

Polystyrene-supported Benzyl Selenide: An Efficient Reagent for Highly Stereocontrolled Synthesis of Substituted Olefins

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Abstract: Polystyrene-supported benzyl selenide has been prepared. This novel reagent was treated with LDA to produce a selenium stabilized carbanion, which reacted with alkyl halide, followed by selenoxide *syn*-elimination, to give substituted olefins stereospecificly.

Keywords: Solid phase synthesis, polystyrene-supported benzyl selenide, substituted olefins.

Solid-phase methodology has been rapidly and extensively applied to the preparation of small organic molecules recently¹. It might be argued that selenoxide *syn*-elimination provided the principal impetus for the development of organoselenium chemistry. In addition, the required selenoxides are readily available from the oxidation of the corresponding selenides, which in turn can be prepared by the reaction of selenium-stabilized carbanions with various electrophilic substrates². However, organic selenides are highly malodorous and generally unpleasant and difficult to handle, especially because of their toxicity. Several groups³ 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 synthesis⁴. Since substituted olefins are important intermediates in organic synthesis, we report here a novel preparation of polystyrene-supported benzyl selenide and its application for a highly stereocontrolled synthesis of substituted olefins with electron withdrawing group, which has significant advantages of easy operation, freedom from odors, and good purities of products.

The preparation of polystyrene-supported benzyl selenide (**Scheme 1a**) is as followed: To a suspension of the swelled resin **1** (2 g) in dry THF (30 mL) was added dropwise benzylselenium bromide under nitrogen at -78°C . After stirring for 0.5 h at -78°C , the resin **2** was collected by filtration and washed with THF (15 mL \times 2), ether (15 mL \times 2), THF/H₂O (3:1) (15 mL \times 2), H₂O (15 mL \times 2), benzene (15 mL \times 2), MeOH (15 mL \times 2), and CH₂Cl₂ (15 mL \times 2), subsequently, and dried in vacuum. Content of Se in resin **2** was 1.01 mmol/g. IR for resin **2** (KBr cm⁻¹): 3024, 2921, 1601, 1492, 1451, 1180, 1069, 1028, 906, 864, 757, 697, 537 cm⁻¹.

Resin **2** reacted smoothly with LDA followed by substitution with electron

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withdrawing group substituted alkyl halides to give resin **3**. The resin **3** was converted to substituted olefins **5** and resin **4** through selenoxide-elimination using hydrogen peroxide (**Scheme 1b**). The results are summarized in **Table 1**. Resin **4** could be recycled.

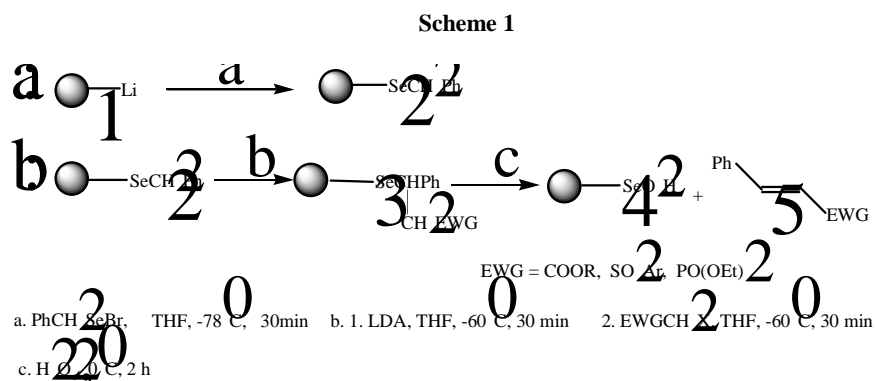


Table 1 Reagents, yields and purities of olefins

Reagents		Products	Yield (%) ^a	Purity (%) ^b
EWG	X			
-COOCH ₃	Br	5a	61	81
-COOCH ₂ CH ₃	Br	5b	70	84
-COOCH ₂ CH=CH ₂	Br	5c	68	78
-SO ₂ C ₆ H ₄ CH ₃ - <i>p</i>	Br	5d	63	81
-SO ₂ Ph	Br	5e	68	82
-PO(OEt) ₂	I	5f	72	87
-PO(OEt) ₂	I	5g^c	70	86

a. Yields of products based on the loading of the resin **2**, the products were identified by ¹H NMR, MS and IR spectra.

b. Determined by ¹H NMR (400MHz).

c. Using regenerated resin **2**.

We have developed a novel method to prepare polystyrene-supported benzyl selenide. It reacted with LDA then substituted alkyl halide, followed by oxidation and stereospecific selenoxide *syn*-elimination, to provide substituted olefins. The novel polystyrene-supported benzyl selenide can be regenerated and reused.

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