128.73 (C(5)); 135.26 (C(1′)); 135.69 (C(2″)); 158.10 (C(7″)); 160.79 (C(3)); 182.45 (C(1)); 190.89 (C(5″)).

2-Chloro-3-dimethylamino-4,4-dimethoxy-(5*Z*)-(prop-2-enylidene)cyclopent-2-enone (5). Found (%): C, 55.72; H, 6.08; Cl, 13.48; N, 5.61. $C_{12}H_{16}ClNO_3$. Calculated (%): C, 55.93; H, 6.25; Cl, 13.76; N, 5.43. IR, ν/cm^{-1}: 1600, 1725. ^1H NMR, δ: 3.18 (s, 6 H, 2 OMe); 3.43 (s, 6 H, NMe_2); 5.53 (dd, 1 H, $=CH_2$, J_1 = 10 Hz, J_2 = 1 Hz); 5.58 (m, 1 H, $=CH_2$); 6.36 (d, 1 H, $CH_2=CH-C\underline{H}=$, J = 11 Hz); 7.04 (ddd, 1 H, $CH_2C\underline{H}-CH=$, J_1 = 17 Hz, J_2 = 11 Hz, J_3 = 10 Hz). ^{13}C NMR, δ: 41.54 (NMe_2); 51.85 (2 OMe); 105.38 (C(4)); 109.50 (C(2)); 126.11 ($=CH_2$); 127.90 (C(5)); 132.15 and 132.20 (=CH—CH=); 157.54 (C(3)); 182.98 (C(1)). MS, *m/z*: 257 $[M]^+$, 242 $[M - Me]^+$, 226 $[M - MeO]^+$, 222 $[M - Cl]^+$.

2-Chloro-3-dimethylamino-4,4-dimethoxy-(5*E*)-(prop-2-enylidene)cyclopent-2-enone (6). Found (%): C, 56.19; H, 6.02; Cl, 13.51; N, 5.28. $C_{12}H_{16}ClNO_3$. Calculated (%): C, 55.93; H, 6.25; Cl, 13.76; N, 5.43. IR, ν/cm^{-1}: 1600, 1725. ^1H NMR, δ: 3.13 (s, 6 H, 2 OMe); 3.43 (s, 6 H, NMe_2); 5.55 (dd, 1 H, $=CH_2$, J_1 = 10.2 Hz, J_2 = 1.5 Hz); 5.63 (dd, 1 H, $=CH_2$, J_1 = 16.8 Hz, J_2 = 1.5 Hz); 6.90 (ddd, 1 H, $CH_2=C\underline{H}-CH=$, J_1 = 16.8 Hz, J_2 = 11.8 Hz, J_3 = 10 Hz); 7.05 (d, 1 H, $CH_2=CH-C\underline{H}=$, J = 11.8 Hz). ^{13}C NMR, δ: 41.68 (NMe_2); 51.88 (2 OMe); 106.56 (C(4)); 108.37 (C(2)); 127.26 ($=CH_2$); 128.22 (C(5)); 130.07 ($CH_2=\underline{C}H$); 131.02 ($CH_2=CH-\underline{C}H=$); 158.20 (C(3)); 182.61 (C(1)).

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P^{III}-Derivatives of methyl mercaptoacetate

A. R. Burilov, I. V. Selezneva, and M. A. Pudovik*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: pudovik@glass.ksu.ras.ru

Dichlorophenylphosphine and dichlorodiethylamidophosphite react with methyl (trimethylsilylthio)acetate to substitute the methoxycarbonylmethylthio group for one Cl atom.

Key words: dichlorophenylphosphine, dichlorodiethylamidophosphite, methyl (trimethylsilylthio)acetate, chloridophosphothioites.

Earlier,[1] we have shown that the reaction of $RPCl_2$ (or PCl_3) with α-mercapto ketones in the presence of a base is accompanied by cyclization involving the carbonyl group. P^{III}-Derivatives of alkyl mercaptoacetates exhibit interesting chemical properties. Refluxing of a mixture of equimolar amounts of PCl_3 and alkyl mercaptoacetates in benzene yields alkoxycarbonylmethylphosphorodichloridothioites, which, when heated to 180—190 °C, cyclize into 2-chloro-5-oxo-1,3,2-oxathiaphospholane. Alkoxycarbonylmethylphosphorothioites and -phosphoramidites synthesized on their basis easily undergo[2] thiophosphite-thiophosphonate isomerization under the action of oxygen at room temperature.

