Brief Communications

Reactions of *O*-methyl tetramethyldiamidophosphite with halo- and thiocyanoalcohols

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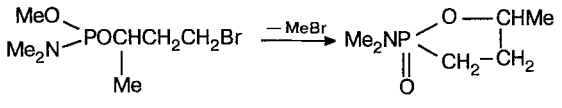
The reaction of *O*-methyl tetramethyldiamidophosphite with 3-bromopropanol or 3-bromo-2-butanol occurs with the liberation of dimethylamine and results in mixed phosphites. The reaction of *O*-methyl tetramethyldiamidophosphite with 3-thiocyano-2-butanol proceeds with the participation of the sulfur atom of the thiocyano group and formation of *S*-(3-hydroxybutyl) tetramethyldiamidothiophosphate.

Key words: *O*-methyl tetramethyldiamidophosphite, 3-bromo-2-butanol, 3-bromo-2-butanol, 3-thiocyano-2-butanol.

Previously, it has been shown that the reaction of *O*-methyl tetramethyldiamidophosphite (**1**) with 3-bromo-2-butanol (**2**) in the presence of Et_3N results in phosphite **3**, which undergoes cyclization in ether at room temperature to give[1] 5-methyl-2-dimethylamino-1,2-oxaphospholane-2-oxide (**4**) (Scheme 1).

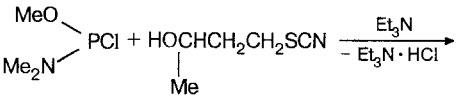
The reaction of compound **1** with 3-thiocyano-2-butanol (**5**) affords[2] 6-methyl-2-dimethylamino-1,3,2-oxathiaphosphorinane-2-oxide (**6**) (Scheme 2).

Scheme 1



3 **4**

Scheme 2



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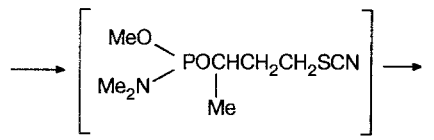

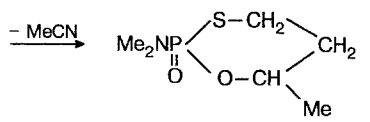

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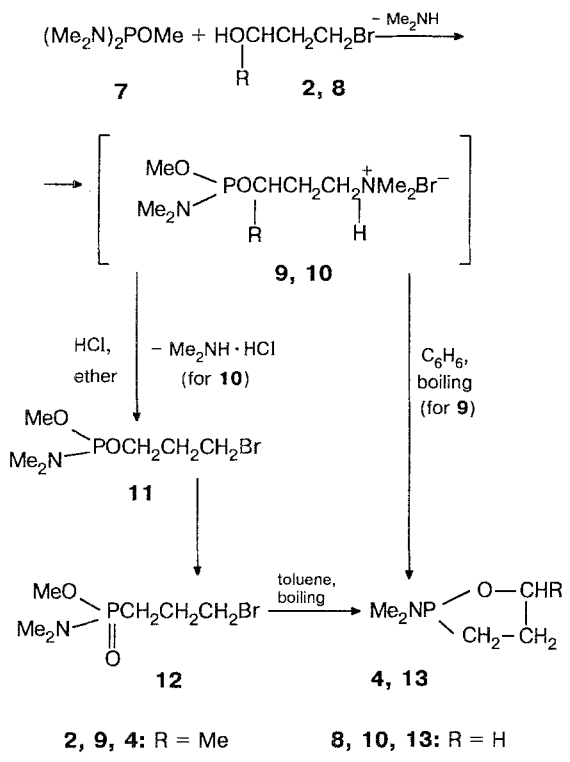
Scheme 3

