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Arylselenenation of conjugated dienes by arylselenenamides in the presence of phosphorus(V) oxyhalides

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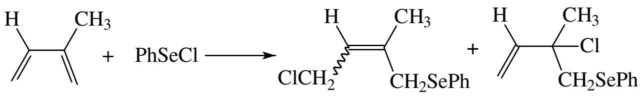
Abstract—Arylselenenation of conjugated and non-conjugated dienes by arylselenenamides in the presence of phosphorus(V) oxyhalides has been studied. Reactions with conjugated dienes lead to 1,4-adducts whilst only addition to double bonds takes place in reactions with non-conjugated dienes.

Arylselenenation reactions of unsaturated compounds are of synthetic interest because the 'selenation–deselenation' sequence is a useful method for obtaining functionally substituted alkenes.[1–3] Selenenyl halide[4–7] and selenenyl triflate[6] are used for the introduction of seleno-containing moieties into alkenes and alkynes. The products of such reactions are usually β-substituted alkyl aryl selenides and are typically obtained in 65–80% yields. However, this type of reaction is characterized by low regioselectivity (85:15).

Electrophilic selenenation of dienes has not been investigated in detail. The only example of conjugated diene selenenation in the literature involves reaction with phenylselenenyl chloride giving either an allylic alcohol or an enone depending on the experimental procedure.[8] The initial products of the reaction of isoprene and PhSeCl are regioisomeric chloroselenides, formed in ratios from 1:1 to 2:5, depending on the reaction temperature:



Earlier, we reported that the reaction of arylsulphenamides[10] and diethylphenylselenenamide **1**[9] with alkenes under activation by $POCl_3$ or $SOCl_2$ resulted in the formation of the 1,2-halosulphenyl- or selenenation products in good yields. The reaction mechanism involves initial coordination of the phosphorus or sulfur Lewis acid with the chalcogen atom of $ArXNR_2$ ($X = S$, Se) as based on NMR data.[10]

In this letter we report a simple and useful method for the synthesis of substituted 1-arylseleno-4-halo-2-enes by the reaction of conjugated dienes with arylselenenamides in the presence of phosphorus oxyhalides.

The reactions of **1** with dienes occur under mild conditions (CH_2Cl_2, −30 °C)[11] and products **2**–**7** are the results of 1,4-addition (see Table 1).

The structures of the unsaturated haloselenides synthesized were determined by NMR and IR spectroscopy. 1,4-Adducts were obtained in high yields in the case of the reaction with conjugated dienes (see Table 1). The structures of the 1,4-adducts were deduced as **2**–**7** based on literature data on the products of analogous sulfenylation reactions[12–14] and (in the cases of **2**, **3**) $^3J_{trans}$ and coupling constants described for substituted cyclopentenes.[15] Two isomeric 1,4-products, differing in the configuration of the substituents around the C=C double bond, were obtained from non-cyclic diene haloselenenation. The observed regioselectivity shows that the direction of initial attack of the electrophile is determined by electronic and not steric factors, as in the reactions with isoprene, the electrophile preferably adds to the C=C double bond adjacent to the donor CH_3-group.

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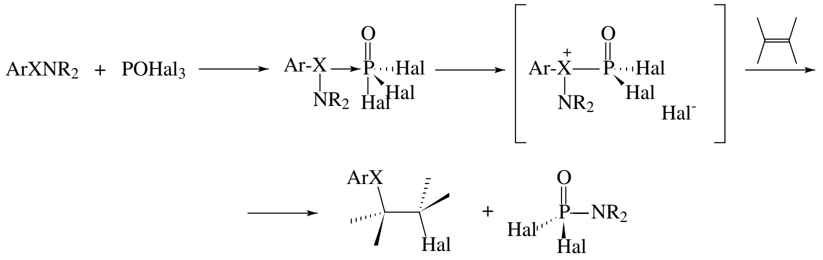
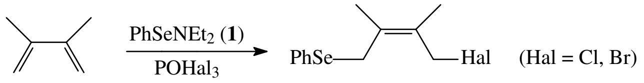
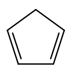
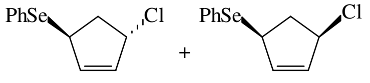
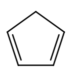
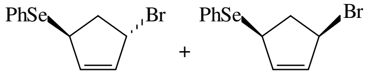
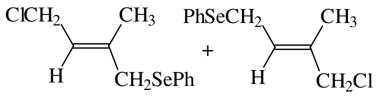
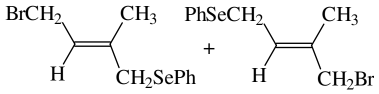
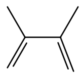
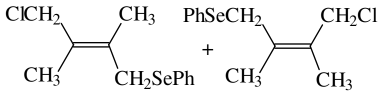
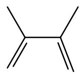
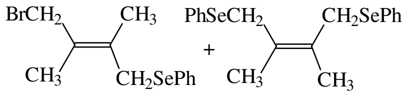


