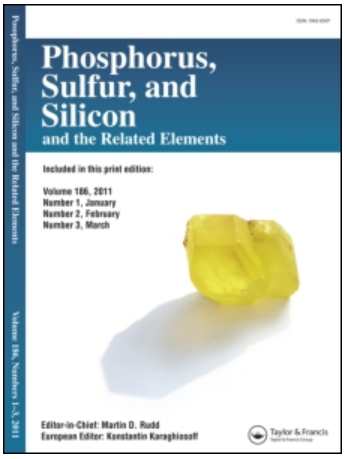

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PHOSPHORYLATED N-PROPARGYLAMINES-SYNTHESIS AND REACTIONS

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PHOSPHORYLATED N-PROPARGYLAMINES-SYNTHESIS AND REACTIONS

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Reaction of N-propargylaminophosphites with methyl iodide or sulfuryl chloride leads to N-propargylaminophosphonates or N-propargylaminophosphates. In the interaction of N-propargylaminophosphites with methyl iodide in the presence of triethylamine hydrochloride three reactivities were noted: 1) cyclization affording azaphospholes; 2) Arbuzov-type reaction giving N-propargylaminophosphonates and 3) addition of HCl to the triple bond leading to N-allylaminophosphonates. Treatment of N-propargylaminophosphonates and -thiophosphates with HCl (gas) leads to phosphorylated N-propargylammonium salts, not to the formation of adducts.

Keywords: N-propargylaminophosphonates; N-propargylaminophosphates; cyclization; azaphospholes; N-allylaminophosphonates; phosphorylated N-propargylammonium salts

INTRODUCTION

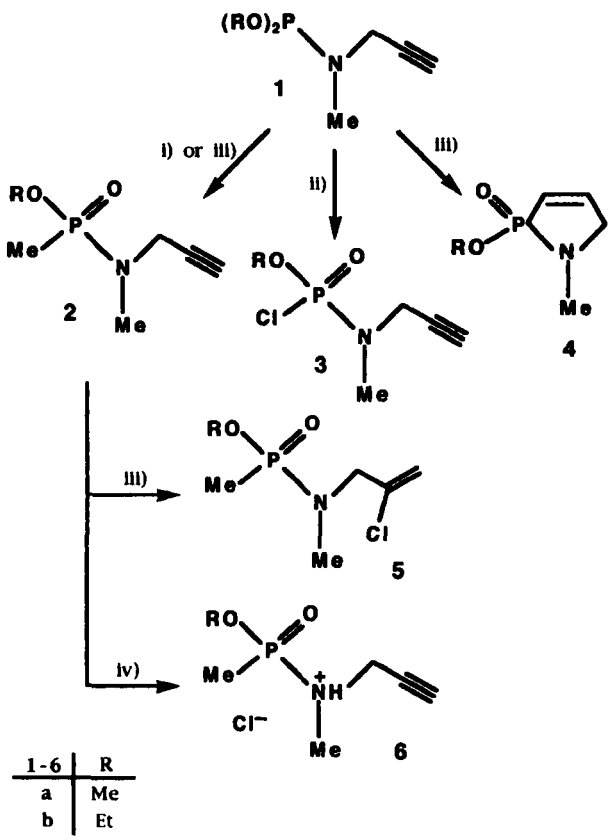
We have recently reported the synthesis and IR spectroscopic study of some S-containing propargyl compounds[1] and the synthesis of S- and Se-containing N-propargylammonium salts and their halogenation products[2]. On the other hand there are some publications[3] concerning the synthesis of phosphorylated N-propargylamines which do not undergo an acetylene-allene rearrangement even at 100°C[4,5], as their O-analogues[6]. There is only one communication[3a] in which the acetylene-allene isomerization of N-propargylaminophosphates caused by sodium hydride in THF and followed by a prototropic isomerization of the obtained allenes to the corresponding acetylene derivatives is described.

*Corresponding author.

N-Propargylaminophosphites **1** are readily available from dialkylchlorophosphites and N-propargylamine in the presence of triethylamine[5]. N-Propargyaminophosphines, synthesized by analogous routes, were found to rearrange to Z-3-alkylphosphino-2-propenal imines.

This rearrangement conceivably proceeds *via* addition of a proton and the phosphino group to the triple bond to give an azaphosphole intermediate, followed by a base catalyzed elimination to give the product[5]. In the absence of an auxiliary base, the base was the amino group of the N-propargyaminophosphites which, therefore, led to the formation of the ammonium salts as intermediates. Upon heating, cyclization took place, leading to the azaphospholes[7].

