$CHCl_3$ with Bu^i_2AlH or dichlorocarbene CCl_2, whose formation has been assumed previously.[9] In order to check experimentally the existence of CCl_2, the reaction was carried out in the presence of the traditional carbene trap, cyclohexene. The product of the reaction of cyclohexene with CCl_2 (dichloronorcarane) was observed by CL-MS along with the main products of addition of the $^{\cdot}CCl_3$ radical to cyclohexene, but its quantity was insignificant.

When the reaction was carried out in the presence of styrene, the yields of $CHCl_3$ and CH_2Cl_2 were substantially lower. This indicates that these products are mainly formed *via* the radical route.

Experimental

A 1 *M* solution of Bu^i_2AlH pre-purified from a triisobutylaluminum admixture by vacuum distillation was used. Entirely deuterated 1,4-dioxane dried by boiling over sodium followed by distillation was used for NMR measurements. CCl_4 was dried with $CaCl_2$ and then distilled. Styrene-d_8 was used in experiments with the radical trap. Cyclohexene dried over $MgSO_4$ was used as the dichlorocarbene trap. The reaction products in the presence of cyclohexene were identified on a Finnigan LC-MS mass spectrometer.

Dichloronorcarane used as the standard in GLC and MS analyses was synthesized by the known procedure.[10]

In the study of CIDNP, the reactions were carried out directly in the probe of a Tesla BS-467 NMR spectrometer (60 MHz, CW) at room temperature. Carbon tetrachloride was added by a syringe to a solution of Bu^i_2AlH in a 5-mm ampule under an argon atmosphere in the detector.

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Synthesis of *O,O*-diethyl *Se*-alkyl selenophosphates by the reactions of diethyl phosphite with alkaneselenenyl halides*

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The reactions of diethyl phosphite with alkaneselenenyl halides in chloroform at 20 °C afforded the corresponding *O,O*-diethyl *Se*-alkyl selenophosphates.

Key words: diethyl phosphite, alkaneselenenyl chlorides, alkaneselenenyl bromides, *O,O*-diethyl *Se*-alkyl selenophosphates.

Several procedures are known for the synthesis of *O,O*-dialkyl *Se*-aryl selenophosphates, most of which have been reported previously.[1] However, only a few examples of the synthesis of compounds $(AlkO)_2P(O)SeAlk$ are available in the literature. Thus, it was reported that ether $(EtO)_2P(O)SeMe$ was obtained by the reaction with halosilanes.[2] *O,O*-Diethyl *Se*-butyl selenophosphate was prepared from *O,O,O*-triethyl selenophosphate and bromobutane.[3] The reac-

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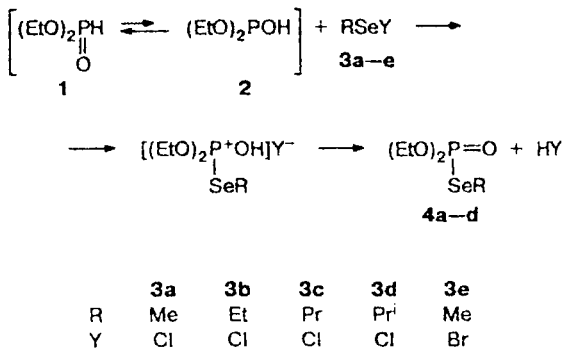
tion of bromoethane with the salt of *O,O*-diethyl selenophosphoric acid afforded ether $(EtO)_2P(O)SeEt$.[4] When diethyl phosphite was heated with butyl selenoisocyanate in benzene, $(EtO)_2P(O)SeBu$ was formed as the reaction product.[5] The reactions of diethyl phosphite with areneselenenyl halides afforded *O,O*-diethyl *Se*-aryl selenophosphates.[1] The data on the use of this reaction for preparing *O,O,Se*-trialkyl selenophosphates as well as the data on the chemical properties of the resulting compounds are unavailable in the literature.

With the aim of developing a simple procedure for the synthesis of *O,O,Se*-trialkyl selenophosphates, we studied the reactions of diethyl phosphite with compounds RSeY, where R = Me, Et, Pr^n, or Pr^i and Y = Cl or Br (**3a—e**). It was found that when selenenyl chlorides **3a—d** and diethyl phosphite were mixed in equimolar amounts at 20 °C, *O,O*-diethyl *Se*-alkyl selenophosphates (**4a—d**) were formed in high yields (72—82%). Methaneselenenyl bromide **3e** also reacted with diethyl phosphite but the yield of product **4a** was lower (50%). Because of this, we used only selenenyl chlorides **3a—d** in subsequent experiments.

The proposed pathway of the formation of the reaction products is analogous to the Arbuzov rearrangement.[6] The first stage of the reaction is the nucleophilic attack of diethyl phosphite on the selenium atom in alkaneselenenyl halide, which leads to replacement of the halogen atom.



