

Reaction of Dialkyl Phosphites with *N*-2-Methyl-2-chloropropylidenealkylamines

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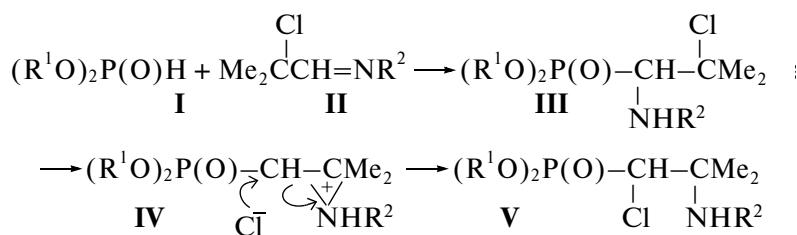
Organophosphorus compounds (OPCs) containing aminoalkylphosphoryl fragments are of large practical and theoretical interest. These compounds show a wide spectrum of useful properties. The addition of dialkyl phosphites to imines is one of the main methods for the preparation of aminoalkylphosphonates.

We have shown recently [1] that 2-halo-substituted alkylpropylidenedamines react with dialkyl phosphites to form new types of OPCs, along with addition products. It was found that the structure of final products is dependent on the halogen nature.

To reveal the effect of the nature of substituents at P(IV) and N(III) on the structure of resulting products and the synthesis of polyfunctional OPCs of new types, we have studied the reactions of dimethyl, diethyl, diisopropyl, di-*n*-butyl-, and di-2-chloroethyl phosphites (**I**) with (2-chloropropylidene)alkylamines (**II**) containing *tert*-butyl, benzyl, and isopropyl substituents at the nitrogen atom.

The reaction of dialkyl phosphites **I** with compounds **II** leads to the initial formation of addition products showing phosphorus resonance signals at 26–29 ppm. Addition product **III** with R² = *t*-Bu and R¹ = Me is a crystalline solid and can be stored in the pure state for a long time without change.

When the reaction mixture was stored for 15–20 days, the primary addition products undergo further transformations and the structure of the reaction products depends on the nature of the substituents at P(IV) and N(III). Thus, the ease of the transformation and the structure of the products are dependent on the nature of the substituents at N(III): if R² = *i*-Pr and Bz, further transformation of the addition product proceeds much more readily as compared with the compound with R² = *t*-Bu. It is likely that cyclic intermediate **IV** in the case of R² = *t*-Bu is more difficult to form as compared with R² = *i*-Pr and Bz on account of steric hindrance.



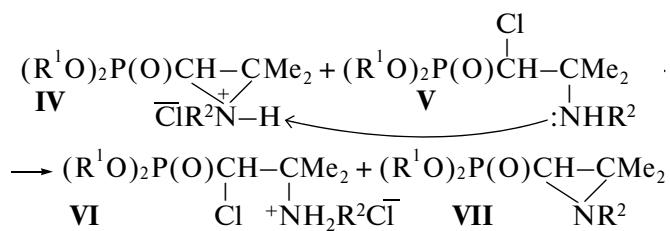
I: R¹ = Me (a), Et (b), *i*-Pr (c), *n*-Bu (d), ClCH₂CH₂ (e).

II: R² = *t*-Bu (a), Bz (b), *i*-Pr (c).

III: R¹ = Me, R² = *t*-Bu (a); R¹ = Et, R² = *t*-Bu (b); R¹ = ClCH₂CH₂, R² = *t*-Bu (c); R¹ = Me, R² = Bz (d); R¹ = *i*-Pr, R² = Bz (e); R¹ = *n*-Bu, R² = Bz (f); R¹ = ClCH₂CH₂, R² = Bz (g); R¹ = ClCH₂CH₂, R² = *i*-Pr (h);