As part of our continuing study on the chemistry of heteroatom-containing propargyl compounds, we report[8] in this paper our results on the synthesis and some reactions of phosphorylated N-propargylamines.

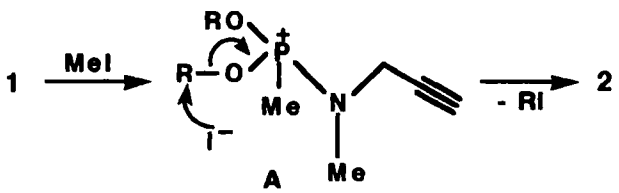


SCHEME 1 Reagents and Conditions: i) MeI, ether, −55°C, 1h, r.t., 1h: ii) SO_2Cl_2, hexane, −55°C, 2h, r.t., 1h: iii) MeI, $Et_3NH.HCl$, ether, −55°C, 3h,r.t., 1h: iv) HCl (gas), CH_2Cl_2, r.t., 3h;

RESULTS AND DISCUSSION

Employing N-methyl-N-propargylaminophosphites **1** as starting material we succeeded in preparing some phosphorylated N-propargylamines, according to the following reaction sequence which is outlined in Scheme 1.

Treatment of N-methyl-N-propargylaminophosphites **1** with methyl iodide under a nitrogen atmosphere and cooling to −55°C leads to formation of propargyl compounds with tetracoordinated phosphorus-N-methyl-N-propargylaminophosphonates **2**. Probably, the reaction proceeds via an intermediate of a quasiphosphonium structure **A** (Scheme 2) followed by nucleophilic attack of the iodide anion on the alkyl group and stabilization of the system with formation of phosphonates **2** takes place (Arbuzov type reaction):

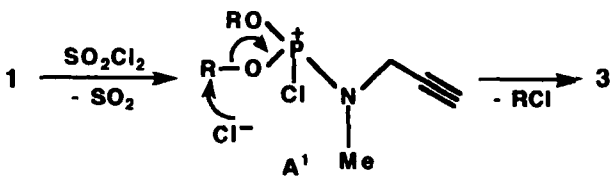


SCHEME 2

Resulting products **2** are isolated by vacuum distillation and identified by ^1H NMR, IR and mass spectra. In the ^1H NMR spectra, the signals for HC≡ and CH_2 protons appear at δ 2.29–2.32 ppm as triplet and δ 3.84–3.85 ppm as two dublets, characteristic of propargyl derivatives[1,5]. A doublet at 1.34–1.36 ppm for the Me-P protons was observed. Furthermore, the doublet for the Me-N group and other signals for the alkoxy group on the phosphorus were also observed. The IR spectra of **2** exhibit characteristic absorption bands for the phosphoryl group, triple bond and P-O-C moiety. The data from mass spectra and the elemental analysis confirm the structure of the obtained compounds.

In a similar way, the interaction between N-methyl-N-propargylamino-phosphites **1** and sulfuryl chloride gives the N-methyl-N-propargylamino-phosphates **3**, probably through the intermediate $\mathbf{A^1}$ (Scheme 3) (Arbuzov type reaction too):

Compounds 3 were isolated by vacuum distillation as yellow liquids and characterized by IR and mass spectra and elemental analyses.



SCHEME 3

Reaction of N-methyl-N-propargylaminophosphites **1** with methyl iodide in the presence of triethylaminehydrochloride under a nitrogen atmosphere and cooled to −55°C proceeds with formation of mixtures of products (yields after distillation 82–84%). Reaction was carried out in one-step using the reaction mixture containing **1** and triethylamine hydrochloride, generated in situ from dialkylchlorophosphite and N-methyl-N-propargylamine in the presence of triethylamine by the procedure described[5]. The yields of the mixture of products after distillation in vacuum were lower (41–46%). The data of TLC investigation (system methanol:ethylacetate:chloroform = 1:1:1) and IR spectra (appearance of absorption bands for double bonds at 1587–1590 cm^{-1} and 1609–1612 cm^{-1}), combined with ^1H NMR spectroscopic investigation of the mixture of products, confirm the formation of following three products: 2-alkoxy-N-methyl-2,5-dihydro-1,2-azaphosphole -2-oxides **4**, N-methyl-N-propargylamino-alkyl-methanephosphonates **2** and N-methyl-N-(2-chloro-1-propene-3-yl)-amino-alkylmethanephosphonates **5**. The prepared mixture of products was chromatographed on preparative TLC (silica gel, Kieselgel GF 254) with methanol/ethylacetate/chloroform 1:1:1 as eluent to give the pure products. The structures of **2**, **4** and **5** were confirmed by their ^1H NMR, IR and mass spectra as well as by elemental analyses. ^1H NMR spectra[7] of 2,5-dihydro-1,2-azaphospholes **4** showed the appearance of signals for H^3 and H^4 protons at low field as two doublets (H^3) and two triplets (H^4), characteristic of azaphosphole derivatives[9]. A multiplet in the range of δ 3.74–3.75 ppm for the H^5 protons was observed. Furthermore, the doublet for the Me-N group and other signals for the alkoxy group were also observed. IR spectra of **4** exhibit characteristic absorption bands for the phosphoryl group, C^3-C^4 double bond and C-O-P moiety.

