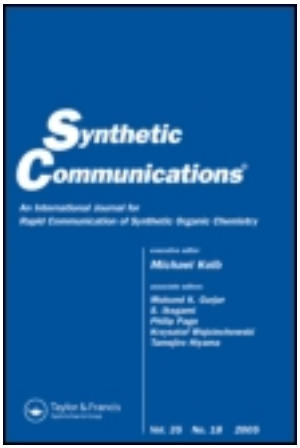

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Convenient One-Pot Synthesis of Vinyl Ethers from Phenyl 2-Hydroxyalkyl Selenides

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Abstract: Vinyl ethers were prepared with good yields in a one-pot, two-step transformation by *O*-alkylation reaction of phenyl 2-hydroxyalkyl selenides with primary or secondary organic halides followed by oxidation elimination with 30% hydrogen peroxide.

Keywords: *O*-Alkylation, oxidation elimination, phenyl 2-hydroxyalkyl selenide, vinyl ether

Vinyl ethers are valuable intermediates that can be used in a wide array of chemical transformations[1] as well as vinyl polymer materials[2] containing oxygen, which are expected to degrade easily in nature. Practically, vinyl ethers are prepared by the reaction of acetylene with alcohols that was developed by Reppe.[3] However, this reaction must be carried out under severe conditions at higher pressure and temperature in the presence of KOH as a catalyst. Several other methods are reported that prepare vinyl and alkenyl ethers: for instance, mercury-catalyzed transvinylation of alcohols with vinyl ethers,[4] elimination of the alcohol moiety or hydrogen

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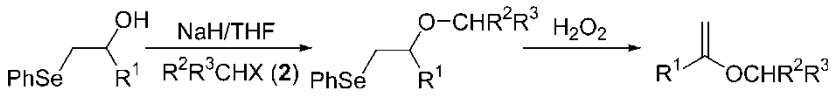
bromide from acetals or α-bromo ethers, respectively,[5,6] isomerization of allyl ethers,[7] carbometalation of alkynic ethers,[8] and ester methylenation promoted by metal complexes.[9] Recently, transformation with coupling of vinyl acetate with alcohols promoted by iridium complexes[10] have also been reported. However, most of these methods involved difficulties such as harsh reactions, laborious manipulation, and low overall yields. In some cases, reactions are unsuitable for sensitive substrates, vigorous toxic compounds are used, or 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.[11] For example, phenylseleno group is readily converted to a leaving group, giving access to carbon–carbon double bond via oxidation followed by β-elimination. In continuation of our interest in organoselenium chemistry,[12] we herein report a convenient and efficient one-pot, two-step preparation of vinyl ethers from phenyl 2-hydroxyalkyl selenides by *O*-alkylation followed by oxidation elimination with 30% hydrogen peroxide (Scheme 1).

Phenyl 2-hydroxyalkyl selenides (**1a**, **1b**, and **1c**) could be easily obtained by the reaction of benzeneselenolate ions with the corresponding epoxides[13] in ethanol at ambient temperature in 84%, 53%, and 90% yields, respectively. With compounds **1a**–**1c** in hand, the *O*-alkylation reaction was investigated starting from phenyl 2-hydroxy-2-phenylethyl selenide (**1a**) with allyl bromide (**2a**) in THF in the presence of sodium hydride, and **1a** was easily *O*-alkylated to afford phenyl 2-(allyloxy)-2-phenylethyl selenide[13d] (**3a**) in 87% yield without competing styrene oxide formation. As expected, 30% hydrogen peroxide was added to the stirred solution of **3a** in THF at 0°C, slowly resulting in a facile oxidation of the selenide to the corresponding selenoxide, and then a *syn*-elimination of the selenoxide effected the release of the 1-phenyl-1-(3-propenoxy)ethene (**4a**) in isolated 83% yield. Although *O*-alkylated intermediate **3a** can be isolated and purified by chromatography, we have found it most convenient to carry out the oxidation elimination in one-pot, which gives almost the same yield. To evaluate the scope of this transformation, a variety of primary or allyl organic halides were subjected to the reaction conditions. The results are outlined in Table 1 It is worth noting the yields of vinyl ethers **4d** and **4e** (Entry 4 and 5) were relative lower under the same reaction conditions, which may have resulted because the corresponding *O*-prop-2-ynylation and *O*-isopropylation were effected in



1 **3** **4**

Scheme 1.