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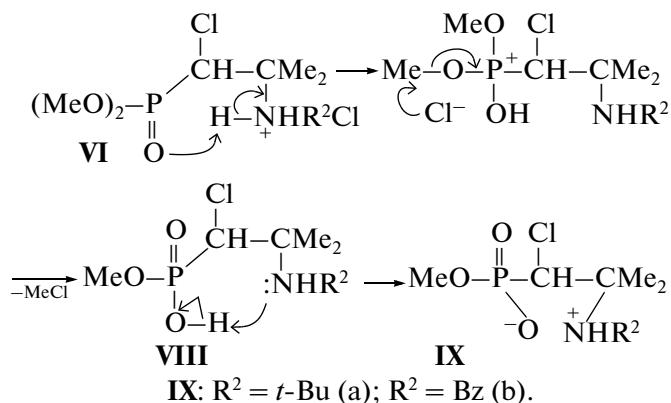
VI: $\text{R}^1 = i\text{-Pr}$, $\text{R}^2 = \text{Bz}$ (a); $\text{R}^1 = n\text{-Bu}$, $\text{R}^2 = \text{Bz}$ (b); $\text{R}^1 = \text{ClCH}_2\text{CH}_2$, $\text{R}^2 = \text{Bz}$ (c); $\text{R}^1 = \text{ClCH}_2\text{CH}_2$, $\text{R}^2 = i\text{-Pr}$ (d).

VII: $\text{R}^1 = \text{Me}$, $\text{R}^2 = t\text{-Bu}$ (a); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Bz}$ (b); $\text{R}^1 = i\text{-Pr}$, $\text{R}^2 = \text{Bz}$ (c); $\text{R}^1 = n\text{-Bu}$, $\text{R}^2 = \text{Bz}$ (d); $\text{R}^1 = \text{ClCH}_2\text{CH}_2$, $\text{R}^2 = \text{Bz}$ (e); $\text{R}^1 = \text{ClCH}_2\text{CH}_2$, $\text{R}^2 = i\text{-Pr}$ (f).

The reaction of dialkyl phosphite **I** with compounds **II** containing isopropyl and benzyl substituents leads to 2-aminoalkylphosphonate hydrochloride (**VI**) and aziridinephosphonate-2 (**VII**). The treatment of the reaction mixture with ether results in salt **VI** as a crystalline product. Compound **VII** with a

small admixture of addition product **III** was isolated from the ethereal mother liquor.

The stability of salt **VI** depends on the nature of substituents at P(IV): when $\text{R}^1 = \text{ClCH}_2\text{CH}_2$ and $\text{R}^2 = i\text{-Pr}$ and *t*-Bu, the salt is stable, while with $\text{R}^1 = \text{Me}$, it converts into betaine **IX**.



The phosphoryl oxygen in compound **VI** deprotonates the ammonium fragment to form quasi-phosphonium center that undergoes dealkylation like the second stage of the Arbuzov reaction. The amino group in intermediate compound **VIII** deprotonates the fragment of phosphonic acid monoester, which leads to betaine compound **IX**.

The structure of the compounds obtained was confirmed by elemental analysis and ^1H and ^{31}P NMR spectra.

EXPERIMENTAL

^1H NMR spectra were recorded on a Tesla BS-567A spectrometer operating at 100 MHz. Proton chemical shifts were referenced to TMS. ^{31}P NMR spectra were recorded on a CXP-100 spectrometer operating at 36.5 MHz; 85% H_3PO_4 was used as an external reference.

Reaction of *N*-(2-methyl-2-chloropropylidene)-*tert*-butylamine (**IIa**) with dimethyl phosphite (**Ia**)

A. Compound **Ia** (118 mmol) and amine **IIa** (118 mmol) were mixed in a dry argon flow. The reaction mixture was slightly warmed up. The mixture was allowed to stand at ambient temperature for 24 h. A slight turbidity was observed when the reaction mixture was dissolved in ether, which was removed by filtration. The precipitate was found to be the second reaction product **Va** formed in considerable amounts when the reaction mixture was allowed to stand for a long time (see item B). The ether was removed from the mother liquor to give 97.6 mmol (83%) of *O,O*-dimethyl (1-*tert*-butylamino-2-methyl-2-chloropropyl)phosphonate **IIIa**, mp 76°C.

