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Reaction Pathways upon Interaction of Allenic Phosphonates with Selenyl Chlorides

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Studies were performed on the reaction between alkyl- and arylselenyl chlorides with esters of allenic phosphonic acids, variously substituted at their terminal C-atom. With the esters of the C-3 diasubstituted acids the reaction is highly regioselective and only oxaphosphol heterocyclization occurs to 2,5-dihydro-1,2-oxaphosphols 21-e. With the esters of the propadiene phosphonic acid the reaction is regio- and (Z)-stereoselective: only the 2,3-adducts 3a-b are formed, where the (Z)-isomer and the allenic phosphonates 4a-b are prevalent, as a result of 1,3-sigmatropic isomerization of 3a-b. With the esters of the C-3 monosubstituted acids, complex reaction mixtures are formed. From them were isolated: (E)- and (Z)-isomers of 2,5-dihydro-1,2-oxaphosphols 2f-j; (E)- and (Z)-isomers of the 2,3-adducts 3c-b; (E)- and (Z)-isomers of 4c-f; and (E)- and (Z)-isomers of the 1,2-adducts 5a-d. The reaction partially loses its regional city, but the (Z)-stereoselectivity is preserved:

The configuration of 3a-h was clarified by ^{13}C NMR spectroscopy.