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Polystyrene-supported Selenides and Selenoxide: Versatile Routes to Synthesize Allylic Alcohols

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Abstract: Several polystyrene-supported selenides and selenoxide have been prepared firstly. These novel reagents were treated with LDA to produce selenium stabilized carbanions, which reacted with aldehydes and alkyl halides, followed by selenoxide *syn*-elimination and [2,3] sigmatropic rearrangement respectively to give *Z*-allylic alcohols stereoselectively.

Keywords: Solid phase synthesis, selenides and selenoxide , allylic alcohol.

Combinatorial chemistry and solid phase synthesis have recently emerged as powerful tools for the drug discovery process[1]. It might be argued that selenoxide *syn*-elimination provided the principal impetus for the development of organoselenium chemistry. [2, 3] Sigmatropic rearrangement[2] of allylic selenium compounds is the most fundamental reaction in the field of synthetic organoselenium chemistry as well as selenoxide *syn*-elimination. However, organic selenides are highly malodorous and generally unpleasant and difficult to handle, especially because of their toxicity. Several groups[3] have developed some organoselenium resins to solve this problem. Recently, our research group has been interested in the application of organic selenium resins in organic synthesis[4,5]. Being the materials of Sharpless-AE reaction[6], allylic alcohols are also important intermediates in organic synthesis. We report here several novel preparations of polystyrene-supported selenides and selenoxide and their applications for highly stereocontrolled synthesis of kinds of *Z*-allylic alcohols[5] with significant advantages of easy operation, free from odors, and good purities of the products.

The preparation of polystyrene-supported selenides and selenoxide is described in **Scheme 1**.

Resin **3** and resin **6** reacted smoothly with LDA followed by substitution with aldehydes and alkyl halides to give resin **7** and resin **10** (**Scheme 2**), which followed by selenoxide *syn*-elimination and [2, 3] sigmatropic rearrangement respectively to give the same type of products-*Z*-allylic alcohols stereoselectively[7]. The results are summarized in **Table 1**. All the resins used could be regenerated and reused[5].

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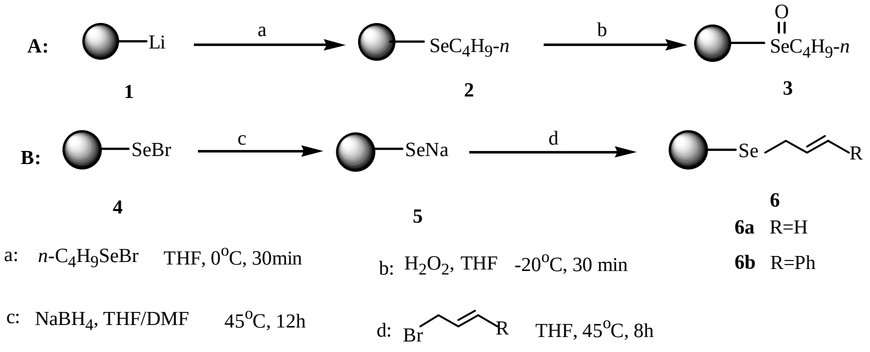
Scheme 1



Scheme 2

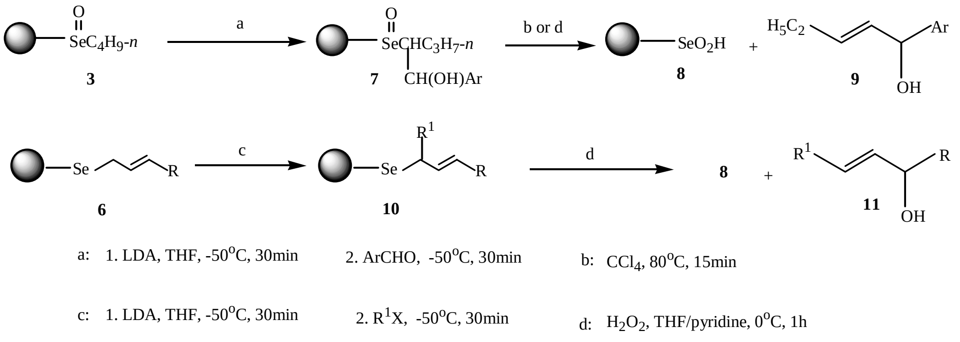


Table 1 Yields and purities of allylic alcohols

Products	Resins	Substrates	Yields (%)[a]	Purities (%)[b]
9a	**3**	PhCHO	88	93
9b	**3**	*p*-CH_3-PhCHO	86	92
9c[c]	**3**	PhCHO	85	91
11a	**6a**	$PhCH_2Br$	81	94
11b	**6b**	CH_3CH_2Br	84	90
11c	**6b**	$PhCH_2Br$	86	92
11d[c]	**6a**	$PhCH_2Br$	80	91

a: Yields of products based on the loading of the resin, the products were identified by ^{1}H NMR, MS and IR spectra. b: Determined by ^{1}H NMR (400MHz). c: Using regenerated resin.

In summary, we have developed several novel methods to prepare polystyrene-supported selenides and selenoxide. They reacted with LDA then aldehydes and alkyl halides, followed by selenoxide *syn*-elimination and [2,3] sigmatropic rearrangement, to provide *Z*-allylic alcohols stereoselectively. These novel polystyrene-supported reagents can be regenerated and reused.

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