^1H NMR (CDCl_3 , δ , ppm, J , Hz): 1.29 (s, 9H, CMe_3), 1.83 and 1.90 (both s, 6H, CMe_2), 1.82–1.87 (br s, 1H, NH), 3.37 (d, 1H, PCH , $^2J_{\text{PH}} = 20$ Hz), 3.93 and 3.94 (both d, 6H, $\text{P}(\text{OMe})_2$, $^3J_{\text{PH}} = 11$ Hz).

^{31}P NMR (CCl_4 , δ , ppm): 29.3.

B. Compound **Ia** (40 mmol) and amine **IIa** (40 mmol) were mixed in a dry argon flow. The reaction mixture was slightly warmed up. The mixture was kept for 30–35 days at ambient temperature. The reaction mixture was treated with ether, the precipitated crystals were separated by filtration and dried in vacuum to give 16.8 mmol (45%) of *O*-methyl (2-*tert*-butylammonio-2-methyl-1-chloropropyl)phosphonate **IX**, mp 150–151°C.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.63 (s, 9H, CMe₃), 1.71 s and 1.80 d (6H, CMe₂, ⁴J_{PH} = 0 and 2.3 Hz), 4.61 (d, 1H, PCH, ²J_{PH} = 9 Hz), 3.93 (d, 3H, POMe, ³J_{PH} = 10 Hz), 9.6 and 10.9 (both br d, 2H, N⁺H₂).

³¹P NMR (CHCl₃, δ, ppm): 11.32.

The residue after ether evaporation (10.2 mmol) according to ¹H and ³¹P NMR spectra is a 2 : 1 mixture of addition product **IIIa** (³¹P NMR (CCl₄, δ, ppm): 28.8) and *O,O*-dimethyl (1-*tert*-butylamino-3,3-dimethylaziridin-2-yl)phosphonate **VIIa** (³¹P NMR (CCl₄, δ, ppm): 26.5).

Synthesis of *O,O*-diethyl (1-*tert*-butylamino-2-methyl-2-chloropropyl)phosphonate **IIIb**

Diethyl phosphite (**Ib**) (40 mmol) and *N*-(2-methyl-2-chloropropylidene)-*tert*-butylamine (**IIa**) (40 mmol) were mixed in a dry argon flow. The temperature of the reaction mixture increased to 31°C. The mixture was allowed to stand at ambient temperature for 24 h. The reaction mixture was treated with ether, and the resulting slight turbidity was removed by filtration. The ether was removed from the mother liquor in vacuum to give 65.8 mmol (81%) of compound **IIIb**, which was identified as a crude product on account of its thermal lability.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.08 (s, 9H, CMe₃), 1.28 (t, 6H, POCH₂Me, ³J_{HH} = 7 Hz), 1.28–1.44 (br s, 1H, NH), 1.60 and 1.64 (both s, 6H, CMe₂), 3.03 (d, 1H, PCH, ²J_{PH} = 19 Hz), 4.05 (quin, 4H, POCH₂, ³J_{HH} = ³J_{PH} = 7 Hz).

³¹P NMR (CDCl₃, δ, ppm): 26.43.

Synthesis of *O,O*-di-2-chloroethyl (1-*tert*-butylamino-2-methyl-2-chloropropyl)phosphonate **IIIc**

By a similar procedure, the reaction of 81 mmol of di-2-chloroethyl phosphite (**Ic**) and 81 mmol of *N*-(2-methyl-2-chloropropylidene)-*tert*-butylamine **IIa** gave 67.9 mmol (84%) of crude compound **IIIc**.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.03 (s, 9H, CMe₃), 1.54 and 1.64 (both s, 6H, CMe₂), 1.58–1.62 (br s overlapped with the signals from CMe₂, 1H, NH), 3.1 (d, 1H, PCH, ²J_{PH} = 18.5 Hz), 3.6 (m, 4H, CH₂Cl), 4.19 (m, 4H, CH₂OP).