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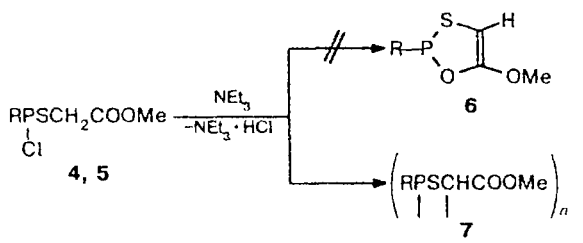
In a continuation of these studies, we attempted to obtain alkoxycarbonylmethylphosphorodichloridothioites (phosphorochloridothioites) by the reaction of Et_2NPCl_2 (**1**) and $PhPCl_2$ (**2**) with alkyl mercaptoacetates in the presence of a base. However, this did not result in the target products; a mixture of phosphorus-containing products was obtained instead (^{31}P NMR). An attempt to synthesize the target products by carrying out the reaction in the absence of a base also failed. In connection with this, we used *S*-silylated methyl mercaptoacetate (**3**) as an object of phosphorylation. Its reactions with acid dichlorides **1** and **2** easily occur at room temperature to give compounds **4** and **5** in high yields. These are light yellow compounds with an unpleasant odor, which are easily hydrolyzed in air.

$$RPCl_2 + Me_3SiSCH_2COOMe \xrightarrow{-Me_3SiCl} RPSCH_2COOMe$$
$$\mathbf{1, 2} \qquad \mathbf{3} \qquad\qquad\qquad\qquad\quad Cl \quad \mathbf{4, 5}$$

R = NEt_2(**1**, **4**); Ph (**2**, **5**)

Their IR spectra exhibit absorption bands corresponding to the P—Cl (575 and 580 cm^{-1}) and C=O (1735 cm^{-1}) stretching vibrations.

Compounds **4** and **5** are thermally stable and do not undergo heterocyclization accompanied by elimination of methyl chloride *via* the pathway described earlier.[2] Owing to the presence of the carbonyl and methylene groups as well as the reactive Cl atom in compounds **4** and **5**, one could expect that the action of a base would lead to the formation of oxathiaphospholene (**6**), as took place in the case of phosphorylated α-mercapto ketones.[1] Compounds **4** and **5** easily react with triethylamine at room temperature to give polymeric products



(**7**) rather than the expected heterocycle **6**. The IR spectra of products **7** show a band at 1735 cm^{-1} corresponding to the C=O stretching vibrations, and their ^1H NMR spectra exhibit signals for the protons of the CH and OMe groups (δ 3.50 and 3.75).

This result attests to the high mobility of the protons of the methylene fragment in compounds **4** and **5**, which is apparently due to the presence of the neighboring thiol S atom. This may also account for the above-described unsuccessful attempts to phosphorylate alkyl mercaptoacetates with acid dichlorides **1** and **2** in the presence of a base.

Experimental

^{31}P NMR spectra were recorded on a nonserial YaMR KGU-4 instrument (10.2 MHz) with 85% H_3PO_4 as the external standard. ^1H NMR spectra were recorded on a Varian T-60 spectrometer (60 MHz) with Me_4Si as the internal standard. IR spectra were obtained on a UR-20 spectrometer in the range 400—3600 cm^{-1}.

Methoxycarbonylmethyl diethyl phosphoroamidochloridothioite (4). A mixture of dichloride **1** (17.4 g, 100 mmol) and ester (17.8 g, 100 mmol) was kept at ~20 °C for 24 h. Chlorotrimethylsilane was removed *in vacuo* (water-jet pump). The mixture was fractionated *in vacuo* to give compound **4** (20.6 g, 85%), b.p. 97—98 °C (0.045 Torr), d_4^{20} 1.1792, n_D^{20} 1.4928. Found (%): C, 34.75; H, 6.30; P, 12.90. $C_7H_{15}ClNO_2PS$. Calculated (%): C, 34.50; H, 6.20; P, 12.71. ^1H NMR (CCl_4), δ: 1.17 (t, 6 H, Me, $^3J_{H,H}$ = 7 Hz); 3.33 (m, 4 H, CH_2N); 3.70 (s, 3 H, OMe); 3.73 (d, 2 H, SCH_2, $^3J_{H,P}$ = 5 Hz). ^{31}P NMR, δ: 160.

Methoxycarbonylmethyl phenylphosphonochloridothioite (5) was obtained in a similar way from dichlorophenylphosphine (**2**) (17.9 g, 100 mmol) and ester **3** (17.8 g, 100 mmol) in 80% yield, b.p. 132—133 °C (0.003 Torr), d_4^{20} 1.2905, n_D^{20} 1.6013. Found (%): C, 43.64; H, 4.35; P, 12.70. $C_9H_{10}ClO_2PS$. Calculated (%): C, 43.47; H, 4.05; P, 12.46. ^1H NMR (CCl_4), δ: 3.50 (d, 2 H, SCH_2, $^3J_{H,P}$ = 14 Hz); 3.67 (s, 3 H, OMe); 7.33—7.77 (m, 5 H, Ph). ^{31}P NMR, δ: 140.

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