Table 1. One-pot synthesis of vinyl ethers from phenyl 2-hydroxyalkyl selenides

Entry	R^1 (**1**)	R^2R^3CHX (**2**)	Product	Yield (%)[a]
1	C_6H_5 (**1a**)	$CH_2{=}CHCH_2Br$ (**2a**)	**4a**	83
2	C_6H_5 (**1a**)	CH_3CH_2Br (**2b**)	**4b**	82
3	C_6H_5 (**1a**)	CH_3I (**2c**)	**4c**	88
4	C_6H_5 (**1a**)	Propargyl bromide (**2d**)	**4d**	73
5	C_6H_5 (**1a**)	$(CH_3)_2CHBr$ (**2e**)	**4e**	70
6	C_6H_5 (**1a**)	3-Cyclohexenyl bromide (**2f**)	**4f**	81
7	C_6H_5 (**1a**)	$C_6H_5CH_2Cl$ (**2 g**)	**4 g**	85
8	$C_6H_5OCH_2$ (**1b**)	$CH_2{=}CHCH_2Br$ (**2a**)	**4 h**	84
9	$C_6H_5OCH_2$ (**1b**)	CH_3CH_2Br (**2b**)	**4i**	83
10	*p*-$CH_3C_6H_4OCH_2$ (**1c**)	CH_3CH_2Br (**2b**)	**4j**	82

[a]Isolated yield based on phenyl 2-hydroxyalkyl selenides **1**.

poorer yields than the other *O*-alkylations or *O*-allylations. On the other hand, secondary halide (2e) may easily take place elimination under basic condition. Further study on the reaction of **1a** with tertiary halide such as *t*-butyl chloride was examined. However, only 21% isolated yield of 1-*tert*-butoxy-1-phenylethene (**4 k**) was obtained. Obviously, *t*-butyl chloride would tend to mainly use the elimination reaction rather than the substitution reaction under sodium alkylate. Additionally, on the basis of these results, an attempt to synthesize of aryl vinyl ether, using phenyl bromide instead of primary or secondary halides, resulted in almost no reaction using similar procedures.

In summary, a facile one-pot procedure for the preparation of vinyl ethers through *O*-alkylation of phenyl 2-hydroxyalkyl selenides with primary or secondary organic halides and subsequent oxidation elimination has been developed. The present method has advantages such as mild reaction conditions, easy manipulation, and good yields.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR (400-MHz) spectra were recorded on a Bruker Avance (400-MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as internal standard. FT-IR spectra were taken on a Perkin-Elmer SP One FT-IR spectrophotometer. Mass spectra (EI, 70eV) were recorded on a HP5989B mass spectrometer. Microanalyses were performed with a PE 2400 elemental analyzer. Styrene oxide was commercially available and the other two epoxides were prepared according to the literature procedure.[13] Diphenyl diselenide[14] and phenyl 2-hydroxyalkyl selenides (**1a** and **1b** are compounds, **1c** is unknown) were prepared according to the literature

methods.[15] THF was distilled under N_2 from sodium/benzophenone immediately prior to use. Organic halides were obtained from commercial suppliers and used without further purification. All reactions were monitored by TLC.

2-Hydroxy-3-(*p*-methylphenoxy)propyl phenyl selenide (1c): Light yellow oil (yield: 90%);^{1}H NMR: $\delta = 7.54–7.52$ (m, 2H), 7.24–7.22 (m, 3H), 7.06 (d, $J = 8.4$ Hz, 2H), 6.76 (d, $J = 8.4$ Hz, 2H), 4.00 (dd, $J = 9.3$, 4.2 Hz, 1H), 3.97 (dd, $J = 9.4$, 5.8 Hz, 1H), 4.09–4.08 (m, 1H), 3.19 (dd, $J = 12.8$, 5.6 Hz, 1H), 3.14 (dd, $J = 12.8$, 6.8 Hz, 1H), 2.81 (bs, 1H), 2.27 (s, 3H);^{13}C NMR: $\delta = 156.3$, 132.9, 130.5, 130.0, 129.4, 129.3, 127.3, 114.5, 70.7, 69.2, 31.9, 20.5; IR (film): $\nu = 3433$, 3058, 2927, 2872, 1599, 1587, 1495, 1384, 1244, 1172, 1074, 1041, 941, 902, 814, 737, 669 cm^{-1}. MS m/z (relative intensity) 322 (M^+, 5.1); anal. calcd. for $C_{16}H_{18}O_2Se$: C, 59.82; H, 5.65. Found: C, 59.62; H, 5.68.