³¹P NMR (CHCl₃, δ, ppm): 27.1.

Reaction of *N*-(2-methyl-2-chloropropylidene)benzylamine (**IIb**) with dimethyl phosphite (**Ia**)

A. Amine **IIb** (77 mmol) was added dropwise on stirring to compound **Ia** (77 mmol) in a dry argon flow. The temperature of the reaction mixture increased to 30°C. The mixture was stirred for 24 h at ambient temperature, and volatile products were removed in a high vacuum to give 71.9 mmol (94%) of crude *O,O*-dimethyl (1-benzylamino-2-methyl-2-chloropropyl)phosphonate **IIIId**.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.69 and 1.70 (both s, 6H, CMe₂), 1.85 (br s, 1H, NH), 2.29 and 3.74 (both d, 1H, PCH, ²J_{PH} = 16.2 Hz), 3.73 and 3.78 (both d, 6H, 2MeO, ³J_{PH} = 10.6 Hz), 4.00 and 3.85 (both d, 2H, CH₂Ph, ²J_{HH} = 12.6 Hz), 7.17–7.29 (m, 5H, Ph).

³¹P NMR (CHCl₃, δ, ppm): 25.5.

B. Compound **Ia** (77 mmol) and amine **IIb** (77 mmol) were mixed in a dry argon flow. The reaction mixture was slightly warmed up. The mixture was kept for 30–35 days at ambient temperature. The reaction mixture was treated with ether five times during this period. The resulting crystals each time were separated by filtration and dried in vacuum. The ether was removed from the mother liquor and the residue was allowed to stand at ambient temperature until next dilution with ether to give 38.2 mmol (63%) of *O*-methyl (2-benzylamino-2-methyl-1-chloropropyl)phosphonate **IXb**, mp 161–163°C.

¹H NMR (CD₃OD, δ, ppm, *J*, Hz): 1.65 and 1.67 (both s, 6H, CMe₂), 3.74 (d, 3H, MeOP, ³J_{PH} = 10.3 Hz), 4.22 (d, 1H, PCH, ²J_{PH} = 10.6 Hz), 4.23 and 4.29 (both d, 2H, CH₂Ph, ²J_{HH} = 12.6 Hz), 7.44–7.56 (m, 5H, Ph), 9.5 (br s, 2H, N⁺H₂).

³¹P NMR (CH₃OH, δ, ppm): 13.6.

For C₁₂H₁₉NCIPO₃ anal. calcd. (%): N, 4.60; Cl, 12.00; P, 10.10. Found (%): N, 5.00; Cl, 11.85; P, 10.45.

After removal of the ether from the mother liquor, the residue (27.4 mmol) was found to be *O,O*-dimethyl (1-benzyl-3,3-dimethylaziridin-2-yl)phosphonate (**VIIb**) of 90% purity.

³¹P NMR (CH₃OH, δ, ppm): 24.9 (90%), 18.3 (3%), 10.5 (7%).

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.45 (d, 1H, PCH, ³J_{PH} = 18 Hz), 1.33 and 1.42 (d and s, respectively, 6H, CMe₂, ⁴J_{PH} = 2.5 and 0 Hz, respectively), 3.7 (d, 2H, CH₂Ph, ⁴J_{PH} = 3.2 Hz), 3.64 and 3.51 (both d, 6H, 2MeO, ³J_{PH} = 10.7 Hz), 7.2–7.4 (m, 5H, Ph).