	3a	3b	3c	3d	3e
R	Me	Et	Pr	Pr^i	Me
Y	Cl	Cl	Cl	Cl	Br

It is known that under the conditions of our study, diethyl phosphite exists in two tautomeric forms.[1] The concentration of form **2** in the initial solution was very small. However, when compounds **3a—e** were added, products **4a—d** were formed, which is, apparently, indicative of a very high rate of the reaction of **2**. This disturbs the equilibrium between the tautomers and leads to the formation of new amounts of **2**.

Compounds **4a—d** are high-boiling liquids. Their structures were established by IR and ^1H and ^{31}P NMR spectroscopy and mass spectrometry and were confirmed by the data of elemental analysis. Compounds **4c,d** are reported for the first time.

Experimental

The ^1H and ^{31}P NMR spectra were recorded on a Jeol FX 90Q spectrometer (operating at 89.55 MHz for ^1H and at 36.23 MHz for ^{31}P); $CDCl_3$ was used as the solvent; HMDS was used as the internal standard.

The initial alkaneselenenyl halides were prepared immediately before use from equimolar amounts of the corresponding dialkyl diselenides and sulfuryl chloride (in the case of RSeCl,) or bromine (in the case of RSeBr).

***O,O*-Diethyl *Se*-methyl selenophosphate (4a).** A solution of SO_2Cl_2 (1.35 g, 0.01 mol) in chloroform (15 mL) was added dropwise to a solution of Me_2Se_2 (1.9 g, 0.01 mol) in chloroform (15 mL). The reaction mixture was stirred for 10 min. The resulting solution of MeSeCl (0.02 mol) was added dropwise to a solution of diethyl phosphite (2.76 g, 0.02 mol) in chloroform (20 mL). The mixture was stirred at 20 °C for 1 h. The solvent was distilled off. The residue was distilled *in vacuo*. Product **4a** was obtained in a yield of 3.31 g (71.8%), b.p. 78 °C (2 Torr). Found (%): C, 26.2; H, 6.3; P, 11.9; Se, 34.0. $C_5H_{13}O_3PSe$. Calculated (%): C, 26.0; H, 5.7; P, 13.4; Se, 34.2. ^1H NMR, δ: 4.16 (m, 4 H, 2 CH_2); 2.16 (d, 3 H, MeSe); 1.37 (t, 6 H, 2 Me). ^{31}P NMR, δ: 19.2 (J = 13.4 Hz). MS, m/z (I_{rel} (%)): 232 $[M]^{\cdot+}$ (17), 155 $[M-77]^+$ (35), 137 $[M-MeSe]^+$ (27), 109 $[M-123]^+$ (100), 93 $[M-139]^+$ (30), 81 $[M-151]^+$ (66). IR, ν/cm^{-1}: 1247 (P=O), 1013 (P—OR), 788 (P—Se).

***O,O*-Diethyl *Se*-ethyl selenophosphate (4b)** was prepared analogously to compound **4a** from Et_2Se_2 (2.16 g, 0.01 mol), SO_2Cl_2 (1.35 g, 0.01 mol), and diethyl phosphite (2.76 g, 0.02 mol). The yield was 3.72 g (75.9%), b.p. 80 °C (2 Torr). Found (%): C, 29.7; H, 6.2; P, 12.1; Se, 32.7. $C_6H_{15}O_3PSe$. Calculated (%): C, 29.4; H, 6.2; P, 12.6; Se, 32.2. ^1H NMR, δ: 4.16 (m, 4 H, 2 CH_2O); 2.87 (m, 2 H, CH_2Se); 1.51 (t, 3 H, Me); 1.36 (t, 6 H, 2 $\underline{Me}CH_2O$). ^{31}P NMR ($CDCl_3$), δ: 19.2 (J_{P-H} = 14.2 Hz). MS, m/z (I_{rel} (%)): 246 $[M]^{\cdot+}$ (12), 138 $[M-EtSe+H]^{\cdot+}$ (18), 109 $[M-137]^+$ (100), 93 $[M-153]^+$ (32), 81 $[M-165]^+$ (62). IR, ν/cm^{-1}: 1255 (P=O), 1014 (P—OR), 788 (P—Se).

