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Three-component reaction between secondary phosphine sulfides, elemental selenium and vinyl ethers: the first examples of Markovnikov addition of thioselenophosphinic acids to double bond

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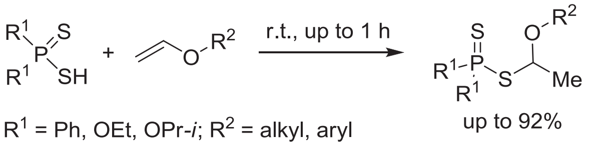
ABSTRACT

Thioselenophosphinic acids, $R_2P(Se)SH$, generated in situ from secondary phosphine sulfides and elemental selenium, easily add to various vinyl ethers (equimolar ratio, 100 °C, 1,4-dioxane, up to 40 min) to give earlier unknown S- and Se-[1-(organyloxy)ethyl]thioselenophosphinates, i.e., $R_2P(Se)SCH(Me)OR'$ and $R_2P(S)SeCH(Me)OR'$ (R, R'=alkyl, aralkyl, hetaralkyl and aryl), the S-esters being predominant (73–95% total yield).

1. Introduction

Currently, vinyl ethers attract increasing attention of researchers as monomers for the preparation of functional polymer materials,[1] precursors for design of pharmaceuticals[2] and convenient building blocks for the synthesis of, in particular, hemilabile mono-[3] and diphosphine ligands.[4] The vinyl ethers as substrates can participate in many reactions such as cycloadditions,[5] metathesis,[6] Claisen rearrangement,[7] metallation,[8] addition of diverse X–H-acids (X=O, N, S, etc.)[9] and Heck-type arylation.[10] One of the most powerful and atom-economic methods for functionalization of vinyl ethers is electrophilic addition of OH-compounds, for example, various acids to the vinyloxy group.[11] This reaction usually proceeds under the mild conditions and creates real prerequisites for direct and controlled modification of vinyl ethers by diverse functional moieties. For instance, the electrophilic addition of carboxylic acids[12] and their thio-analogues[13] to vinyl ethers is shown to provide a direct, efficient and facile short-cut to acetals including functional and optically active ones.

However, little is known about the addition of organophosphorus acids and its thio- or selenoanalogues to vinyl ethers. Phosphinic acids, $R_2P(O)OH$, do not add to the vinyloxy group, nevertheless, dithiophosphinic and -phosphoric acids easily react with vinyl ethers (room temperature, without catalyst and solvent) to give regioselectively the corresponding Markovnikov-type adducts in quantitative yields[14] (Scheme 1).



Scheme 1. Electrophilic addition of dithiophosphinic and -phosphoric acids to vinyl ethers.

Recently,[15] it has been shown that diselenophosphinic acids, generated in situ from secondary phosphines (or their selenides) and elemental selenium (90 °C, 1,4-dioxane), add to a diverse array of vinyl ethers to afford previously unknown diselenophosphinic esters in high yields (Scheme 2).

At the same time, precedent for the addition of thioselenophosphinic acids, $R_2P(Se)SH$ or $R_2P(S)SeH$, to vinyl ethers is

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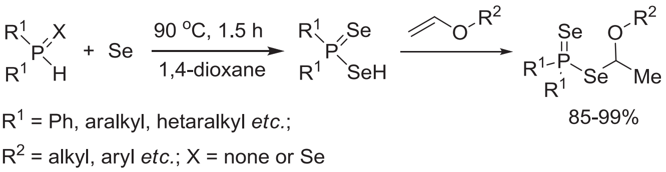
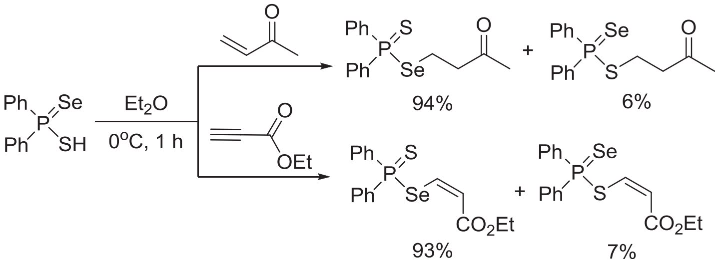


