Polymer-Supported β-Bromoethyl Selenide: An Efficient Reagent for the Synthesis of Aryl Vinyl Ethers

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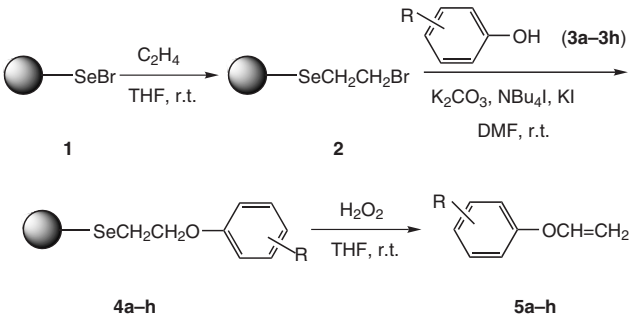
Abstract: A simple and efficient procedure for the solid-phase synthesis of aryl vinyl ethers using polymer-supported β-bromoethyl selenide with traceless linker strategy is described.

Key words: solid-phase organic synthesis, polymer-supported β-bromoethyl selenide, aryl vinyl ether, oxidation-elimination

Vinyl ethers are valuable intermediates that can be used in a wide array of chemical transformations.[1] More specifically, aryl vinyl ethers with unsubstituted vinyl moiety, have been involved in reactions such as [2+2],[2] [2+4][3] and 1,3-dipolar cycloadditons,[4] and hydroformylation,[5] etc. Aryl vinyl ethers are usually prepared according to either of the following procedures: the dehydrohalogenation of aryl 2-haloethyl ethers[6] or the addition of phenols to acetylene.[7] Recently, other transformations with copper (II)-promoted coupling of arylboronic acids[8] and tributyl(vinyl)tin[9] with phenols have also been reported. However, most of these methods involved difficulties such as harsh reactions, laborious manipulation and low overall yields, or in some cases, reactions are unsuitable for sensitive substrates, vigorous toxic compounds are used or some reagents are not readily available. It is well known that phenylseleno group is readily converted to a leaving group giving access to carbon-carbon double bond via oxidation followed by β-elimination.[10] However, organoselenium reagents always have a foul smell and are quite toxic, which is often problematic in organic synthesis. Recently, the use of the selenium reagents immobilized on polymer-resin has provided significant advantages, including decrease volatility and simplification of product work-up.[11] In connection with our interest in solid-phase organoselenium chemistry,[12] herein, we wish to report a convenient and efficient solid-phase synthetic approach to aryl vinyl ethers based on a novel polymer-supported β-bromoethyl selenide (Scheme 1).

Simple stirring of polymer-supported selenium bromide **1** in THF at room temperature with a excess of anhydrous ethene resulted in a rapid decolorization of the resin (less than five minutes) to produce a yellow β-bromoethyl selenide resin **2** in nearly quantitative yield, as monitored by FT-IR spectroscopy showing a moderate strong C-Br absorption at 572 cm^{-1}. Resin **2** can be stored at room temperature for long time without diminution of capacity or the liberation of disagreeable odors. With the resin **2** in hand, the preparation of phenolic ethers resin **4**, the key for the success of this protocol was investigated. Usually the synthesis of phenolic ethers has been efficiently accomplished by alkylation reaction in the presence of a base. Here, the alkylation reaction was investigated starting from resin **2** and 4-cyanophenol (**3f**). In our case, when potassium carbonate and DMF were employed as a base and a solvent, respectively, the alkylation on solid-phase at room temperature for 24 hours was complete as monitored by FT-IR spectra with a single strong CN peak at 2210 cm^{-1} and the complete disappearance of the C-Br



Scheme 1

Table 1 Preparation of Aryl Vinyl Ethers on a Polymeric Support

Entry	Phenol	R	Product	Yield (%)[a]	Purity (%)[b]
1	**3a**	H	**5a**	95	> 95
2	**3b**	3-CH_3	**5b**	94	> 95
3	**3c**	4-*t*-C_4H_9	**5c**	96	> 95
4	**3d**	4-Br	**5d**	93	> 95
5	**3e**	4-NO_2	**5e**	93	> 95
6	**3f**	4-CN	**5f**	95	> 95
7	**3g**	4-CO_2CH_3	**5g**	94	> 95
8	**3h**	4-$NHCOCH_3$	**5h**	92	> 95

[a] Overall yield based on polymer-supported β-bromoethyl selenide (1.14 mmol Br/g).
[b] Determined by ^{1}H NMR of crude cleavage product.

