Facile Solid-Phase Organic Synthesis of 5-Vinyl-Substituted 1,2,4-Oxadiazoles from Polymer-Bound α-Selenopropionic Acid

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Cyclocondensation of polystyrene-supported α-selenopropionic acid with amidoximes in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) followed by oxidative deselenation efficiently afforded 5-vinyl 1,2,4-oxadiazoles in good yield and purity with a facile work-up procedure.

Keywords: Solid-phase organic synthesis; Polystyrene-supported α-selenopropionic acid; 5-Vinyl-substituted 1,2,4-oxadiazole.

Polymer-supported reagents have attracted growing interest because they can provide attractive and practical methods for combinatorial chemistry and solid-phase organic synthesis (SPOS) in recent years.[1] SPOS using insoluble solid supports such as polystyrene resins takes advantage of the simple removal of excess or consumed reagents by a simple filtration workup operation. The design and synthesis of pharmacologically relevant heterocyclic molecules using SPOS methodology is now recognized as a valuable tool for acceleration of drug discovery. 1,2,4-Oxadiazoles are a class of important heterocycles, which have been well documented throughout the literature due to their biological importance. 1,2,4-Oxadiazoles have often been used as bioisosteres of esters and amides[2] and as dipeptide mimetics[3] in a number of pharmacologically important molecules. They can also be found in a number of biologically important molecules, such as muscarinic agonists,[4] serotoninergic (5-HT_3) antagonists,[5] benzodiazepine receptor agonists,[6] and dopamine ligands.[7] Generally, 1,2,4-oxadiazoles are synthesized by (i) cyclodehydration of *O*-acylamidoximes; (ii) cyclization of *N*-acylamidoximes; (iii) 1,3-dipolar cycloaddition of nitrile oxides to nitriles; (iv) electrocyclic ring closure of nitrenoids; and (v) oxidation of 4,5-dihydro-1,2,4-oxadiazoles.[8] Recently, the use of a polymer support for the preparation of 5-isoxazol-4-yl-[1,2,4]oxadiazole diheterocyclics, which proceed through an alkynoate intermediate has been reported.[9] However, in view of the fact that vinyl substituted heterocycles are used as versatile organic synthetic intermediates,[10] the incorporation of vinyl substituent into 1,2,4-oxadiazole ring using SPOS methodology, has little been investigated. In recent years, polymer-bound phenylseleno group has been proven to be a versatile pro-vinyl safety-catch traceless linker, which can give access to carbon-carbon double bond *via* oxidation followed by β-elimination.[11] Meanwhile, the use of the selenium reagents immobilized on polymer-resin has provided significant advantages, including decrease volatility and simplification of product work-up. As a continuation of our studies toward the development of new methods for the synthesis of heterocyclic compounds based on solid-phase organoselenium chemistry,[12] we report herein a convenient and efficient approach to 5-vinyl 1,2,4-oxadiazoles from polystyrene-supported α-selenopropionic acid (Scheme I).

Polymer-supported α-selenopropionic acid **2** was prepared by treatment of a THF-swollen suspension of cross-linked (1%) polystyrene bound selenium bromide **1**[11b] with $LiBH_4$, followed by treatment with 2-bromopropionic acid according to our previous method.[12a] The minimum loading of COOH of resin **2** verified by their FT-IR spectra showing a strong carbonyl absorption at 1726 cm^{-1} were determined by acid-base titration[13] to be 1.20 mmol/g. With resin **2** in hand, the secondary condensation reaction of polymeric α-selenopropionic acid **2** with various amidoximes, the key for the success of this protocol was investigated. Ordinarily, dicyclohexyl carbodiimide (DCC), 1-

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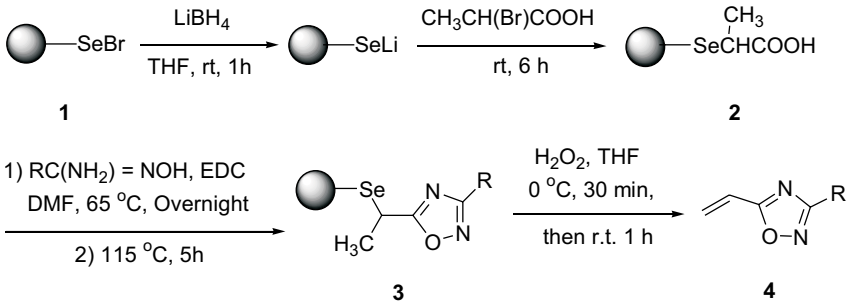
Scheme I