General Procedure for the Preparation of Vinyl Ethers

To a solution of phenyl 2-hydroxyalkyl selenide (1.0 mmol) in dry THF (20 mL) at room temperature was added sodium hydride (0.04 g, 60% dispersion, 1.0 mmol). The resulting mixture was stirred for ca. 1 h at room temperature. A solution of the organic halide (1.0 mmol) in dry THF (2 mL) was then added dropwise, and the reaction flask was placed in an oil bath preheated to 80°C. The mixture was refluxed for 1 h and then cooled gradually to 0°C. The 30% hydrogen peroxide (1.0 mL, 11.6 mmol) was added over 10 min. After an additional stirring for 20 min at room temperature, water (20 mL) was added and the solution was extracted with ether (20×3 mL). The combined organic phase was washed with saturated $NaHCO_3$ solution, brine, and water (twice) and then dried over magnesium sulfate. The solvent was removed in vacuo, and the residue was purified by flash silica-gel column chromatography (CH_2Cl_2/hexane, 10 : 90) to give the pure product.

1-Phenyl-1-(3-propenoxy)ethene (4a):[9b] Colorless oil;^{1}H NMR: $\delta = 6.88–6.45$ (m, 2H), 7.01–6.84 (m, 3H), 5.81–6.27 (m, 1H), 5.60–5.14 (m, 2H), 4.65 (d, $J = 3.1$ Hz, 1H), 4.40–4.11 (m, 2H), 4.16 (d, $J = 3.1$ Hz, 1H); IR (film): $\nu = 3056$, 2974, 2850, 1645, 1622, 1595, 1495, 1242, 1100, 1044, 991, 912, 812 cm^{-1}.

1-Ethoxy-1-phenylethene (4b):[9b] Colorless oil;^{1}H NMR: $\delta = 7.68–7.56$ (m, 2H), 7.19–7.07 (m, 3H), 4.60 (d, $J = 2.1$ Hz, 1H), 4.20 (d, $J = 2.1$ Hz, 1H), 3.74 (q, $J = 7.1$ Hz, 2H), 1.34 (t, $J = 7.1$ Hz, 3H); IR (film): $\nu = 3056$, 2975, 2852, 1632, 1592, 1495, 1378, 1244, 1096, 1045, 990, 813 cm^{-1}.

1-Methoxy-1-phenylethene (4c):[9b] Colorless oil;^{1}H NMR: $\delta = 7.65–7.52$ (m, 2H), 7.18–7.04 (m, 3H), 4.58 (d, $J = 2.0$ Hz, 1H), 4.21 (d, $J = 2.0$ Hz, 1H), 3.71 (s, 3H); IR (film): $\nu = 3057$, 2974, 2855, 1634, 1593, 1495, 1380, 1243, 1094, 1045, 988, 812 cm^{-1}.

1-Phenyl-1-(3-propynyloxy)ethene (4d): Colorless oil;^{1}H NMR: $\delta = 6.92–6.57$ (m, 2H), 7.04–7.02 (m, 3H), 4.68 (d, $J = 3.0$ Hz, 1H), 4.22 (d, $J = 3.0$ Hz, 1H), 4.16 (dd, $J = 15.6$, 2.4 Hz, 1H), 3.90 (dd, $J = 15.6$, 2.4 Hz, 1H), 2.41 (t, $J = 2.4$ Hz, 1H);^{13}C NMR: $\delta = 158.7$, 136.7, 132.1, 129.2, 126.8, 126.0, 80.1, 74.5, 56.7; IR (film): $\nu = 3280$, 3059, 2972, 2851, 2212, 1636, 1595, 1495, 1354, 1245, 1102, 1044, 990, 910, 665 cm^{-1}; anal. calcd. for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.60; H, 6.43.