Table 1. Haloselenenation of conjugated dienes with arylselenenamide **1** and phosphorus oxyhalides[a,b]



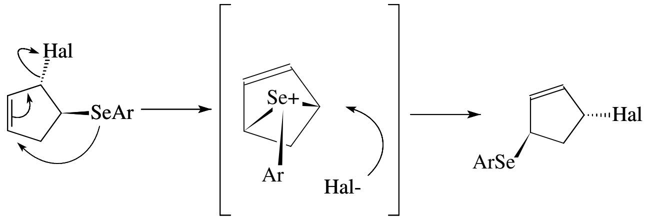
Diene	$POHal_3$	Products	Ratio **a**:**b**	Yield (%)
	$POCl_3$	 **2a** **2b**	3/1	52
	$POBr_3$	 **3a** **3b**	3/1	60
	$POCl_3$	 **4a** **4b**	2/1	63
	$POBr_3$	 **5a** **5b**	2/1	69
	$POCl_3$	 **6a** **6b**	1/1	67
	$POBr_3$	 **7a** **7b**	1/1	79

[a] See Ref. 11 for typical reaction conditions.

[b] The ratios of the isomers were determined by NMR spectroscopy.

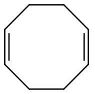
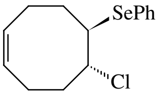
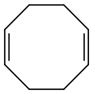
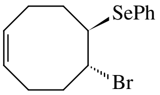
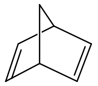
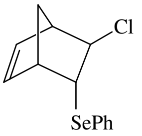
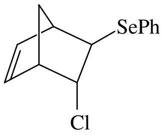
Reaction with conjugated dienes leads to 1,4-adducts, but in the first step of the reaction the intermediate from 1,2-addition is formed, which is rapidly isomerized to the 1,4-adduct. In the case of the addition to 1,3-cyclopentadiene, the trans-isomer is the major product. This can be explained through interaction of one of the lone pairs of selenium with the carbocation centre, proceeding at the 4-position of the cyclopentane ring, as has previously been described.[12]

Addition to only one double bond takes place in the case of the reaction with non-conjugated dienes (see Table 2).



Thus, $POHal_3$-activated *N*,*N*-diethylphenylselenenamide **1** has been utilized for the haloselenenation of dienes resulting in the formation of 1,4-haloselenenation products in the case of conjugated dienes and mono-

Table 2. Haloselenenation of non-conjugated dienes with arylselenenamide **1** and phosphorus oxyhalides[a]

Diene	$POHal_3$	Products	Ratio **a**:**b**	Yield (%)
	$POCl_3$	 **8**	—	72
	$POBr_3$	 **9**	—	76
	$POCl_3$	 +  **10a** **10b**	1:5	75

[a] See Ref. 11 for typical reaction conditions.

haloselenides in the case of non-conjugated dienes. The simplicity of the experimental procedure and of product purification makes this reaction a convenient method for obtaining seleno-containing unsaturated compounds.

References and notes

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11. *Typical reaction procedure*: To a solution of *N*,*N*-diethylselenenamide **1** (2.5 mmol) in dry methylene chloride (10 ml) at −30 °C, a solution of phosphorus(V) oxychloride (2.5 mmol) in CH_2Cl_2 (10 ml) was added. The resulting mixture was stirred for 10 min and a solution of diene (2.5 mmol) in the same solvent (10 ml) was added. After 30 min, the temperature of the reaction mixture was gradually raised to rt and the mixture was passed through a short column of silica gel. Evaporation of the solvent in vacuo gave the product of 1,4-addition as based on ^1H NMR data.
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