

Solid-phase Synthesis of Diethyl *Trans*-1-Alkenephosphonates Using Polymer-bound α -Diethoxyphosphoryl Methyl Selenide

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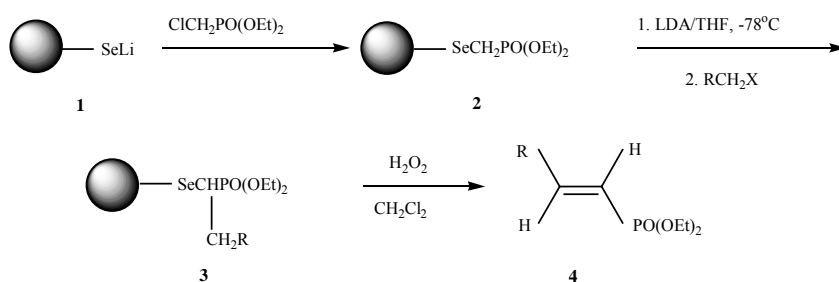
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Abstract: The solid-phase preparation of diethyl *trans*-1-alkenephosphonates *via* seleno-polymer reagent has been reported.

Keywords: Solid-phase organic synthesis, polymer-bound α -diethoxyphosphoryl methyl selenide, diethyl *trans*-1-alkenephosphonate.

Polymer-supported organic reagents have been applied to the rapid preparation of small organic molecules because they can provide attractive and practical methods for combinatorial chemistry and solid-phase synthesis¹. Vinylphosphonates bearing an electron withdrawing groups at the α -position are versatile intermediates for the synthesis of some hetero- and carbocyclic compounds². Many methods have been developed for preparing their parent compounds, 1-alkenephosphonates. Among those methods, an important methodology involves oxidative elimination of organoselenyl moieties in α -selenylphosphonates³. However, organic selenides are highly malodorous and generally unpleasant and difficult to handle, especially because of their toxicity. Polymer-bound selenium reagents have been recently developed to solve this problem⁴. In connection our research with the application of seleno-resins in organic synthesis⁵, here we report a facile synthetic approach to diethyl *trans*-1-alkenephosphonate using polymer-bound α -diethoxyphosphoryl methyl selenide **2** (Scheme 1).

Scheme 1



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Table 1 Yields and purities of *trans*-1-alkenephosphonates

Entry	RCH ₂ X	Product	Yield (%) ^a	Purity (%) ^b
1	<i>n</i> -C ₃ H ₇ CH ₂ Br	4a	85	>95
2	C ₆ H ₅ CH ₂ Cl	4b	91	>95
3	<i>p</i> -ClC ₆ H ₄ CH ₂ Cl	4c	91	>95
4	C ₆ H ₅ CH ₂ CH ₂ Br	4d	90	>95

a) Overall yields based on the loading of resin **2**. b) Determined by ¹H NMR (400 MHz).

Reaction of polystyrene-bound lithium selenide **1**⁴ with diethyl chloromethylphosphonate afforded polymer reagent **2**, which exhibited a characteristic P=O absorption at 1245 cm⁻¹ in FT-IR spectrum and contained 1.24 mmol P/g by elemental analysis. Treatment of the lithio derivative of resin **2** (1.0 mmol) with representative primary alkyl halides (2.0 mmol) furnished the α -selenylated alkanephosphonate resin **3**, which was converted into the corresponding diethyl 1-alkenephosphonates **4** by oxidation-elimination with 30% H₂O₂ (1.0 mL) at room temperature in good yields (85-91%) and with high purities of crude materials in all cases (>95 % by ¹H NMR analysis) as shown in **Table 1**. It should be noted that *trans*-1-alkenephosphonates are formed exclusively. The residual resin with no residual P=O absorption in FT-IR spectrum indicated the oxidation-elimination was complete.

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