Scheme 2. One-pot synthesis of Se-[1-(organyloxy)ethyl]diselenophosphinates.

absent in the literature. It is pertinent to note that until recently only two examples of such acids, namely $Ph_2P(Se)SH$ and *t*-Bu(Ph)P(Se)SH, have been prepared (both by acidification of the corresponding salts with HCl).[16] Murai et al. have demonstrated that $Ph_2P(Se)SH$ acids add selectively to methyl vinyl ketone or ethyl propiolate in an anti-Markovnikov fashion to afford Se-esters with a small amount of the *S*-isomers (up to 7%), Scheme 3.[16]



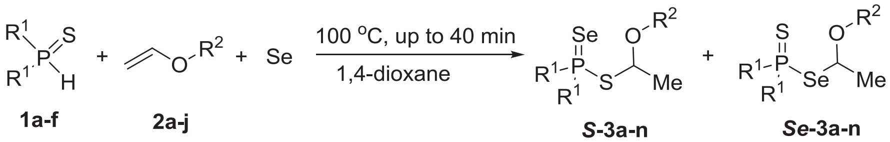
Scheme 3. Nucleophilic addition of thioselenophosphinic acids to methyl vinyl ketone and ethyl propiolate.

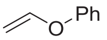
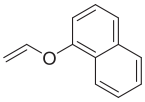
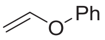
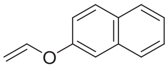
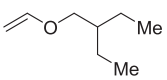
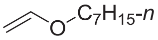
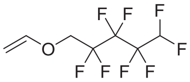
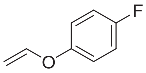
In the present work we have implemented for first time the electrophilic addition of thioselenophosphinic acids to alkenes (on example of vinyl ethers). For this purpose, we have studied the reaction of secondary phosphine sulfides with selenium in the presence of vinyl ethers aiming at (i) the development of an atom-economic route to thioselenophosphinic esters and (ii) the investigation of the competition between thioselenophosphinic S- and Se-esters formation.

2. Results and discussion

We have found that the thioselenophosphinic esters may be successfully synthesized via the three-component reaction between secondary phosphine sulfides, elemental selenium and vinyl ethers. Experiments have shown that the thioselenophosphinic acids, $R_2P(Se)SH$, generated in situ from secondary phosphine sulfides **1a**–**f** and elemental selenium, easily add to various vinyl ethers **2a**–**j** in a Markovnikov fashion (1,4-dioxane, 100 °C, up to 40 min) to give a mixture of thioselenophosphinic S- and Se-esters **3a**–**n** in high yield (^{31}P NMR data). The isolated yields of the products **3a**–**n** and ratio of S- and Se-esters in the reaction mixtures are presented in Table 1.

Table 1
One-pot synthesis of thioselenophosphinic S- and Se-esters **3a**–**n**



Entry	Phosphine sulfide	R^1	Vinyl ether	Product	Molar ratio of S-/Se-ester[a]	Overall yield[b] (%)
1	**1a**	Cy	 (**2a**)	**3a**	58:42	93
2	**1a**	Cy	 (**2b**)	**3b**	50:50	93
3	**1b**	$(CH_2)_2Ph$	 (**2a**)	**3c**	70:30	90
4	**1b**	$(CH_2)_2Ph$	 (**2c**)	**3d**	63:37	95
5	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 (**2d**)	**3e**	75:25	73
6	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 (**2e**)	**3f**	72:28	90
7	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 (**2f**)	**3g**	62:38	93
8	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 (**2g**)	**3h**	61:39	91