Reaction of *N*-(2-methyl-2-chloropropylidene)benzylamine (**IIb**) with diisopropyl phosphite (**Ic**)

Compound **Ia** (23 mmol) was mixed with amine **IIb** (23 mmol) in a dry argon flow. The mixture was kept for 60 days at ambient temperature. The reaction

mixture was treated with ether four times during this period to give 4.7 mmol (21%) of *O,O*-diisopropyl (2-benzylamino-2-methyl-1-chloropropyl)phosphonate hydrochloride **VIA**, mp 145°C.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.36 and 1.38 (both d, 6H, CH¹₃CH²₃CH⁵OP, ³*J*_{H¹H⁵} = ³*J*_{H²H⁵} = 6.0 Hz), 1.38 and 1.43 (both d, 6H, CH³₃CH⁴₃CH⁶OP, ³*J*_{H³H⁶} = ³*J*_{H⁴H⁶} = 6.1 Hz), 1.6 and 1.82 (both s, 6H, CMe₂), 4.01 and 4.29 (both d, 2H, CH₂, ²*J*_{HH} = 12.7 Hz), 4.83 (sextet, 1H, POCH⁵CH¹₃CH²₃, ³*J*_{PH⁵} = ³*J*_{H¹H⁵} = ³*J*_{H²H⁵} = 6.0 Hz), 4.98 (sextet, 1H, POCH⁶CH³₃CH⁴₃, ³*J*_{PH⁶} = ³*J*_{H³H⁶} = ³*J*_{H⁴H⁶} = 6.0 Hz), 5.18 (d, 1H, PCH, ²*J*_{PH} = 9.5 Hz), 8.84 and 12.04 (both br s, 2H, NH₂).

³¹P NMR (CHCl₃, δ, ppm): 16.29.

For C₁₇H₃₀NCl₂PO₃ anal. calcd. (%): N, 3.50; Cl, 17.80; P, 7.80. Found (%): N, 3.65; Cl, 17.50; P, 7.45.

The residue (5.8 mmol) after the last removal of the ether was established by ³¹P and ¹H NMR spectroscopy to be a 3 : 1 mixture of addition product **IIIe** [³¹P NMR (CH₃CH₂OCH₂CH₃, δ, ppm): 21.9.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.29 and 1.32 (both d, 6H, CH¹₃CH²₃CH⁵OP, ³*J*_{H¹H⁵} = ³*J*_{H²H⁵} = 6.3 Hz), 1.32 and 1.34 (both d, 6H, CH³₃CH⁴₃CH⁶OP, ³*J*_{H³H⁶} = ³*J*_{H⁴H⁶} = 6.3 Hz), 1.75 and 1.71 (both s, 6H, CMe₂), 2.1 (br s, 1H, NH), 2.93 (d, 1H, PCH, ²*J*_{PH} = 17.34 Hz), 4.10 and 4.89 (both d, 2H, CH₂Ph, ²*J*_{HH} = 12.3 Hz), 4.75 (hept, 1H, POCH⁵CH¹₃CH²₃, ³*J*_{PH⁵} = ³*J*_{H¹H⁵} = ³*J*_{H²H⁵} = 6.3 Hz), 4.78 (hept, 1H, POCH⁶CH³₃CH⁴₃, ³*J*_{PH⁶} = ³*J*_{H³H⁶} = ³*J*_{H⁴H⁶} = 6.3 Hz), 7.28–7.38 (m, 5H, Ph) and *O,O*-diisopropyl (1-benzyl-3,3-dimethylaziridin-2-yl)phosphonate **VIIc** [³¹P NMR (CH₃CH₂OCH₂CH₃, δ, ppm): 22.3.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.25 and 1.24 (d and s, respectively, 6H, CMe₂, ⁴*J*_{PH} = 3 and 0 Hz, respectively), 1.44 (d, 1H, PCH, ²*J*_{PH} = 17.3 Hz), 3.64 and 3.74 (both d, 2H, CH₂Ph, ²*J*_{HH} = 14.2 Hz), 4.59 (hept, 1H, POCH⁵CH¹₃CH²₃, ³*J*_{PH⁵} = ³*J*_{H¹H⁵} = ³*J*_{H²H⁵} = 6.0 Hz), 4.61 (hept, 1H, POCH⁶CH³₃CH⁴₃, ³*J*_{PH⁶} = ³*J*_{H³H⁶} = ³*J*_{H⁴H⁶} = 6.0 Hz), 1.24 and 1.26 (both d, 6H, CH¹₃CH²₃CH⁵OP, ³*J*_{H¹H⁵} = ³*J*_{H²H⁵} = 6.0 Hz), 1.29 and

1.31 (both d, 6H, CH³₃CH⁴₃CH⁶OP, ³*J*_{H³H⁶} = ³*J*_{H⁴H⁶} = 6 Hz), 7.20–7.26 (m, 5H, Ph)].

