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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### The Reactions of Phosphorus Selenonoesters, $>P(Se)OR$ , with Halogens. New Five-Co-Ordinate and Phosphonium Intermediates Containing P-Se Bond

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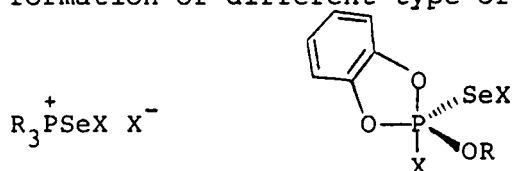
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# THE REACTIONS OF PHOSPHORUS SELENONOESTERS, $>P(Se)OR$ , WITH HALOGENS. NEW FIVE-CO-ORDINATE AND PHOSPHONIUM INTERMEDIATES CONTAINING P-Se BOND

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As a continuation of our investigation on the chemistry of  
 thiono- and selenonophosphorus acid esters, the reactions  
 of phosphoroselenoates with various halogens were studied  
 (1). Depending on the structure of selenonophosphoryl com-  
 pound and on the nature of halogen these reactions involve  
 the formation of different type of intermediates like:

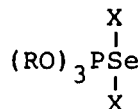


X = Cl, Br, I

R = Alkyl, Aryl, Alkoksyl

X = Cl

R = Alkyl



X = Br

R = Alkyl =  $Bu^tCH_2$

The structure of above intermediates was established by  
 means of  $^{31}P$  NMR and IR spectroscopy and by their synthe-  
 sis on an independent way via the Arbusov reaction between  
 corresponding tricoordinate phosphorus compounds and sele-  
 nium (II) chloride ( $Se_2Cl_2$ ) or phenylselenyl chloride.  
 $^1J(PSe)$  values were used as a structural criterion. The  
 mechanism of interaction between selenonoesters,  $>P(Se)OR$ ,  
 and halogens, involving ligand exchange at phosphorus  
 center will be discussed.

- (1) J.Michalski, J.Mikołajczak, A.Skowrońska, J.Am.Chem.  
 Soc., 100, 5386 (1978) and references cited therein.