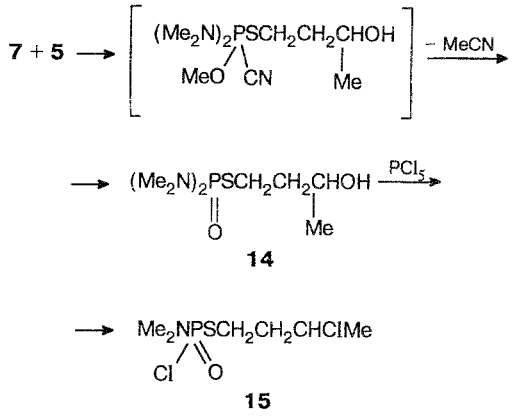


The reaction of *O*-methyl tetramethyldiamidophosphite (**7**) with bromoalkanols can proceed *via* replacement of the methoxy or dimethylamino group at the P atom. It was found that the action of compound **2** on **7** results in the abstraction of dimethylamine followed by cyclization of the phosphite formed (Scheme 3). When the starting compounds are heated in benzene at 60 °C, a white bulky precipitate is formed (the ^{31}P NMR spectrum of a sample of the reaction mixture displays one signal at δP +146). If the benzene is evaporated *in vacuo*, the pasty white precipitate decomposes with self-heating. We assume that an ammonium salt (**9**) is formed, whose transformation to compound **4** requires a higher temperature (heating in boiling C_6H_6).

The reaction of phosphite **7** with 3-bromopropanol (**8**) in benzene results in salt **10** at the first stage. This salt is more stable to heating in benzene than compound **9** and is transformed on boiling in C_6H_6 to cyclization product **13** in a minor yield. Therefore, it is more expedient to perform the reaction of compounds **7** and **8** in ether with subsequent treatment of salt **10** with an ethereal solution of HCl. Boiling in toluene results in the transformation of the phosphite **11** formed to the respective phosphate (**12**), which undergoes cyclization under these conditions to give compound **13**.

Haloalcohols react with phosphite **7** without changes in the phosphorus coordination, but thiocyanoalcohols react with compound **7** by the Arbuzov reaction scheme. The reaction starting from compounds **5** or **7** affords

Scheme 4



S-(3-hydroxybutyl)tetramethyldiamidothiophosphate (**14**), which withstands distillation *in vacuo*. The IR spectrum of compound **14** confirms the presence of an OH group (a band at 3390 cm^{-1}). The reaction of thiophosphate **14** with PCl_5 gave acid chloride **15**.

Experimental

Reaction of *O*-methyl tetramethyldiamidophosphite (7) with 3-bromo-2-butanol (2). Compound **2** (10.52 g) was slowly added with stirring to phosphite **7** (10.31 g) in C_6H_6 (20 mL). A white precipitate of salt **9** formed. The stirred reaction mixture was heated to boiling, refluxed for 15—20 min, and cooled. The precipitate was filtered off, and the residue was distilled to give 4 g of 5-methyl-2-dimethylamino-1,2-oxaphospholane-2-oxide (**4**), b.p. 85—90 °C (0.15 Torr), d_4^{20} 1.1468; n_D^{20} 1.4672. ^{31}P NMR, δ: + 49. *Cf.* Ref. 1: d_4^{20} 1.1486; n_D^{20} 1.4607. The IR spectrum of compound **4** is identical to that of a sample obtained previously.[1]

Reaction of phosphite 7 with 3-bromopropanol (8). Compound **8** (6 g) was added with stirring to phosphite **7** (6.47 g) in ether (30 mL), and a white precipitate of salt **10** formed immediately. HCl (1.5 g) in ether (20 mL) was added with stirring and cooling (ice-water) to the reaction mixture, and the amount of the precipitate increased. The ^{31}P NMR spectrum of a sample of the reaction mixture predominantly displays a signal of phosphite **11** at δ 146. The ether was evaporated *in vacuo* without heating, then C_6H_6 (10 mL) was added, and the mixture was refluxed for 45 min. The ^{31}P NMR spectrum of the reaction mixture displayed two signals at δ 50 and 36. Distillation gave a fraction (3.2 g) with b.p. 60—98 °C (0.07 Torr) whose spectrum contained the same signals. This fraction was refluxed with toluene (^{31}P NMR monitoring) to give 2-dimethylamino-1,2-oxaphospholane-2-oxide **13**: b.p. 74—79 °C (0.1 Torr), d_4^{20} 1.1725; n_D^{20} 1.4732. ^{31}P NMR, δ: + 49. *Cf.* Ref. 1: d_4^{20} 1.1718; n_D^{20} 1.4718.

