Dibutyl-2-dimethylamino-5,6-dihydro-1,3,2-diazaphosphindane 2-sulfide VI. A 0.217-g portion of sulfur was gradually added to a solution of 2 g of diazaphospholane **IV** in 20 ml of benzene. The mixture was left for 12 h, after which the solvent was removed in vacuo. The residue was distilled, and 1.73 g (78%) of **VI** was obtained, bp 196–198°C (0.1 mm Hg), d_4^{20} 1.05824, n_D^{20} 1.54874. IR spectrum, ν, cm^{-1}: 745 (P=S), 1595, 1670 (=C–C=), 3050 (H–C=). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.82 t (6H, C*H*$_3$CH$_2$CH$_2$CH$_2$, $^3J_{HH}$ 6.5 Hz), 1.18–1.59 m (8H, CH$_3$C*H*$_2$C*H*$_2$CH$_2$), 2.21 m (4H, *cyclo*-CH$_2$); 2.35 d (6H, N–CH$_3$, $^3J_{PH}$ 8 Hz), 3.14 d.t (4H, CH$_3$·CH$_2$CH$_2$C*H*$_2$, $^3J_{HH}$ 6, $^3J_{PH}$ 10 Hz), 4.35 br.s (4H, =CH). ^{31}P NMR spectrum: δ_P 74 ppm. Found P, %: 9.14. $C_{16}H_{30}N_3PS$. Calculated P, %: 9.48.

1,3-Dibutyl-2-ethoxy-4,5,6,7-tetrahydro-1,3,2-diazaphosphindane 2-oxide X. A solution of 2.45 g of diethyl phosphorous chloride in 50 ml of benzene was added dropwise with stirring to a solution of 3.33 g of **II** in 100 ml of benzene, cooled to ~10°C. The mixture was left for 12 h, after which the solvent was removed in vacuo, and the residue was distilled. Diazaphospholine **X** was obtained; yield 2.01 g

(43%), bp 150–151°C (0.06 mm), n_D^{20} 1.4979. IR spectrum, ν, cm^{-1}: 1040 (POC), 1230 (P=O), 1680 (C=C). ^1H NMR spectrum (C_6D_6), δ, ppm: 0.77 t (6H, $CH_3CH_2CH_2CH_2$, $^3J_{HH}$ 6 Hz), 1.01 t (3H, CH_3CH_2O, $^3J_{HH}$ 7 Hz), 1.21–1.60 m (8H, $CH_3CH_2 \cdot CH_2CH_2$), 1.65 m (4H, *cyclo*-CH_2CH_2), 2.03 m (4H, *cyclo*-CH_2C=), 2.71 d.t (4H, $CH_3CH_2CH_2CH_2$, $^3J_{HH}$ 6, $^3J_{PH}$ 12 Hz), 2.93 d.q (2H, CH_3CH_2O, $^3J_{HH}$ 7, $^3J_{PH}$ 14 Hz). ^{31}P NMR spectrum: δ_P 18.9 ppm. Found P, %: 9.42. $C_{16}H_{31}N_2O_2P$. Calculated P, %: 9.87.

1,3-Dibutyl-2-chloro-4,5,6,7-tetrahydro-1,3,2-diazaphosphindane 2-oxide XI. A solution of 1.96 g of ethyl phosphorous dichloride in 50 ml of benzene was added dropwise with stirring to a solution of 3 g of **II** in 100 ml of benzene, cooled to ~10°C. The mixture was left for 2 h, after which the solvent was removed in vacuo, and the residue was distilled. Diazaphospholene **XI** was obtained; yield 1.96 g (48%), bp 155–158°C (0.06 mm), n_D^{20} 1.5196. IR spectrum, ν, cm^{-1}: 530 (P–Cl), 1235 (P=O), 1680 (C=C). ^1H NMR spectrum (C_6D_6), δ, ppm: 0.87 t (6H, $CH_3CH_2CH_2 \cdot CH_2$, $^3J_{HH}$ 7 Hz), 1.16–1.62 m (8H, $CH_3CH_2CH_2 \cdot CH_2$), 1.78 m (4H, *cyclo*-CH_2CH_2), 2.05 m (4H, *cyclo*-CH_2C=), 3.03 d.t (4H, $CH_3CH_2CH_2CH_2$, $^3J_{HH}$ 7, $^3J_{PH}$ 7 Hz). ^{31}P NMR spectrum: δ_P 25 ppm. Found, %: Cl 10.84; P 9.42. $C_{14}H_{26}ClN_2OP$. Calculated, %: Cl 11.66; P 10.18.

1,3-Dimethyl-2-ethyl-4,5,6,7-tetrahydro-1,3,2-diazaphosphindane 2-oxide XIII. A solution of 6.01 g of ethyldichlorophosphine in 50 ml of diethyl ether was added dropwise with stirring to a solution of 6.33 g of **I** in 150 ml of diethyl ether, cooled to ~10°C. Salt **XII** precipitated; mp 53°C. ^{31}P NMR spectrum ($CHCl_3$): δ_P 75.4 ppm. After 1 h, we added 9.27 g of triethylamine and then, dropwise, 0.82 g of water with cooling to 0–5°C. The mixture was left overnight, after which the precipitate of triethylamine hydrochloride (12.5 g, 99%) was filtered off. The solvent was removed in vacuo, and the residue was distilled. Diazaphospholine **XIII** was obtained; yield 7.5 g (76%), bp 133°C (0.05 mm Hg), n_D^{20} 1.5300. IR spectrum, ν, cm^{-1}: 1240 (P=O), 1675 (C=C). ^1H NMR spectrum (CCl_4), δ, ppm: 1.10 t (3H, CH_3CH_2), 1.61 m (4H, *cyclo*-CH_2CH_2), 1.90 m (2H, CH_3CH_2), 2.33 m (4H, *cyclo*-CH_2=C), 2.76 d (6H, NCH_3, $^3J_{PH}$ 10 Hz). ^{31}P NMR spectrum: δ_P 44 ppm. Found P, %: 14.32. $C_{10}H_{19}N_2OP$. Calculated P, %: 14.49.

REFERENCES

1. Kibardin, A.M., Gazizov, T.Kh., and Pudovik, A.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, no. 6, p. 1452.
2. Kibardin, A.M., Mikhailov, Yu.B., Gryaznova, T.V., and Pudovik, A.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, no. 7, p. 1684.
3. Kibardin, A.M., Gryaznova, T.V., Enikeev, K.M., Mikhailov, Yu.B., and Pudovik, A.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, no. 7, p. 1684.
4. Kibardin, A.M. and Pudovik, A.N., *Zh. Obshch. Khim.*, 1993, vol. 63, no. 11, pp. 2430–2441.
5. Lodochnikov, V.G., Gryaznova, T.V., Gryaznov, P.I., Musin, R.Z., and Kibardin, A.M., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 12, pp. 1970–1974.
6. Kibardin, A.M., Litvinov, I.A., Naumov, V.A., Efremov, Yu.Ya., Gryaznova, T.V., and Pudovik, A.N., *Dokl. Akad. Nauk SSSR*, 1987, vol. 297, no. 2, pp. 376–379.
7. Burgada, R., *Ann. Chim.*, 1963, vol. 8, nos. 5–6, pp. 347–381.
8. Kibardin, A.M., Gryaznova, T.V., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 3, pp. 376–382.