

Solid-Phase Stereoselective Synthesis of (E)-1, 2-Disubstituted Ethenes from Polymer-Supported α -Selenoaldehydes

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Abstract: Reaction of polymer-supported α -selenoaldehydes with Grignard reagents afforded polymer-bound β -hydroxyalkyl selenides, which treated with thionyl chloride and triethylamine leading to (E)-1, 2-disubstituted ethenes in good yield.

Keywords: Solid phase organic synthesis, α -selenoaldehyde, (E)-1, 2-disubstituted ethene.

Polymer-supported reagents have found increasing applications for the preparation of small organic molecules during the past few years¹. Many solution-phase synthetic methods have been developed for the stereoselective synthesis of 1, 2-disubstituted ethenes. As we know so far, however, little effort has been made for the stereoselective preparation of 1, 2-disubstituted ethenes *via* polymer-resins. β -Hydroxyalkyl selenides are useful precursors for the synthesis of olefins²⁻⁴. However, organic selenium reagents always have a foul smell and are quite toxic, which is often problematic in organic synthesis. In connection our research with the preparation of polymer-supported α -selenoaldehydes⁵ and their applications in solid-phase organic synthesis, we wish to report here the first stereoselective synthesis of (E)-1, 2-disubstituted ethenes *via* α -selenoaldehyde resin (**Scheme 1**). Use of these selenium reagents has been proved to provide significant advantages, including decrease volatility and simplification of product work-up.

Reaction of resin **1** (loading = 1.02, 1.10 mmol CHO/g, R¹ = Ph, Et) with Grignard reagents at room temperature formed β -hydroxyalkyl selenides resin **2**, which shown strong hydroxyl absorption at 3430-3440 cm⁻¹ in their infrared spectra. Treatment of resin **2** with *p*-toluenesulfonic acid or perchloric acid² afforded the products **3** in poor yields. While methanesulfonyl chloride² or trifluoroacetic anhydride and triethylamine⁴ were adopted, the yields of **3** were 50-60%. (E)-1, 2-disubstituted ethenes **3a-3d** were obtained in high yields when thionyl chloride³ was used in the presence of triethylamine (**Table 1**), which are even higher than those of the liquid-phase synthesis.

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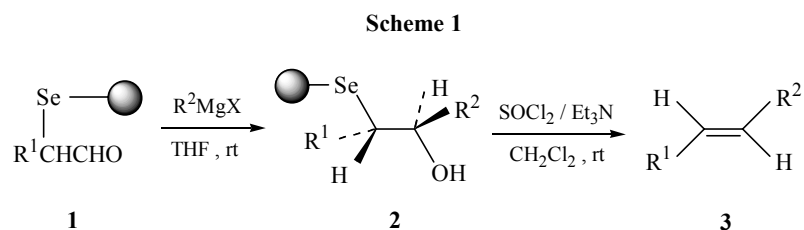


Table 1 Preparation of (E)-1, 2-disubstituted ethenes

NO.	R ¹	R ²	Yield (%) ^a	E/Z ratio ^b
3a	C ₆ H ₅	C ₆ H ₅	85	97/3
3b	C ₆ H ₅	CH ₃	80	95/5
3c	CH ₃ CH ₂	C ₆ H ₅	76	96/4
3d	CH ₃ CH ₂	C ₆ H ₅ CH ₂	81	95/5

a) Overall yields based on the loading of resin **1**. b) Determined by ¹H NMR (400 MHz).

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References

1. S. J. Shuttleworth, S. M. Allin, P. K. Sharma, *Synthesis*, **1997**, 1217.
2. J. Rémon, W. Dumont, A. Krief, *Tetrahedron Lett.*, **1976**, 1385.
3. J. Rémon, A. Krief, *Tetrahedron Lett.*, **1976**, 3743.
4. H. J. Reich, F. Chow, *J. Chem. Soc., Chem. Commun.*, **1975**, 790.
5. S. R. Sheng, L. L. Wu, X. Huang, *Chin. Chem. Lett.*, **2002**, In Press.

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