(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), 1,1-carbonyldiimidazole (CDI), *O*-(1H-benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium tetrafluoroborate, 1,2,3-benzotriazole-1-hydroxide (HOBt), or *O*-benzotriazol-1-yl-*N,N,N',N'*-tetr-amethyluronium hexafluorophosphate (HBTU) have been used as a coupling reagent to promote the condensation of carboxylic acids with amidoximes.[14,15] After considerable experimentation, the best result was obtained by treatment of resin **2** with amidoximes in the presence of excess EDC in DMF through a two-step one-pot condensation. The cyclocondensation on polymer was complete as monitored by FT-IR study of the resin **3** showing a new moderate strong absorption near 1654 cm^{-1} corresponding to C=N stretch group in oxadiazole ring, with disappearance of the band at 1726 cm^{-1}. As expected, subsequent oxidation-elimination of resin **3** was very rapid and efficient with excess of 30% hydrogen peroxide to afford the corresponding 5-vinyl 1,2,4-oxadiazoles **4** in good yields (72-80%) and purities (90-96%) of crude materials in all cases (Table 1). The residual resin, polystyrene-supported phenylseleninic acid, was obtained as a by-product, whose infrared data was identical to the previously reported data.[16] The polystyrene-supported phenylseleninic acid could be converted to resin **1** for recycle by treatment of it with $KI/Na_2S_2O_3$ [17] followed by bromine.[11b] For example, 3-phenyl-5-vinyl-1,2,4-oxadiazole (**4a**) was obtained in 75% yield under the same reaction condition using the recovered selenenyl bromide resin **1** (second run), and in 70% 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**.

Table 1. The yields and purities of 5-vinyl 1,2,4-oxadiazoles **4**

Entry	R	Product	Yield (%)[a]	Purity (%)[b]
1	C_6H_5	**4a**	78	95
2	4-$CH_3OC_6H_4$	**4b**	80	96
3	4-$CH_3C_6H_4$	**4c**	79	93
4	4-ClC_6H_4	**4d**	76	93
5	2-ClC_6H_4	**4e**	77	94
6	3-BrC_6H_4	**4f**	74	90
7	4-FC_6H_4	**4g**	74	92
8	$C_6H_5CH_2$	**4h**	73	92
9	*i*-C_3H_7	**4i**	72	91

[a] Overall yields based on polystyrene-supported α-selenopropionic acid **2** (1.20 mmol COOH/g).
[b] Determined by HPLC of crude cleavage product (λ = 254 nm).

In conclusion, a novel and efficient method for the solid-phase traceless synthesis of 5-vinyl 1,2,4-oxadiazoles in good yields and purities by cyclocondensation of polymer-supported α-selenopropionic acid with amidoximes and subsequent oxidation-elimination has been developed. The advantages of the present method include decreasing volatility and simplification of product work-up.

EXPERIMENTAL SECTION

Melting points were determined on X_4 melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer using $CDCl_3$ as the solvent and TMS as an 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. Mass spectra (EI, 70 eV) were recorded on a HP5989B mass spectrometer. HPLC analysis was carried out on Agilent 1100 (250 × 4.6 mm C_{18} Column, gradient elution 50/20/30 THF/CH_3OH/H_2O (v/v), 1 mL/min, UV detection at λ = 254 nm). Polystyrene (H 1000, 100-200 mesh, cross-linked with 1% divinylbenzene) for the preparation of polystyrene-supported selenium bromide[11b] and other starting materials were purchased from commercial suppliers and used without further purification. DMF was distilled from calcium hydride and THF was stilled from sodium-benzophenone immediately prior to use.

General procedure for the synthesis of vinyl-substituted 1,2,4-oxadiazoles (4a-4i)

Under a positive pressure of nitrogen, amidoximes (1.5 mmol) and EDC (0.48 g, 2.5 mmol) was added to a suspension of the swollen polymeric α-phenylselenopropionic acid **2** (0.5 g, 0.60 mmol) in anhydrous DMF (20 mL) and heated to 65 °C overnight. The mixture was then refluxed at 115 °C for another 5 h at which time the new formed resin **3** was washed thoroughly successively with DMF (2 × 10 mL), DCM (2 × 10 mL), MeOH (2 × 10 mL), and DCM (2 × 10 mL). The washed resin **3** was then suspended in THF (15 mL), and 30% hydrogen peroxide (0.5 mL, 5.8 mmol) was added; the mixture was stirred for 30 min at 0 °C, followed by 1 h at room temperature. The mixture was filtered, and the residual resin was washed with CH_2Cl_2 (3 × 10 mL). The filtrate was washed with H_2O (2 × 20 mL), dried over $MgSO_4$, and evaporated to dryness under vacuum to obtain the crude products **4**. Further purification was *via* flash chromatography with EtOAc/*n*-hexane (1/10-1/20 v/v) as the eluent for ^{1}H NMR, ^{13}C NMR, and microanalysis.

