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Reaction of Polymer-supported Selenovinyl Bromide with Grignard Reagents: A Facile Route to the Synthesis of (*E*)-1, 2-Disubstituted Olefins

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Abstract: Polymer-supported selenovinyl bromide, easily prepared from polymer-supported selenenyl bromide with acetylene, reacts with different Grignard reagents using a step-by-step strategy to obtain (*E*)-1, 2-disubstituted ethenes in good yields.

Keywords: Polymer-supported selenovinyl bromide, Grignard reagents, disubstituted ethenes.

During the last few years, solid-phase methodology has been rapidly and extensively applied to the preparation of small organic molecules[1]. Organoselenium reagents are powerful tools for introducing new functional groups into organic substrates under extremely mild condition[2]. Among them, vinyl selenides are important precursors of alkenes because the selenenyl groups can be easily substituted by various reagents. There have been many reports about the stereoselective synthesis of vinyl selenide and its utilization in the synthesis of alkene[3]. However, it is often problematic in organic synthesis that organic selenium reagents always have a foul smell and are quite toxic. Our research group has been interested in the application of organic selenium resins in organic synthesis[4]. Here we reported a simple preparation of polystyrene-supported (*E*)-1-bromo-2-selenoethylene and its application to react with different Grignard reagents using a step-by-step strategy to obtain (*E*)-1, 2-disubstituted ethenes. Evident advantages of this reaction are easy operations, odorlessness, good yields of the products.

Simple stirring of polystyrene-supported selenenyl bromide (resin **1**)[5] with acetylene in DMF for 12 h resulted in the polystyrene-supported (*E*)-1-bromo-2-arylselenoethylene (resin **2**), which was evidenced by the formation of (*E*)-stilbene (**4a**) through its reaction with phenyl magnesium bromide (8.0 equiv) at room temperature for 24 h in the presence of $NiCl_2(PPh_3)_2$ catalyst (**Scheme 1**).

The unsymmetrical olefins were prepared when different Grignard reagents were used in a step-by-step way because the coupling reactivity of the vinyl bromide was much higher than that of the vinyl selenide. The polystyrene-supported (*E*)-1-bromo-2-

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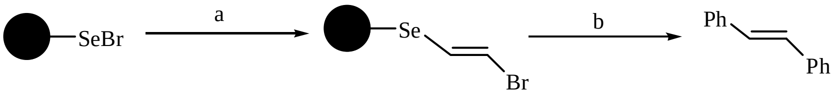
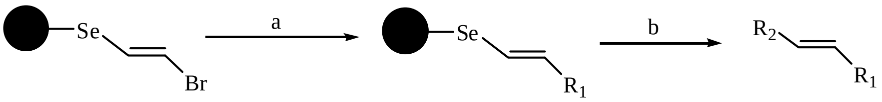
Scheme 1



1 **2** yield: 85%

a. HC≡CH, DMF, r.t., 12h; b. PhMgX, THF, $NiCl_2(PPh_3)_2$, r.t. 24h.

Scheme 2



2 **3** **4**

a. R_1MgX, THF, $NiCl_2(PPh_3)_2$, r.t. 2h; b. R_2MgX, THF, $NiCl_2(PPh_3)_2$, r.t. 24h.

Table 1 Preparation of (*E*)-1,2-disubstituted ethenes [a]

Products	R^1	R^2	Yield (%)[a]
4a	Ph	$4\text{-}ClC_6H_4$	80
4b	Ph	$4\text{-}CH_3C_6H_4$	81
4c	Ph	$3\text{-}CH_3C_6H_4$	81
4d	Ph	CH_3	80
4e	$4\text{-}ClC_6H_4$	CH_3CH_2	78

a.The products are known and identified by ^{1}H NMR and IR spectra.
b.Isolated yields based on the minimum loading of polymer-supported selenobromide(1.02 mmol/g).

arylselenoethylene **2** was first treated with a Grignard reagnt in the presence of $NiCl_2(PPh_3)_2$ as the catalyst. After stirred at rt for 2 hours, the vinyl bromide coupling reaction on solid-phase completed to obtain polystyrene-supported vinyl selenide **3**, which was determined by the elemental analysis (Br was undetectable). After filtration, polystyrene-supported vinyl selenide **3** was then treated with another Grignard reagent to obtain unsymmetrical olefins. Results are summarized in **Table 1**.

In conclusion, we have developed an SPOS (solid phase organic synthesis) route to synthesize (*E*)-1,2-disubstituted ethenes stereoselecively. Evident advantages of this reaction are easy operations, odorlessness, good yields of the products.

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