Reaction of *N*-(2-methyl-2-chloropropylidene)-benzylamine (**IIb**) with dibutyl phosphite (**Id**)

By a similar procedure, the reaction of compound **Id** (30.7 mmol) with amine **IIb** (30.7 mmol) afforded 7.6 mmol (27%) of *O,O*-dibutyl (2-benzylamino-2-methyl-1-chloropropyl)phosphonate hydrochloride **VIc**, mp 122°C.

¹H NMR (CHCl₃, δ, ppm, *J*, Hz): 0.945 and 0.950 (both t, 6H, 2CH₂CH₃, ³*J*_{HH} = 7.0 Hz), 1.69 (quin, 4H, 2CH₃CH₂, ³*J*_{HH} = 7.0 Hz), 1.43 (m, 4H, 2OCH₂CH₂), 1.63 and 1.82 (both s, 6H, CMe₂), 4.03 and the second doublet is overlapped with POCH₂ signals (2H, CH₂Ph, ²*J*_{HH} = 12.7 Hz), 4.19–4.35 (m, 4H, 2CH₂OP), 5.25 (d, 1H, PCH, ²*J*_{PH} = 10 Hz), 7.42–7.58 (m, 5H, Ph), 11.9 and 8.9 (both br s, 2H, NH₂).

³¹P NMR (CHCl₃, δ, ppm): 17.91.

For C₁₇H₃₄NCl₂PO₃ anal. calcd. (%): N, 3.30; Cl, 16.70; P, 7.30. Found (%): N, 3.65; Cl, 16.90; P, 7.40.

The residue (7.6 mmol) after removal of the ether was shown by ³¹P and ¹H NMR to be a 3 : 1 mixture of addition product **IIIIf** (^d_p 23.3 ppm) and *O,O*-dibutyl (1-benzyl-3,3-dimethylaziridin-2-yl)phosphonate **VIIId** (^d_p 22.5 ppm).

Reaction of *N*-(2-methyl-2-chloropropylidene)-benzylamine (**IIb**) with di-2-chloroethyl phosphite (**Ie**)

By a similar procedure, the reaction of compound **Ie** (68.3 mmol) with amine **IIb** (68.3 mmol) gave 32.7 mmol (45%) of *O,O*-di-2-chloroethyl (2-benzylamino-2-methyl-1-chloropropyl)phosphonate hydrochloride **VIc**, mp 152–153°C.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.67 and 1.81 (both s, 6H, CMe₂), 3.76 (m, 4H, CH₂OP), 4.50 and 4.59 (m, 4H, CH₂Cl), 4.02 and 4.29 (both d, 2H, CH₂Ph, ²*J*_{HH} = 12.3 Hz), 5.5 (d, 1H, PCH, ²*J*_{PH} = 9 Hz), 7.28–7.57 (m, 5H, Ph), 8.5 and 12.1 (both br s, 2H, NH₂).

³¹P NMR (CDCl₃, δ, ppm): 18.7.

For C₁₅H₂₄NCl₄PO₃ anal. calcd. (%): N, 3.00; Cl, 32.25; P, 6.70. Found (%): N, 3.25; Cl, 32.00; P, 7.05.

The residue (84.3 mmol, 21%) after removal of the ether was established by ³¹P and ¹H NMR to be a 1 : 4 mixture of addition product **IIIg** [³¹P NMR (CDCl₃, δ, ppm): 24.5.