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absorption and was found to have lost all its bromine by elemental analysis. Furthermore, it has been found that the alkylation was carried out completely in only about ten hours in the presence of catalytic amounts of NBu_4I/KI. But in other solvents such as CH_3CN, CH_2Cl_2 and THF under the same conditions as above, or at reflux temperature even for longer time, the alkylation was not complete according to the FT-IR spectrum of the isolated resin with CBr and CN absorptions.

As expected, oxidation–elimination of resins **4a–h** was very rapid and efficient with excess of 30% hydrogen peroxide at room temperature to afford the corresponding aryl vinyl ethers **5a–h** in good yields (92–96%) and high purity of crude materials in all cases (> 95% by ^{1}H NMR analysis) (Table 1). The residual resin, polystyrene-supported phenylseleninic acid, was obtained as a by-product, whose FT-IR data was identical to the previously reported data.[13] The polystyrene-supported phenylseleninic acid could be converted to resin **1** for recycle by treatment of it with KI/$Na_2S_2O_3$[12c,14] followed by bromine.[12a] For example, phenyl vinyl ether (**5a**) was obtained in 84% yield under the same reaction condition using the recovered selenenyl bromide resin **1** (second run), and in 71% yield after second recycle (i.e. third run). It was shown that recycling 2–3 times led to a gradual deterioration of the resin **1**.

Similarly, the treatment of resin **2** with 1-naphthol (**3i**) gave 1-naphthyl vinyl ether (**5i**) in 93% yield and with >95% purity. With our successful synthesis of aryl vinyl ethers, we studied the reaction of resin **2** with benzyl alcohol in the same procedure, but no reaction was observed. However, when sodium hydride was used instead of K_2CO_3, 80% isolated yield of benzyl vinyl ether (**5j**) was obtained. The yield of **5j** did not improved greatly on enhancing the reaction temperature or prolonging the reaction time.

In conclusion, a convenient and efficient method for the solid-phase traceless synthesis of aryl vinyl ethers from alkylation of polymer-supported β-bromoethyl selenide with phenols and subsequent oxidation–elimination has been developed. Simple workup procedure replaces the time-consuming isolation and purification steps in the corresponding solution-phase synthesis.

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. Microanalyses were performed with a PE 2400 elemental analyzer. Polystyrene for the preparation of polystyrene-supported selenium bromide according to the procedure described by Nicolaou[11a] was purchased from Aldrich (100–200 mesh, cross-linked with 1% divinylbenzene). Phenols were purchased from commercial sources or prepared in our laboratory.

Preparation of Aryl Vinyl Ethers; General Procedure

To THF (10 mL) saturated with anhyd ethane was added the polystyrene-bound selenenyl bromide **1** (1.0 g, 1.18 mmol). The deep red coloration of the polymer disappeared instantly and the mixture was stirred at r.t. for 5 min. After removal of the solvent, the yellow resin **2** containing Br (1.14 mmol) was obtained and then swelled in DMF (8 mL). K_2CO_3 (0.25 g, 1.8 mmol), NBu_4I (0.018 g, 0.05 mmol), KI (0.025g, 0.15 mmol) and a solution of phenols **3a–i** (2.0 mmol) in DMF (2 mL) was added under a nitrogen atmosphere. The mixture was stirred at r.t. for 10 h and then filtered, the polymer was washed successively with HOAc (ca 2.0 equiv), H_2O, THF (2 × 5 mL), MeOH (2 × 5 mL) and CH_2Cl_2 (2 × 5 mL). The washed resin **4** was pre-swollen with THF (15 mL), followed by the treatment with 30% hydrogen peroxide (1.5 mL, 17.4 mmol) and stirred at r.t. for 30 min. Then the resin was filtered off and rinsed with Et_2O (4 × 3 mL). The filtrate was extracted with Et_2O and the organic extracts were washed with water, dried over anhyd $MgSO_4$ and concentrated to afford product **5a–i**.

Phenyl Vinyl Ether (5a)

Colorless oil (lit.[7a] oil).