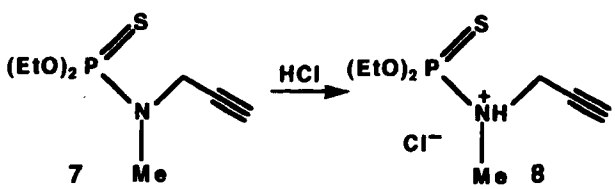
Structural assignment for the N-allylamino-alkylmethanephosphonates **5** was based on their ^1H NMR and IR spectral data. The signals for protons of Me-P (δ 1.30–1.33) and Me-N (δ 2.68–2.71) groups appear as doublets in the ^1H NMR spectra. Multiplets for the CH_2 (δ 3.73–3.75) and $=CH_2$ (δ 3.95–3.98) protons and signals for the alkoxy group were also observed. There are absorption bands for the P=O and C=C groups and P-O-C moiety in the IR spectra of **5**.

Therefore, in the reaction of N-methyl-N-propargylaminophosphites **1** with methyl iodide in the presence of triethylaminehydrochloride three type transformations proceed: (1) heterocyclization of N-methyl-N-propargylaminophosphites **1** with the hydrogen chloride of triethylaminehydrochloride[5] affording the 2,5-dihydro-1,2-azaphosphole 2-oxides **4** and elimination of alkyl chloride; (2) Arbuzov reaction of N-methyl-N-propargylaminophosphites **1** with methyl iodide giving the N-methyl-N-propargylaminophosphonates **2** and elimination of alkyl iodide; and (3) addition of hydrogen chloride upon the triple bond of N-methyl-N-propargylaminophosphonates **2** (in accordance with the Markovnikov rule) leading to the N-methyl-N-allylaminophosphonates **5**.

Treatment of the N-methyl-N-propargylamino-ethylmethanephosphonate **2a** with hydrogen chloride (gas) in methylene chloride for 3 hours leads to the phosphorylated N-methyl-N-propargylammonium salts **6a**, but no adduct **5a** was formed. A complex multiplet of bands at 2315–2778 cm^{-1} which is typical for the ammonium structure[10], is observed in the IR spectra of **6a**, along with the absorption bands for C≡C, HC≡ and P-O-C bonds and P=O group.

The adduct **5b** was obtained by treatment of the isolated N-methyl-N-propargylamino-ethylmethanephosphonate **2b** with triethylamine hydrochloride with a yield of 62%.

Analogous ammonium salt **8** was obtained by the reaction of N-methyl-N-propargylamino-diethylthiophophate **7**[5] with hydrogen chloride (gas) as well as with triethylamine hydrochloride (Scheme 4) - no adduct **5** was found in the reaction mixture:



7 8

One of the probable explanations of the fact, that in the interaction of phosphorylated N-methyl-N-propargylamines **2** and **7** with hydrogen chloride (gas), reactions of formation of phosphorylated ammonium salts take place and no addition reactions, is the more basic strength of the nitrogen atom in comparison with the triple bond in compounds **2** and **7**. The formation of the ammonium salt **8** in the reaction with hydrogen chloride (gas) as well as with triethylamine hydrochloride could be explaned with the more basic strength of nitrogen atom in the thiophosphate **7** in comparison with the one in the phosphonates **2**. The

addition of hydrogen chloride to the triple bond in the N-propargylaminophosphonates **2**, probably is due to the "softer" hydrochlorination with triethylamine hydrochloride than the direct one with hydrogen chloride (gas).