¹H NMR (CDCl₃, δ, ppm, *J*, Hz): 1.75 and 1.76 (both s, 6H, CMe₂), 3.08 (d, 1H, PCH, ²*J*_{PH} = 16.3 Hz), 7.10–7.26 (m, 5H, Ph) and *O,O*-di-2-chloroethyl (1-benzyl-3,3-dimethylaziridin-2-yl)phosphonate (**VIIe**) [³¹P NMR (CDCl₃, δ, ppm): 25.6.

¹H NMR (CDCl_3 , δ , ppm, J , Hz): 1.21 and 1.32 (both s, 6H, CMe_2), 1.47 (m, 1H, PCH, $^2J_{\text{PH}} = 18.9$ Hz), 3.44 and 3.67 (both d, 2H, CH_2Ph , $^2J_{\text{HH}} = 13.5$ Hz), 7.16–7.24 (m, 5H, Ph)].

Reaction of *N*-(2-methyl-2-chloropropylidene)isopropylamine (IIc**) with di-2-chloroethyl phosphite (**Ie**)**

Compound **Ie** (97.3 mmol) was mixed with amine **IIc** (97.3 mmol) in a dry argon flow. The reaction mixture was slightly warmed up. The mixture was kept for three weeks at ambient temperature. The reaction mixture was treated with ether five times during this period and the precipitated reaction product was isolated by filtration each time to give 46.7 mmol (53%) of *O,O*-di-2-chloroethyl (2-isopropylamino-2-methyl-1-chloropropyl)phosphonate hydrochloride (**VId**), mp 101°C.

¹H NMR (CDCl_3 , δ , ppm, J , Hz): 1.88 (d, 6H, CMe_2), 1.58 and 1.82 (both d, 6H, $\underline{\text{CH}}$ Me_2 , $^3J_{\text{HH}} = 7.0$ Hz), 2.3 (m, 1H, CHMe_2), 3.9 (m, 4H, CH_2OP), 4.7 (m, 4H, CH_2Cl), 5.85 (d, 1H, PCH, $^2J_{\text{PH}} = 13$ Hz), 8.3 and 11.2 (br d and br s, respectively, 2H, NH_2).

³¹P NMR (CHCl_3 , δ , ppm): 18.89.

For $\text{C}_{11}\text{H}_{24}\text{NCl}_4\text{PO}_3$ anal. calcd. (%): N, 3.82; Cl, 38.65; P, 8.44. Found (%): N, 3.62; Cl, 38.25; P, 8.58.

The residue (17.8 mmol) after removal of the ether was established by ³¹P and ¹H NMR to be a 1 : 4 mixture of addition product **IIIh** [³¹P NMR (CDCl_3 , δ , ppm): 25.9. ¹H NMR (CDCl_3 , δ , ppm, J , Hz): 1.75 and 1.76 (both s, 6H, CMe_2), 3.08 (d, 1H, PCH, $^2J_{\text{PH}} = 16.3$ Hz)] and *O,O*-di-2-chloroethyl (1-isopropyl-3,3-dimethylaziridin-2-yl)phosphonate (**VIIIf**). The mixture was identified in a crude state on account of its thermal instability.

³¹P NMR (CDCl_3 , δ , ppm): 25.6.

¹H NMR (CDCl_3 , δ , ppm, J , Hz): 1.08 and 1.14 (both d, 6H, $\underline{\text{CH}}$ Me_2 , $^3J_{\text{HH}} = 7.0$ Hz), 1.38 (s, 6H, CMe_2), 1.43 (d, 1H, PCH, $^2J_{\text{PH}} = 18$ Hz), 2.3 (m, 1H, $\underline{\text{CH}}$ Me_2), 3.68 (m, 4H, CH_2O), 4.35 (m, 4H, CH_2Cl).

REFERENCES

1. Gazizov, M.B., Khairullin, R.A., Alekhina, A.I., Litvinov, I.A., Krivolapov, D.B., Latypov, Sh.K., Balandina, A.A., Musin, R.Z., and Sinyashin, O.G., *Mendeleev Commun.*, 2008, vol. 18, no. 5, pp. 262–264.