IR: 3045, 1640, 1623, 1600, 1495, 1230, 1212, 1165, 1155, 1145, 956, 942 cm^{-1}.

^{1}H NMR: δ = 7.15–7.02 (m, 5 H), 6.58 (dd, *J* = 14.0, 6.0 Hz, 1 H), 4.70 (dd, *J* =14.0, 1.5 Hz, 1 H), 4.34 (dd, *J* = 6.0, 1.5 Hz, 1 H).

^{13}C NMR: δ = 154.0, 144.4, 133.1, 120.5, 115.3, 95.3.

Anal. Calcd for C_8H_8O: C, 79.98; H, 6.71. Found: C, 80.06; H, 6.80.

3-Methylphenyl Vinyl Ether (5b)

Colorless oil (lit.[7a] oil).

IR: 3050, 1640, 1622, 1600, 1500, 1380, 1230, 1160, 1149, 960, 822 cm^{-1}.

^{1}H NMR: δ = 6.83–7.20 (m, 4 H), 6.50 (dd, *J* = 14.2, 6.5 Hz, 1 H), 4.32 (dd, *J* = 14.2, 1.8 Hz, 1 H), 4.04 (dd, *J* = 6.5, 1.8 Hz, 1 H), 2.30 (s, 3 H).

^{13}C NMR: δ = 154.6, 140.4, 132.1, 123.7, 122.6, 119.5, 115.3, 95.6, 21.5.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.66; H, 7.60.

4-t-Butylphenyl Vinyl Ether (5c)

Colorless oil (lit.[6a] oil).

IR: 3045, 2940, 1640, 1600, 1600, 1500, 1378, 1240, 1180, 1149, 825 cm^{-1}.

^{1}H NMR: δ = 6.80 (d, *J* = 8.2 Hz, 2 H), 7.18 (d, *J* = 8.2 Hz, 2 H), 6.51 (dd, *J* = 14.0, 6.2 Hz, 1 H), 4.28 (dd, *J* = 14.0, 1.6 Hz, 1 H), 4.24 (dd, *J* = 6.2, 1.6 Hz, 1 H), 1.31 (s, 9 H).

^{13}C NMR: δ = 157.1, 145.5, 133.7, 120.0, 117.3, 95.8, 38.0, 28.5.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.86; H, 9.20.

4-Bromophenyl Vinyl Ether (5d)

Colorless oil (lit.[15] oil).

IR: 3050, 1636, 1578, 1475, 1230, 1160, 1140, 1060, 1000, 950, 820 cm^{-1}.

^{1}H NMR: δ = 7.40 (d, *J* = 8.5 Hz, 2 H), 6.95 (d, *J* = 8.5 Hz, 2 H), 6.60 (dd, *J* = 13.8, 6.1 Hz, 1 H), 4.78 (dd, *J* = 13.8, 1.8 Hz, 1 H), 4.48 (dd, *J* = 6.1, 1.8 Hz, 1 H).

^{13}C NMR: δ = 155.9, 147.7, 132.6, 118.5, 115.7, 96.0.

Anal. Calcd for C_8H_7BrO: C, 48.27; H, 3.55. Found: C, 48.36; H, 3.63.

4-Nitrophenyl Vinyl Ether (5e)

Colorless oil (lit.[15] oil).

IR: 3060, 1638, 1600, 1580, 1498, 1481, 1330, 1230, 1160, 1120, 1100, 945, 840 cm^{-1}.

^1H NMR: δ = 8.25 (d, *J* = 8.9 Hz, 2 H), 7.10 (d, *J* = 8.9 Hz, 2 H), 6.68 (dd, *J* = 13.6, 6.0 Hz, 1 H), 5.01 (dd, *J* = 13.6, 1.9 Hz, 1 H), 4.70 (dd, *J* = 6.0, 1.9 Hz, 1 H).

^{13}C NMR: δ = 161.3, 145.5, 142.8, 125.7, 116.3, 99.1.

Anal. Calcd for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.25; H, 4.35; N, 8.52.

4-Cyanophenyl Vinyl Ether (5f)
Colorless oil (lit.[16] oil).

IR: 3050, 2200, 1635, 1595, 1492, 1300, 1235, 1160, 1125, 950, 824 cm^{-1}.