EXPERIMENTAL

Method of Analysis

^{1}H-NMR spectra were obtained on a BRUCKER WM-250 spectrometer for solutions in $CDCl_3$ operating at 250.1 MHz with Me_4Si as internal standard. IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena, Germany). Mass spectra were taken with a JEOL DX-300 spectrometer.

Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory. The melting and boiling points are uncorrected. All reactions were performed in oven-dried glassware under an atmosphere of nitrogen. The preparations were carried out under exclusion of moisture. The solvents were purified by standard methods. All compounds were checked for their purify on TLC plates.

Starting Materials

N-methyl-N-propargylamino-dialkylphosphites (**1**) were synthesized by following the procedure described earlier[5].

Synthesis of N-methyl-N-propargylamino-alkylmethanephosphonates (2a,b) General procedure

To a solution of N-methyl-N-propargylaminophosphite (**1**) (10 mmol) in dry diethyl ether (5 ml) at −55°C during 0.5 h, was added dropwise with stirring a solution of methyl iodide (1.42 g, 10 mmol) in dry ether (3 ml). The reaction mixture was stirred for 1 h at the same temperature and 1 h at room temperature. Then the solvent was removed using a rotatory evaporater, and the residue was distilled under vacuum to give the product as a light yellow liquid. The products had the following properties:

N-methyl-N-propargylamino-methylmethanephosphonate (2a)

Yield: 67%, b.p. 72–73°C/0.5 mm Hg, $C_6H_{12}O_2NP$, Calcd., %: N 8.69, P 19.22; Found, %: N 8.85, P 19.34; IR spectra (neat), cm^{-1}: 1027 (P-O-C), 1250 (P=O), 2108 (C≡C), 3216 (HC≡). ^{1}H NMP spectra, δ, ppm: 1.34 (d, $^2J_{HP}$ 13.9 Hz, 3H,

Me-P), 3.21 (d, 3H, MeO-P), 2.32 (t, $^4J_{HH}$ 2.3 Hz, 1H, HC≡), 2.75 (d, $^3J_{HP}$ 9.7 Hz, 3H, Me-N), 3.84 (dd, $^4J_{HH}$ 2.4 Hz, $^3J_{HP}$ 10.5 Hz, 2H, CH_2); MS, m/z 161 (M^+).

N-methyl-N-propargylamino-ethylmethanephosphonate (2b)

Yield: 69%, b.p. 78–79°C/0.5 mm Hg, $C_7H_{14}O_2NP$, Calcd., %: N 7.99, P 17.68; Found, %: N 8.14, P 17.61; IR spectra (neat), cm^{-1}: 1022 (P-O-C), 1247 (P=O), 2103 (C≡C), 3214 (HC≡); ^1H NMP spectra, δ, ppm: 1.36 (d, $^2J_{HP}$ 14.1 Hz, 3H, Me-P), 1.38 (t, 3H, $MeCH_2O$-P), 2.29 (t, $^4J_{HH}$ 2.4 Hz, 1H, HC≡), 2.74 (d, $^3J_{HP}$ 9.5 Hz, 3H, Me-N), 3.85 (dd, $^4J_{HH}$ 2.4 Hz, $^3J_{HP}$ 10.5 Hz, 2H, CH_2), 4.14 (m, 2H, CH_2O); MS, m/z 175 (M^+).

Synthesis of N-methyl-N-propargylamino-alkylchlorophosphates (3a,b) General procedure

To a solution of N-methyl-N-propargylaminophosphite (**1**) (10 mmol) in dry hexane (5 ml) at −55°C during 0.5 h, was added dropwise with stirring a solution of sulfuryl chloride (1.48 g, 11 mmol) in dry hexane (5 ml). The reaction mixture was stirred for 2 h at the same temperature and 1 h at room temperature. Then the solvent was removed using a rotatory evaporater, and the residue was distilled under vacuum to give the product as a yellow liquid. The products had the following properties:

N-methyl-N-propargylamino-methylchlorophosphate (3a)

Yield: 53%, b.p. 92–93°C/0.5 mm Hg, $C_5H_9O_2NClP$, Calcd., %: N 7.71, P 17.06, Found, %: N 7.84, P 17.34; IR spectra (neat), cm^{-1}: 1023 (P-O-C), 1275 (P=O), 2119 (C≡C), 3238 (HC≡).