***O,O*-Diethyl *Se*-propyl selenophosphate (4c)** was prepared analogously to compound **4a** from Pr_2Se_2 (2.44 g, 0.01 mol), SO_2Cl_2 (1.35 g, 0.01 mol), and diethyl phosphite (2.76 g, 0.02 mol). The yield was 4.27 g (82%), b.p. 84 °C (2 Torr). Found (%): C, 32.4; H, 5.8; P, 11.1; Se, 30.8. $C_7H_{17}O_3PSe$. Calculated (%): C, 32.4; H, 6.6; P, 11.9; Se, 30.5. ^1H NMR, δ: 4.16 (m, 4 H, 2 $\underline{CH_2}O$); 2.85 (t, 2 H, CH_2Se); 1.79 (m, 2 H, $\underline{CH_2}CH_2Se$); 1.35 (t, 6 H, 2 $\underline{Me}CH_2O$); 1.0 (t, 3 H, Me). ^{31}P NMR, δ: 19.8 (J_{P-H} = 14.0 Hz). MS, m/z (I_{rel} (%)): 260 $[M]^{\cdot+}$ (11), 218 $[M-Pr+H]^{\cdot+}$ (15), 162 $[M-98]^{\cdot+}$ (28), 109 $[M-151]^+$ (53), 81 $[M-179]^+$ (35), 43 $[M-217]^+$ (100). IR, ν/cm^{-1}: 1250 (P=O), 1010 (P—OR), 790 (P—Se).

***O,O*-Diethyl *Se*-isopropyl selenophosphate (4d)** was prepared analogously to compound **4a** from $Pr^i_2Se_2$ (2.44 g, 0.01 mol), SO_2Cl_2 (1.35 g, 0.01 mol), and diethyl phosphate (2.76 g, 0.02 mol). The yield was 3.74 g (72.2%), b.p. 86—88 °C (2 Torr). Found (%): C, 33.0; H, 7.0; P, 10.9; Se, 30.0. $C_7H_{17}O_3PSe$. Calculated (%): C, 32.4; H, 6.6; P, 11.9; Se, 30.5. ^1H NMR, δ: 4.16 (m, 4 H, 2 $\underline{CH_2}O$); 3.6 (m, 1 H, CHSe); 1.55 (d, 6 H, 2 Me); 1.36 (t, 6 H, 2 $\underline{Me}CH_2O$). ^{31}P NMR, δ: 19.4 (J_{P-H} = 13.8 Hz). MS, m/z (I_{rel} (%)): 260 $[M]^{\cdot+}$ (18), 219 $[M-41]^+$ (54), 191 $[M-69]^+$ (46), 163 $[M-97]^+$ (100), 110 $[M-140]^{\cdot+}$ (46), 81 $[M-179]^+$ (51). IR, ν/cm^{-1}: 1250 (P=O), 1015 (P—OR), 789 (P—Se).

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(*N*-Benzoyl)trichloroacetimidoylphosphonate

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A method for the synthesis of *O,O*-diethyl (*N*-benzoyl)trichloroacetimidoylphosphonate (**1**) by successive reaction of *N*-(1-diethoxyphosphoryl-2,2-dichlorovinyl)benzamide with Me_3SiCl and Cl_2 was proposed. The reaction of phosphonate **1** with R_3P follows the [4+1] cycloaddition mechanism to give phosphoranes, whose stability and further transformations are controlled by the nature of R.

Key words: acyl imines, imidoylphosphonates, cycloaddition, phosphoranes.

The first representatives of compounds containing the C-phosphorylated azomethine group were synthesized by M. I. Kabachnik *et al.* in 1945.[1] Important among those compounds are imidoylphosphonates, whose electron-withdrawing phosphoryl group predetermines their higher reactivity compared to ordinary azomethines.

Most of the known methods for the synthesis of imidoylphosphonates consist in nucleophilic replacement of the Cl atom of imidoyl chlorides under the action of trialkyl phosphites.[2] However, this method cannot be used for the synthesis of trichloroacetimidoylphosphonates because the reaction of phosphites with trichloroacetimidoyl chlorides involves the Cl atoms of the trichloromethyl group.[3]

Similarly to the earlier published procedure,[4] we attempted to obtain (*N*-benzoyl)trichloroacetimidoylphosphonate **1** from the known phosphonate **2** under the action of the complex of chlorine with pyridine. However, it turned out that the reaction was not completed under these conditions even with prolonged stirring (5 h) and a two-fold excess of chlorinating agent, which may be due to its instability and low rate of chlorination. The reaction is completed only when additional portions of freshly prepared complex are added from time to time, but its course is ambiguous and its reproducibility low.

We elaborated a more convenient method for the synthesis of imidoylphosphonate **1**, based on available[5] dichlorophosphonate **3**. Essentially, this method includes mild chlorination (Cl_2, benzene, 20—25 °C) of a silyl derivative of this compound, existing as a mixture of *N*- and *O*-isomers (δ^1P 8.0, δ^2P 8.7, $\delta^1 : \delta^2 = 6 : 1$), with subsequent elimination of Me_3SiCl. Unlike this, nonsilylated amide **3** cannot be chlorinated with chlorine even under more drastic conditions (heating, UV irradiation). Silyl derivative **4** is thermally unstable. When distilled (160—168 °C, 0.05 Torr), it is partially (up to 30%) converted into the known[6] oxazaphospholine **5** (δP = 19.96), which was isolated in the individual state (Scheme 1).

The thermal instability of compound **4** does not prevent the formation of phosphonate **1** because the

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