^1H NMR: δ = 7.70 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H), 6.66 (dd, *J* = 13.7, 6.1 Hz, 1 H), 4.98 (dd, *J* = 13.7, 2.0 Hz, 1 H), 4.68 (dd, *J* = 6.1, 2.0 Hz, 1 H).

^{13}C NMR: δ = 159.8, 145.8, 134.1, 118.6, 117.1, 106.1, 98.6.

Anal. Calcd for C_9H_7NO: C, 74.46; H, 4.86; N, 9.65. Found: C, 74.53; H, 4.91; N, 9.70.

Methyl 4-(Vinyloxy)benzoate (5g)
Colorless oil (lit.[16] oil).

IR: 3050, 2985, 2940, 1710, 1635, 1596, 1498, 1425, 1300, 1272, 1235, 1156, 1132, 1100, 840 cm^{-1}.

^1H NMR: δ = 8.00 (d, *J* = 8.3 Hz, 2 H), 7.15 (d, *J* = 8.3 Hz, 2 H), 6.88 (dd, *J* = 13.6, 6.0 Hz, 1 H), 4.85 (dd, *J* = 13.6, 1.6 Hz, 1 H), 4.55 (dd, *J* = 6.0, 1.6 Hz, 1 H), 3.84 (s, 3 H).

^{13}C NMR: δ = 166.5, 160.2, 146.6, 131.5, 124.5, 116.1, 97.3, 51.8.

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.50; H, 5.71.

***N*-[4-(Vinyloxy)phenyl]acetamide (5h)**
Mp 102–103 °C (lit.[17] mp 103–103.5 °C).

IR: 3258, 3188, 3130, 3055, 1650, 1600, 1495, 1300, 1235, 1210, 1162, 1145, 940, 830 cm^{-1}.

^1H NMR: δ = 7.40–7.50 (m, 2 H), 7.26 (br s, 1 H), 6.95–7.05 (m, 2 H), 6.63 (dd, *J* = 13.7, 6.1 Hz, 1 H), 4.75 (dd, *J* = 13.7, 1.7 Hz, 1 H), 4.55 (dd, *J* = 6.1, 1.7 Hz, 1 H), 2.18 (s, 3 H).

^{13}C NMR: δ = 169.2, 153.2, 148.5, 133.4, 122.1, 117.3, 94.6, 24.1.

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.87; H, 6.36; N, 7.96.

1-Naphthyl Vinyl Ether (5i)
Mp 31–32 °C (lit.[18] mp 32 °C).

IR: 3050, 1630, 1600, 1495, 1255, 1226, 1172, 1152, 1142, 942 cm^{-1}.

^1H NMR: δ = 7.00–7.50 (m, 7 H), 6.71 (dd, *J* = 14.1, 6.0 Hz, 1 H), 4.81 (dd, *J* = 14.1, 1.6 Hz, 1 H), 4.45 (dd, *J* = 6.0, 1.6 Hz, 1 H).

^{13}C NMR: δ = 152.7, 144.9, 133.9, 132.6, 128.9, 128.7, 128.3, 126.7, 125.9, 123.5, 115.8, 95.7.

Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.74; H, 6.01.

Benzyl Vinyl Ether (5j)
Colorless oil (lit.[18] oil).

IR: 2986, 1642, 1596, 1500, 1425, 1302, 1235, 1150, 1100, 965 cm^{-1}.

^1H NMR: δ = 7.20–7.12 (m, 5 H), 6.50 (dd, *J* = 13.9, 6.7 Hz, 1 H), 4.55 (s, 2 H), 4.22 (dd, *J* = 13.9, 2.0 Hz, 1 H), 3.97 (dd, *J* = 6.7, 2.0 Hz, 1 H).

^{13}C NMR: δ = 139.5, 131.1, 128.6, 127.5, 114.8, 95.2, 73.9.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.65; H, 7.61.

