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A Facile One-pot Method for the Synthesis of Vinyl Ethers from 2-Hydroxyalkyl Phenyl Selenides

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Abstract: A mild, one-pot procedure for the synthesis of vinyl ethers in good yields from 2-hydroxyalkyl phenyl selenides with primary or secondary organic halides has been developed.

Keywords: One-pot, vinyl ethers, 2-hydroxyalkyl selenides phenyl, synthesis.

Vinyl ethers are valuable intermediates that can be used in a wide array of chemical transformation[1]. Many methods for preparing vinyl ethers have been reported by the reaction of acetylene with alcohols, mercury-catalyzed transvinylation of alcohols with vinyl ethers, elimination of the alcohol moiety or hydrogen bromide from acetals or α-bromo ethers, isomerization of allyl ethers, carbometalation of alkynic ethers or ester methylenation promoted by metal-complexes, *etc.*[2]. However, most of these methods involved difficulties, such as harsh reactions, laborious manipulation and low overall yields, or in some cases, the reactions are unsuitable for sensitive substrates, some reagents are not readily available. Organoselenium reagents are now commonly used as a powerful tool for introducing new functional groups into organic substrates under extremely mild conditions[3]. In a continuation of our interest in organoselenium chemistry[4], here we report a mild, convenient protocol to prepare vinyl ethers from 2-hydroxyalkyl phenyl selenides **1** in one-pot, two-steps transformation (**Scheme 1**). To our knowledge, this synthetic method has not been prepared.

2-Hydroxyalkyl phenyl selenides **1** (1.0 mmol), easily prepared from PhSeNa with the corresponding epoxides[5], were *O*-alkylated by treatment of primary or secondary organic halides (1.0 mmol) in THF (20 mL) in the presence of sodium hydride (1.0 mmol) at 80 °C for 1 h to afford *O*-alkylated intermediate **3**, which was easily converted into the corresponding vinyl ethers **4** [6] by oxidation-elimination with 30 % hydrogen peroxide [7] at 0 °C and then at room temperature for 30 min in good yields (70-88%) as shown in **Table 1**. Although **3** can be isolated and purified by chromatography, we have found it most convenient to carry out the oxidation-elimination giving almost the same yield in one-pot. The present method has advantages such as mild reaction condition, easy manipulation and good yields. However, it should be noted that using tertiary halide such as *t*-butyl

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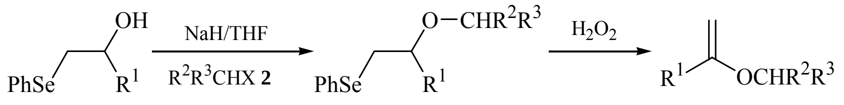
chloride instead of primary or secondary organic halide, only 21% isolated yield of 1-*tert*-butoxy-1-phenylethene was obtained. Obviously, *t*-butyl chloride would tend to mainly take place the elimination reaction rather than the substitution reaction under sodium alkylate.

Scheme 1



1 **3** **4**

Table 1 Preparation of vinyl ethers from 2-hydroxyalkyl phenyl selenides

Entry	R^1	R^2R^3X	Product [a]	Yield (%) [b]
1	C_6H_5	$CH_2{=}CHCH_2Br$	**4a**	83
2	C_6H_5	CH_3I	**4b**	88
3	C_6H_5	$(CH_3)_2CHBr$	**4c**	70
4	C_6H_5	$C_6H_5CH_2Cl$	**4d**	85
5	C_6H_5	3-Cyclohexenyl bromide	**4e**	81
6	$C_6H_5OCH_2$	CH_3CH_2Br	**4f**	83
7	*p*-$CH_3C_6H_4OCH_2$	CH_3CH_2Br	**4g**	82

[a] Purified by flash silica gel column chromatography (CH_2Cl_2/hexane, 10: 90); [b] Isolated yield.

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References and Notes

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6. Compounds **4a-d** are known and their physical spectral data were identical to those reported in the literature [8]. Compound **4e.** Colorless oil; ^1H NMR (400 Mz, $CDCl_3$, δ ppm): 7.77-7.73 (m, 2 H), 7.15-7.06 (m, 3 H), 5.94 (dd, 1H, $J = 10, 2.4$ Hz), 5.70 (dt, 1H, $J = 10, 2.8$ Hz), 4.75 (d, 1H, $J = 2.4$ Hz), 4.56 (bs, 1 H), 4.20 (d, 1H, $J = 2.4$ Hz), 1.88-1.60 (m, 5 H), 1.36-1.31 (m, 1 H); ^{13}C NMR (125 Mz, $CDCl_3$, δ ppm): 158.9, 137.7, 131.3, 128.5, 128.3, 126.8, 126.0, 83.3, 70.4, 28.3, 25.3, 19.4; IR (film): $\nu = 3059$, 2972, 2851, 1643, 1620, 1590, 1496, 1241, 1101, 1042, 978, 910, 810 cm^{-1}; Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.90; H, 8.15. Compound **4f.** Colorless oil. ^1H NMR (400 Mz, $CDCl_3$, δ ppm): 7.52-7.19 (m, 2 H), 6.86-7.00 (m, 3 H), 4.08 (d, 2H, $J = 4.8$ Hz), 3.59 (q, 2H, $J = 7.1$ Hz), 3.26 (dd, 1H, $J = 12.8, 6.0$ Hz), 3.23 (dd, 1H, $J = 12.8, 6.0$ Hz), 1.18 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (125 Mz, $CDCl_3$, δ ppm): 158.6, 132.5, 129.4, 126.9, 121.0, 114.6, 65.9, 29.5, 15.2. IR (film): $\nu = 3059$, 2975, 2872, 1625, 1600, 1495, 1383, 1243, 1094, 1045, 882, 813, 691 cm^{-1}. Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.08; H, 7.99. Compound **4g.** Colorless oil; ^1H NMR

(400 Mz, $CDCl_3$, δ ppm): 7.52 (d, 2H, *J* = 8.8 Hz), 6.77 (d, 2H, *J* = 8.4 Hz), 4.06 (d, 2H, *J* = 3.2 Hz), 3.60 (q, 2H, *J* = 7.2 Hz), 3.24 (dd, 1H, *J* = 12.8, 6.0 Hz), 3.17 (dd, 1H, *J* = 12.8, 6.0 Hz), 2.31 (s, 3H), 1.17 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 Mz, $CDCl_3$, δ ppm): 156.7, 132.6, 129.2, 127.2, 121.1, 114.5, 70.0, 29.6, 20.5, 15.3; IR (film): ν = 3057, 2975, 2871, 1624, 1600, 1494, 1385, 1244, 1095, 1045, 880, 812, 690 cm^{-1}; Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.03; H, 8.44.

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