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B-Substituted Carboranyl Thio- and Selenophosphites. Synthesis and Chemical Properties

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B-SUBSTITUTED CARBORANYL THIO- AND SELENOPHOSPHITES. SYNTHESIS AND CHEMICAL PROPERTIES

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The first examples of B-substituted carboranyl thio- and selenoesters of trivalent phosphorus acids were synthesized. On the basis of these samples, a series of new corresponding pentavalent phosphorus acids derivatives, potentialy bioactive compounds, was obtained. S- and Se-carborane-9-yl-diethylthiophosphites (I) were obtained by the interaction of diethylchlorphosphites with 9-mercapto- or 9-selenocarboranes in the presence of triethylamine.

$$(EtO)_{2} PCI + V/ \longrightarrow HC-CH B_{10}H_{9}XH \longrightarrow B_{10}H_{9}XP(OEt)_{2}$$

$$X = S, Se$$

$$(I)$$

Compounds (I) add easily oxygen, sulphur, and selen despite of the presence of the bulk carboranyl substituent. The interaction of (I) with alkyliodides leads to the usual Arbuzov reaction products. The interaction of thiophosphites (I) with chloral give the mixture of the product of the starting compound (I) oxydation along with vinylthiophosphate.

$$\begin{array}{c} O \\ \parallel \\ HC-CH + HC-CCl_3 \longrightarrow HC-CH O + HC-CH O \\ \backslash / & \parallel \\ B_{10}H_9SP(OEt)_2 & B_{10}H_9SP & B_{10}H_9SP(OEt)_2 \\ \end{array}$$

$$\begin{array}{c} O \\ \downarrow / & \parallel \\ OCH=CCl_2 \end{array}$$

These compounds participate in the reactions mentioned above easier than corresponding C-phosphorilated carboranes due to electron donor ability of the B-carborane-9-yl group.