N-methyl-N-propargylamino-ethylchlorophosphate (3b)

Yield: 57%, b.p. 97–98°C/0.5 mm Hg, $C_6H_{11}O_2NClP$, Calcd., %: N 7.16, P 15.84, Found, %: N 7.24, P 16.02; IR spectra (neat), cm^{-1}: 1019 (P-O-C), 1271 (P=O), 2117 (C≡C), 3243 (HC≡); MS m/z 195 (M^+).

Reaction of N-methyl-N-propargylamino-dialkylphosphites 1a,b with methyl iodide in the presence of triethylaminehydrochloride

To the mixture containing the N-methyl-N-propargylamino-dialkylphosphite (**1**) (10 mmol) and triethylaminehydrochloride (1.38 g, 10 mmol) in dry ether (10 ml) at −55°C was added dropwise with stirring a solution of methyl iodide (1.42

g, 10 mmol). The reaction mixture was stirred for 3 h at the same temperature and 1 h at room temperature. Then the precipitate was filtered off, the solvent was removed using a rotatory evaporater, and the residue was distilled under vacuum to give the mixture of products as a light yellow liquid. Yield: 82–84%.

Reaction was carried out in one-step using the reaction mixture containing the N-methyl-N-propargylamino-dialkylphosphite **1** and triethylaminehydrochloride, generated *in situ* from dialkylchlorophosphite and N-methyl-N-propargylamine in the presence of triethylamine by the procedure described above[5]. The yields of the mixture of products after distillation in vacuum were 41–46%.

The prepared mixtures of products were chromatographed on preparative TLC (silica gel, Kieselgel GF 254) with methanol/ethylacetate/chloroform 1:1:1 as eluent to give the pure products with the following properties:

R = Me: Yield: 82%, b.p. 78–79°C/0.5 mm Hg; Ratio of the products: **4a**:**5a**:**2a** = 2.4:1.2:1.

2-Methoxy-N-methyl-2,5-dihydro-1,2-azaphosphole 2-oxide (4a)

oil, $C_5H_{10}O_2NP$, Calcd., %: P 21.05, N 9.52, Found, %: P 20.94, N 9.48; IR spectra (neat), cm^{-1}: 1018 (P-O-C), 1226 (P=O), 1587 (C=C); ^1H NMR spectra, δ, ppm: 2.80 (d, $^3J_{HP}$ 7.7 Hz, 3H, Me-N), 3.02 (d, 3H, MeO-P), 3.74 (m, 2H, H^5), 6.05 (dd, $^3J_H{}^3{}_{-P}$ 28.5 Hz, $^3J_H{}^3{}_{-H}{}^4$ 9.0 Hz, 1H, H^3), 7.00 (tt, $^2J_H{}^4{}_{-P}$ 42.1 Hz, $^3J_H{}^3{}_{-H}{}^4$ 9.0 Hz, $^3J_H{}^4{}_{-H}{}^5$ 2.1 Hz, 1H. H^4); MS m/z 147 (M^+).

N-Methyl-N-(2-chloro-1-propene-3-yl)amino-methylmethanephosphonate (5a)

oil, $C_6H_{13}O_2NPCl$, Calcd., %: P 15.68, Cl 17.94, N 7.09, Found, %: P 15.74, Cl 18.03, N 7.01; IR spectra (neat), cm^{-1}: 1038 (P-O-C), 1249 (P=O), 1609 (C=C); ^1H NMR spectra, δ, ppm: 1.30 (d, $^2J_{HP}$ 11.7 Hz, 3H, Me-P), 2.68 (d, $^3J_{HP}$ 8.3 Hz, 3H, Me-N), 3.68 (d, $^3J_{HP}$ 10.8 Hz, 3H, MeO-P), 3.73 (m, 2H, CH_2), 3.98 (m, 2H, CH_2=); MS m/z 197 (M^+).

R = Et: Yield: 84%, b.p. 81–82°C/0.5 mm Hg; Ratio of the products: **4b**:**5b**:**2b** = 2.6:1.3:1.