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References

(1) *Comprehensive Organic Synthesis*, Vol. 9; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991**, Cumulative Indexes, see: enol ethers; ethers, phenyl vinyl; ethers, vinyl; vinyl ethers.
(2) For selected examples of [2+2] cylcoadditons, see: (a) Brückner, R.; Huisgen, R. *Tetrahedron Lett.* **1990**, *31*, 2557. (b) El-Nabi, H. A. A. *Tetrahedron* **1997**, *53*, 1813. (c) Futamura, S.; Ohta, H.; Kamiya, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2190.
(3) For selected examples of Diels–Alder reactions, see: (a) Markó, I. E.; Evans, G. R.; Declercq, J.-P. *Tetrahedron* **1994**, *50*, 4557. (b) Wada, E.; Yasuoka, H.; Kanemasa, S. *Chem. Lett.* **1994**, 145. (c) Hojo, M.; Masuda, R.; Okada, E. *Synthesis* **1990**, 347.
(4) For selected examples of 1,3-dipolar cycloadditons, see: (a) Savinov, S. N.; Austin, D. J. *Chem. Commun.* **1999**, 1813. (b) Shimizu, T.; Hayashi, Y.; Teramura, K. *J. Org. Chem.* **1983**, *48*, 3053.
(5) (a) Nait Ajjou, A.; Alper, H. *J. Am. Chem. Soc.* **1998**, *120*, 1466. (b) Abu-Gnim, C.; Amer, I. *J. Organomet. Chem.* **1996**, *516*, 235. (c) Basoli, C.; Botteghi, C.; Cabras, M. A.; Chelucci, G.; Marchetti, M. *J. Organomet. Chem.* **1995**, *488*, C20.
(6) (a) Mizuno, K.; Kimura, Y.; Otsuji, Y. *Synthesis* **1979**, 688. (b) Dombroski, J. R.; Hallensleben, M. L. *Synthesis* **1972**, 693. (c) McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 548. (d) Oae, S.; Yano, Y. *Tetrahedron* **1968**, *24*, 5721. (e) Fueno, T.; Matsumura, I.; Okuyama, T.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 818.
(7) (a) Reppe, W. *Liebigs Ann. Chem.* **1956**, *601*, 81. (b) Andriyankov, M. A.; Skvortsova, G. G.; Malkova, T. I.; Platonova, A. T. *Pharm. Chem. J. (Engl. Transl.)* **1981**, *15*, 190. (c) Turner, J. O.; Glickman, S. A. DE Patent, 1802602, **1969**.
(8) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett.* **1998**, *39*, 2937.
(9) Blouin, M.; Frenette, R. *J. Org. Chem.* **2001**, *66*, 9043.
(10) (a) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. (b) Liotta, D. *Acc. Chem. Res.* **1984**, *17*, 28. (c) *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, **1987**. (d) Back, T. G. *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 2; Patai, S., Ed.; Wiley: Chichester, **1987**, Chap 3.
(11) (a) Nicolaou, K. C.; Pastor, J.; Barluenga, S.; Winssinger, N. *Chem. Commun.* **1998**, 1947. (b) Ruhland, T.; Andersen, K.; Pedersen, H. *J. Org. Chem.* **1998**, *63*, 9204. (c) Fujita, K.-I.; Hashimoto, S.; Oishi, A.; Taguchi, Y. *Tetrahedron Lett.* **2003**, *44*, 3793. (d) Uehlin, L.; Wirth, T. *Org. Lett.* **2001**, *3*, 2931.

(12) (a) Huang, X.; Sheng, S.-R. *Tetrahedron Lett.* **2001**, *42*, 9035. (b) Huang, X.; Sheng, S.-R. *J. Comb. Chem.* **2003**, *5*, 273. (c) Huang, X.; Xu, W.-M. *Tetrahedron Lett.* **2002**, *43*, 5495.
(13) Zundel, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 499.
(14) Ferranti, F.; Filippo, D. D. *J. Chem. Soc. B* **1971**, 1925.
(15) Afonin, A. V.; Vashchenko, A. V.; Tagaki, T.; Kimura, A.; Fujiwara, H. *Can. J. Chem.* **1999**, *77*, 416.
(16) Bzhezovskii, V. M.; Finkel'shtein, B. L.; Kushnarev, D. F.; Kalabin, G. A.; Troffimov, B. A. *J. Org. Chem. USSR (Engl. Transl.)* **1990**, *26*, 15.
(17) Skvortsova, G. G.; Kurov, G. N.; Samoilova, M. Y. *J. Org. Chem., USSR (Engl. Transl.)* **1966**, *2*, 1046.
(18) Christol, H.; Cristau, H.-J.; Soleiman, M. *Synthesis* **1975**, 736.