Chemistry

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Abstract

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DIETHYL-*Se*-CHLOROSELENOPHOSPHATES

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Several years ago, a new type of organophosphorus compound containing the grouping of atoms $> P(O)SCl$ was obtained in our laboratory. These compounds were prepared by the action of chlorine or sulfuryl chloride on dialkyl monothiophosphates ($^{1-5}$), and also on dialkoxyphosphinyl disulfides (^{1,2,6}) and trialkyl thiophosphates (^{7}). The substances obtained possessed high chemical activity. As typical thiophosphorylating reagents of electrophilic character, they readily added to unsaturated compounds ($^{8-10}$), underwent reactions of electrophilic aromatic substitution (^{11}), replaced hydrogen atoms in an active methylene group (^{1,12}), and reacted with other typical nucleophilic reagents: mercaptans and thio acids (^{13}), amines (^{11}), trialkyl and dialkyl phosphites (^{12}), and similar substances.

The subject of the present communication is experiments leading to the preparation of the selenium analogs of the compounds mentioned. Diethyl-*Se*-chloroselenophosphates are formed by the action of chlorinating agents on esters of phosphorus seleno acids, quite analogously to the sulfur compounds. However, we were unable to isolate these substances in pure form, since they readily decompose. They are more stable in solution. Thus, diethyl-*Se*-chloroselenophosphate, formed by the action of an equivalent amount of sulfuryl chloride on triethyl selenophosphate, is relatively stable in benzene solution at a temperature of −5°, and in this form it can be used in subsequent reactions:

$$(C_2H_5O)_2P(Se)OC_2H_5 + SO_2Cl_2 \rightarrow (C_2H_5O)_2P(O)SeCl + SO_2 + C_2H_5Cl.$$

Complete distillation of the solvent leads to decomposition of the substance with liberation of selenium:

$$(C_2H_5O)_2P(O)SeCl \xrightarrow{\Delta} (C_2H_5O)_2P(O)Cl + Se.$$

Diethyl-*Se*-chloroselenophosphate decomposes in the presence of the slightest traces of moisture; however, in other reactions it is a less active compound than the corresponding diethyl-*S*-chlorothiophosphate. Its addition to cyclohexene, chosen as an example of an addition reaction to ethylenic hydrocarbons, proceeds considerably more slowly than in the case of the thio analog:

$$(C_2H_5O)_2P(O)SeCl + \overline{\ CH\ } = CH(CH_2)_3CH_2 \xrightarrow{80\%}$$

$$\rightarrow (C_2H_5O)_2P(O)Se - CH - \overline{CHCl - (CH_2)_3}CH_2.$$

The addition reaction of diethyl-*Se*-chloroselenophosphate to ethyl vinyl ether also proceeds relatively slowly. The addition product (I), however, was not isolated because of its instability, but was isolated

the product of its reaction with ethyl alcohol—a stable acetal (II):

$$(C_2H_5O)_2P(O)SeCl{+}CH_2{=}CH{-}O{-}C_2H_5 \xrightarrow{75\%} [(C_2H_5O)_2P(O)SeCH_2CHClOC_2H_5] \xrightarrow{C_2H_5OH}$$

$$\rightarrow (C_2H_5O)_2P(O)Se{-}CH_2{-}CH(OC_2H_5)_2.$$

(II)

The ease of formation of the acetal may be regarded as confirmation of the proposed direction of the addition reaction.

Experimental Part

1. Diethyl-Se-chloroselenophosphate $(C_2H_5O)_2P(O)SeCl$. To a solution of triethyl selenophosphate (15.9 g, 0.065 mole) in benzene (1 : 1), a solution of sulfuryl chloride (8.8 g, 0.065 mole) in benzene (1 : 1) was added dropwise, the temperature of the exothermic reaction being maintained below 0°. The initially colorless solution gradually turned yellow. After the entire amount of sulfuryl chloride had been added, the volatile reaction products were distilled off under reduced pressure (about an hour). An attempt to distill off the benzene completely on a water bath heated to 30° led to decomposition of the product with liberation of selenium. In the following experiments diethyl-Se-chloroselenophosphate was not isolated and was used in subsequent reactions in the form of a benzene solution.

2. Addition reaction of diethyl-Se-chloroselenophosphate to cyclohexene.
O,O-Diethyl-Se-(2-chlorocyclohexyl)-selenophosphate

$$(C_2H_5O)_2P(O)Se{-}CH{-}CH(Cl){-}(CH_2)_3{-}CH_2.$$

To a benzene solution of diethyl-Se-chloroselenophosphate, obtained as in experiment 1, a solution of cyclohexene (6.6 g, 0.08 mole) in benzene (1 : 1) was added dropwise, the temperature of the mildly exothermic reaction being maintained below 20°. Decolorization of the reaction mixture occurred only after 3 days of standing at room temperature. Volatile products were distilled off under reduced pressure. The benzene solution was washed with acid sodium carbonate, with water, and dried ($MgSO_4$). Benzene was distilled off under reduced pressure. Fifteen grams of O,O-diethyl-Se-(2-chlorocyclohexyl)-selenophosphate was obtained as a colorless oil (69.3% of theory, calculated relative to the initial triethyl selenophosphate); b.p. 93–94°/0.07 mm; n_D^{18} 1.5166.

Found, %:	P 9.5;	Se 23.5
$C_{10}H_{20}O_3ClPSe$. Calculated, %:	P 9.3;	Se 23.7

3. Addition reaction of diethyl-Se-chloroselenophosphate to vinyl ethyl ether.

O,O-Diethyl-Se-(2,2-diethoxyethyl)-selenophosphate $(C_2H_5O)_2P(O)SeCH_2CH(OC_2H_5)_2$.

To a benzene solution of diethyl-Se-chloroselenophosphate, obtained analogously to experiment 1, a solution of vinyl ethyl ether (5.8 g, 0.08 mole) in benzene (1 : 1) was added dropwise; the temperature of the mildly exothermic reaction was maintained below 0°. After the entire amount of diethyl-Se-chloroselenophosphate had been added, the solution did not decolorize. Complete decolorization occurred only after 24 hours of standing at room temperature. The solvent was distilled off under reduced pressure. Ethyl alcohol (25 ml) was added to the oily residue of O,O-diethyl-Se-(2-ethoxy-2-chloroethyl)-selenophosphate, and the reaction mixture was left for 1/2 hour at room temperature, then neutralized with solid acid sodium carbonate. The liquid was decanted from the precipitate, and the precipitate was washed twice with benzene. The benzene extracts were combined with the oil, washed twice with water, and dried ($MgSO_4$). Benzene was distilled off in a va-

···in vacuum and the residue was fractionated. 17 g of O,O-diethyl-Se-(2,2-diethoxyethyl) selenophosphate was obtained as a thick light-yellow oil (78.7% of theory, based on the initial triethyl selenophosphate); b.p. 81—81.5°/0.05 mm; $n_D^{20.5}$ 1.4710.

$C_{10}H_{23}O_5PSe$.	Found, %:	P 9.5;	Se 23.4
	Calculated, %:	P 9.3;	Se 23.7

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CITED LITERATURE

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