Solid-phase Synthesis of Vinyl Sulfones Using Polystyrene-supported Selenomethyl Phenyl Sulfone

Shou Ri SHENG*, Wei ZHOU, Xiao Ling LIU, Qin XIN, Cai Sheng SONG

Institutes of Chemistry, Jiangxi Normal University, Nanchang 330027

Abstract: The solid-phase preparation of vinyl sulfones *via* a novel polystyrene-supported selenomethyl phenyl sulfone reagent has been reported.

Keywords: Solid-phase organic synthesis, polystyrene-supported selenomethyl phenyl sulfone, vinyl sulfone.

Synthesis on a polymer support shows a number of advantages as compared to solution chemistry. The most important one is the possibility to apply and remove the excess of reagents and removing them without involving time-consuming separation techniques¹. Vinyl sulfones have now become generally accepted useful intermediates in organic synthesis, *e.g.*, serving efficiently as both Michael acceptors and π partners in cycloaddition reaction. Among many methods for preparing vinyl sufones the ionic and radical addition of selenosulfonate to alkenes and alkynes is important procedure². However, organic selenium reagents usually have a foul smell and are quite toxic, which is often problematic in organic synthesis. Polymer-supported selenium reagents have been recently developed to solve this problem³. In connection our research with the application of seleno-resins in organic synthesis⁴, we here report a novel facile route to vinyl sulfone using polystyrene-supported selenomethyl phenyl sulfone regent **2** (Scheme 1).

Reaction of polystyrene-supported lithium selenide 1^3 with chloromethyl phenyl sulfone afforded polymer reagent 2, which exhibited two strong characteristic sulfone stretches at 1317 and 1145 cm⁻¹ in FT-IR spectrum and contained a loading of 1.25 mmol S/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 alkyl phenyl sulfone resin 3, which was easily converted into the corresponding vinyl sulfones 4 by oxidation-elimination with 30 % hydrogen peroxide at 0 °C and then at room temperature in good yields (86-93%) and the crude materials (in 92-96 % of purities) was shown in **Table 1**. It should be noted that *trans*-1-alkenylsulfones are formed exclusively except for compound 4e. The residual resin with no $-SO_2$ - absorption in FT-IR spectrum indicated the oxidation-elimination was complete.

^{*} E-mail: shengsr@163.com



 Table 1
 Yields and purities of vinyl sulfones

Entry	RCH ₂ X	Product	Yield (%) ^a	Purity (%) ^b
1	C ₆ H ₅ CH ₂ Br	4 a	90	92
2	NCCH ₂ Cl	4b	86	95
3	CH ₃ OCOCH ₂ Br	4 c	91	92
4	CH ₃ CH ₂ Br	4d	93	96
5	CH ₃ I	4 e	93	96

a) Overall yields based on the loading of resin 2. b) Determined by HPLC.

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