1-Isopropoxy-1-phenylethene (4e):[9b] Colorless oil;^{1}H NMR: $\delta = 7.48–7.21$ (m, 2H), 7.10–7.01 (m, 3H), 4.56 (d, $J = 2.1$ Hz, 1H), 4.25–4.32 (m, 1H), 4.03 (d, $J = 2.1$ Hz, 1H), 1.32 (d, $J = 7.2$ Hz, 6H); IR (film): $\nu = 3058$, 2976, 2845, 1635, 1558, 1495, 1384, 1375, 1240, 1101, 1042, 989, 810 cm^{-1}.

1-(3-Cyclohexenoxy)-1-phenylethene (4f): Colorless oil;^{1}H NMR: $\delta = 7.77–7.73$ (m, 2H), 7.15–7.06 (m, 3H), 5.94 (dd, $J = 10$, 2.4 Hz, 1H), 5.70 (dt, $J = 10$, 2.8 Hz, 1H), 4.75 (d, $J = 2.4$ Hz, 1H), 4.56 (bs, 1H), 4.20 (d, $J = 2.4$ Hz, 1H), 1.88–1.60 (m, 5H), 1.36–1.31 (m, 1H); ^{13}C NMR: $\delta = 158.9$, 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.

1-Benzoxy-1-phenylethene (4 g):[9b] Colorless oil;^{1}H NMR: $\delta = 7.60–7.01$ (m, 10H), 4.81 (s, 2H), 4.52 (d, $J = 3.2$ Hz, 1H), 4.12 (d, $J = 3.2$ Hz, 1H); IR (film): $\nu = 3059$, 2975, 2844, 1632, 1559, 1494, 1445, 1241, 1100, 1039, 985, 812 cm^{-1}.

1-Phenoxymethyl-1-(3-propenoxy) ethene (4 h): Colorless oil;^{1}H NMR: $\delta = 6.95–6.86$ (m, 2H), 7.27–7.20 (m, 3H), 5.94–5.84 (m, 1H), 5.25 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.15 (d, $J = 10.4$ Hz, 1H), 4.12 (s, 2H), 4.09 (d, $J = 4.8$ Hz, 2H), 3.15–3.26 (m, 2H);^{13}C NMR: $\delta = 158.6$, 134.7, 132.6, 129.2, 127.0, 121.0, 117.5, 114.6, 71.4, 29.3; IR (film): $\nu = 3060$, 2923, 2856, 1622, 1600, 1495, 1244, 1096, 1079, 925, 814, 737, 691 cm^{-1}; anal. calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.78; H, 7.51.

1-Ethoxy-1-phenoxymethylethene (4i): Colorless oil;^{1}H NMR: $\delta = 7.52–7.19$ (m, 2 H), 6.86–7.00 (m, 3H), 4.08 (d, $J = 4.8$ Hz, 2H), 3.59 (q, $J = 7.1$ Hz, 2H), 3.26 (dd, $J = 12.8$, 6.0 Hz, 1H), 3.23 (dd, $J = 12.8$, 6.0 Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H);^{13}C NMR: $\delta = 158.6$, 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.

1-Ethoxy-1-(*p*-methylphenoxymethyl) ethene (4j): Colorless oil;^{1}H NMR: $\delta = 7.52$ (d, $J = 8.8$ Hz, 2H), 6.77 (d, $J = 8.4$ Hz, 2H), 4.06 (d, $J = 3.2$ Hz, 2H), 3.60 (q, $J = 7.2$ Hz, 2H), 3.24 (dd, $J = 12.8$, 6.0 Hz, 1H), 3.17 (dd, $J = 12.8$, 6.0 Hz, 1H), 2.31 (s, 3H), 1.17 (t, $J = 7.2$ Hz, 3H);^{13}C NMR: $\delta = 156.7$, 132.6, 129.2, 127.2, 121.1, 114.5, 70.0, 29.6, 20.5, 15.3; IR (film): $\nu = 3057$, 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.

1-*tert*-Butoxy-1-phenylethene (4 k):[9b] Colorless oil;^{1}H NMR: $\delta = 7.44–7.19$ (m, 2H), 7.12–6.95 (m, 3H), 4.65 (d, $J = 2.0$ Hz, 1H), 4.28 (d, $J = 2.0$ Hz, 1H), 1.34 (s, 9H); IR (film): $\nu = 3058$, 2976, 2845, 1635, 1558, 1500, 1390, 1365, 1240, 1101, 1042, 990, 810 cm^{-1}.

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