2-Ethoxy-N-methyl-2,5-dihydro-1,2-azaphosphole 2-oxide (4b)

oil, $C_6H_{12}O_2NP$, Calcd., %: P 19.22, N 8.69, Found, %: P 19.38, N 8.78; IR spectra (neat), cm^{-1}: 1016 (P-O-C), 1232 (P=O), 1590 (C=C); ^1H NMR spectra, δ, ppm: 1.31 (t, 3H, $MeCH_2O$-P), 2.79 (d, $^3J_{HP}$ 7.8 Hz, 3H, Me-N), 3.75 (m,

2H, H^5), 4.02 (m, 2H, CH_2O-P), 6.03 (dd, $^3J_{H^3\text{-}P}$ 29.1 Hz, $^3J_{H^3\text{-}H^4}$ 8.9 Hz, 1H, H^3), 7.00 (tt, $^2J_{H^4\text{-}P}$ 42.2 Hz, $^3J_{H^3\text{-}H^4}$ 8.9 Hz, $^3J_{H^4\text{-}H^5}$ 2.1 Hz, 1H. H^4); MS m/z 147 (M^+).

N-Methyl-N-(2-chloro-1-propene-3-yl)amino-ethylmethanephosphonate (5b)

oil, $C_7H_{15}O_2NPCl$, Calcd., %: P 14.64, Cl 16.75, N 6.62, Found, %: P 14.51, Cl 16.91, N 6.57; IR spectra (neat), cm^{-1}: 1040 (P-O-C), 1251 (P=O), 1612 (C=C); ^1H NMR spectra, δ, ppm: 1.33 (d, $^2J_{HP}$ 11.9 Hz, 3H, Me-P), 1.34 (t, 3H, $MeCH_2O$-P), 2.71 (d, $^3J_{HP}$ 8.6 Hz, 3H, Me-N), 3.75 (m, 2H, CH_2), 3.95 (m, $^4J_{HP}$ 2.3 Hz, 2H, CH_2=), 4.09 (m, 2H, CH_2O-P); MS m/z 211 (M^+).

The compound **5b** was also obtained by the following procedure: To triethylaminehydrochloride (1.38 g, 10 mmol) and dry ether (10 ml) at −55°C was added dropwise with stirring a solution of N-methyl-N-propargylamino-ethylmethanephosphonate (**2b**) (0.88 g, 5 mmol) in dry ether (10 ml). The reaction mixture was stirred for 1 h at the same temperature and 2 h at room temperature. Then the precipitate was filtered off, the solvent was removed using a rotatory evaporater and the residue was chromatographed on preparative TLC with methanol/ethylacetate/chloroform 1:1:1 as eluent to give the pure product as a yellow oil. Yield: 62%.

Synthesis of N-methyl-N-propargylamino-N-(ethoxymethanephosphoryl)-ammonium chloride (6)

Through a stirred solution of N-methyl-N-propargylamino-ethylmethanephosphonate (**2b**) (0.88 g, 5 mmol) in dry methylene chloride (10 ml) at room temperature dry hydrogen chloride (gas) was bubbled for 3 h. Then the precipitate was filtered, washed with 20 ml of methylene chloride and dried. Yield: 76%, m.p. 74–75°C, $C_7H_{15}O_2NPCl$, Calcd., %: N 6.61, Found, %: N 6.47; IR spectra (nujol), cm^{-1}: 1029 (P-O-C), 1233 (P=O), 2125 (C≡C), 2315–2778 (ammonium), 3244 (HC≡);

Synthesis of N-methyl-N-propargylamino-N-(diethoxythiophosphoryl)-ammonium chloride (8)

Method a: Through a stirred solution of N-methyl-N-propargylamino-diethylthiophosphate (**7**)[5] (1.11 g, 5 mmol) in dry 1,2-dichloroethane (10 ml) at 45–50°C dry hydrogen chloride (gas) was bubbled for 7 h. The flask was stoppered and kept at room temperature during six days. Then the precipitate was filtered, washed with 20 ml of 1,2-dichloroethane and dried. Yield: 65%.

Method b: To triethylaminehydrochloride (1.38 g, 10 mmol) and dry 1,2-dichloroethane (10 ml) at 45–50°C was added dropwise with stirring a solution of N-methyl-N-propargylamino-diethylthiophosphate (**7**) (1.11 g, 5 mmol) in dry 1,2-dichloroethane (10 ml). The reaction mixture was stirred for a week at the same temperature. Then the precipitate, containing the ammonium salt **8** and triethylaminehydrochloride, was washed quickly with water, filtered, washed with 10 ml 1,2-dichloroethane and dried. Yield: 45%.

m.p. 81–82°C, $C_8H_{17}O_2SNPCl$, Calcd., %: N 5.43, Found, %: N 5.60; IR spectra (nujol), cm^{-1}: 1026 (P-O-C), 2127 (C≡C), 2321–2785 (ammonium), 3258 (HC≡);

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