Reaction of phosphite 7 with 3-thiocyano-2-butanol (5). Compound **5** (3.18 g) was added with stirring to phosphite **7** (3.64 g) in C_6H_6 (20 mL); this was accompanied by self-heating of the reaction mixture. Evaporation of C_6H_6 *in vacuo* left 2.57 g (44 %) of *S*-(3-hydroxybutyl)tetramethyldiamidothiophosphate (**14**), b.p. 120—122 °C (0.1 Torr), d_4^{20} 1.1184; n_D^{20} 1.5035. Found (%): C, 39.84; H, 8.98; N, 11.70; P, 12.07. $C_8H_{21}N_2O_2PS$. Calculated (%): C, 40.00; H, 8.75; N, 11.67; P, 12.92. ^{31}P NMR, δ: +42.

Reaction of thiophosphate 14 with PCl_5. PCl_5 (3.97 g) was cautiously added to a solution of thiophosphate **14** in $CHCl_3$ (20 mL). The mixture was refluxed for 30 min. The volatile compounds were distilled off *in vacuo* (10 Torr) at 70 °C. $CHCl_3$ was added to the residue, and the solution was passed through a porous funnel with SiO_2 to remove resinous admixtures. The solvent was evaporated *in vacuo*, and the residue was distilled to give acid chloride **15**, b.p. 98—110 °C (0.1 Torr), d_4^{20} 1.2261; n_D^{20} 1.5080. Found (%): C, 28.56; H, 5.40; P, 12.09. $C_6H_{14}Cl_2NOPS$. Calculated (%): C, 28.80; H, 5.60; P, 12.40. ^{31}P NMR, δ: +38.

References

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Synthesis of 1-morpholino-1-(phenylethynyl)cycloalkanes from enamines and phenylacetylene in the presence of Cu(I) halides

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1-Morpholino-1-(phenylethynyl)cyclopentane and 1-morpholino-1-(phenylethynyl)cyclohexane were obtained by reactions of enamines, derivatives of cyclic ketones, with phenylacetylene in the presence of CuI. A scheme for catalysis by Cu(I) compounds with the intermediate formation of copper phenylacetylide and iminium salts was suggested.

Key words: 1-amino-1-(phenylethynyl)cycloalkanes; enamines; phenylacetylene, copper(I) halides; copper acetylides; Mannich reaction; iminium salts.

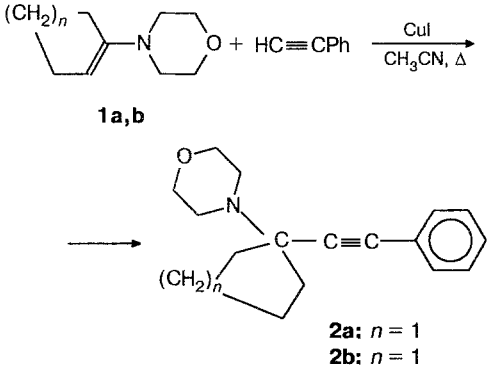
The addition of nonactivated terminal acetylenes to the double bond of enamines, derivatives of butyric and isobutyric aldehydes, catalyzed by Cu(I) compounds has been described previously.[1]

We have found that enamines **1a,b**, the derivatives of cyclic ketones, also readily react with phenylacetylene on heating in acetonitrile in the presence of stoichiometric or catalytic amounts of CuI to give 1-morpholino-1-(phenylethynyl)cycloalkanes **2a,b** (Scheme 1).

It was shown by chromatography that compounds **2** are also formed if CuCl or CuBr are used. In Ref. 1, only the catalytic action of Cu(I) compounds was stated.

It is noted in a review[2] devoted to the Mannich reaction (which can also occur *via* enamines as intermediate compounds) that Cu(I) salts increase the nucleophilicity of acetylene substrates toward Mannich rea-

Scheme 1



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