3-Phenyl-5-vinyl-1,2,4-oxadiazole (4a)

Oil; ^{1}H NMR: δ = 8.11-8.08 (m, 2H), 7.51-7.46 (m, 3H), 6.80-6.57 (m, 2H), 6.00-5.97 (m, 1H); ^{13}C NMR = 174.5, 168.4, 131.2, 128.8, 128.5, 127.3, 126.8, 120.5; IR (neat): ν_{max} = 3070, 2926, 1646, 1543, 1445, 1360, 956, 910, 770, 705 cm^{-1}; EI-MS: *m/z* (%) = 172 (M^+); Anal. Calcd for $C_{10}H_8N_2O$: C, 69.76; H, 4.68; N, 16.27. Found: C, 69.82; H, 4.77; N, 16.33.

3-(4-Methoxylphenyl)-5-vinyl-1,2,4-oxadiazole (4b)

White solid, mp 50-51 °C; ^{1}H NMR: δ = 7.98 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.76-6.72 (m, 1H), 6.58-5.71 (m, 2H), 3.85 (s, 3H); ^{13}C NMR = 174.2, 168.5, 161.2, 129.1, 128.5, 120.4, 119.0, 114.2, 55.3; IR (KBr): ν_{max} = 3320, 3035, 2925, 1615, 1540, 1478, 1415, 1358, 810, 787, 695 cm^{-1}; EI-MS: *m/z* (%) = 202 (M^+); Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.41; H, 5.07; N, 13.92.

3-(4-Methylphenyl)-5-vinyl-1,2,4-oxadiazole (4c)

Oil; ^{1}H NMR: δ = 8.01 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.78-6.72 (m, 1H), 6.60-5.95 (m, 2H), 2.42 (s, 3H); ^{13}C NMR = 174.1, 168.5, 141.5, 129.5, 128.4, 127.1, 123.8, 120.3, 21.3; IR (neat): ν_{max} = 3000, 2935, 2841, 1614, 1540, 1476, 1422, 1358, 1254, 1108, 840, 787, 690 cm^{-1}; EI-MS: *m/z* (%) = 186 (M^+); Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.99; H, 5.48; N, 15.12.

3-(4-Chlorophenyl)-5-vinyl-1,2,4-oxadiazole (4d)

White solid, mp 58-60 °C; ^{1}H NMR: δ = 8.01 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.78-6.73 (m, 1H), 6.60-6.54 (m, 1H), 6.01-5.98 (m, 1H); ^{13}C NMR = 174.4, 167.5, 137.5, 129.1, 128.7, 128.5, 125.2, 120.2; IR (KBr): ν_{max} = 3060, 2925, 1815, 1545, 1470, 1412, 1093, 982, 838, 790, 500 cm^{-1}; EI-MS: *m/z* (%) = 206 (M^+); Anal. Calcd for $C_{10}H_7ClN_2O$: C, 58.13; H, 3.41; N, 13.56. Found: C, 58.20; H, 3.49; N, 13.63.

3-(2-Chlorophenyl)-5-vinyl-1,2,4-oxadiazole (4e)

Oil; ^{1}H NMR: δ = 7.92-7.90 (m, 1H), 7.55-7.52 (m, 1H), 7.42-7.37 (m, 2H), 6.80-6.78 (m, 1H), 6.63-6.58 (m, 1H), 6.04-6.01 (m, 1H); ^{13}C NMR = 173.8, 167.5, 133.5, 131.5, 131.2, 130.9, 128.8, 126.7, 125.7, 120.2; IR (neat): ν_{max} = 3065, 2925, 2855, 1645, 1542, 1470, 1344, 1055, 955, 767, 735 cm^{-1}; EI-MS: *m/z* (%) = 206 (M^+); Anal. Calcd for $C_{10}H_7ClN_2O$: C, 58.13; H, 3.41; N, 13.56. Found: C, 58.19; H, 3.50; N, 13.63.

3-(3-Bromophenyl)-5-vinyl-1,2,4-oxadiazole (4f)

White solid, mp 62-63 °C; ^{1}H NMR: δ = 8.26-8.24 (m, 1H), 8.06-8.04 (m, 1H), 7.66-7.64 (m, 1H), 7.37-7.34 (m, 1H), 6.81-6.74 (m, 1H), 6.62-6.14 (m, 2H); ^{13}C NMR = 174.6, 167.4, 134.2, 130.5, 130.3, 129.1, 128.6, 125.7, 122.7, 120.2; IR (KBr): ν_{max} = 2925, 1645, 1542, 1470, 1398, 1360, 956, 786, 730, 675 cm^{-1}; EI-MS: *m/z* (%) = 250 (M^+); Anal. Calcd for $C_{10}H_7BrN_2O$: C, 47.84; H, 2.81; N, 11.16. Found: C, 47.90; H, 2.90; N, 11.22.

3-(4-Fluorophenyl)-5-vinyl-1,2,4-oxadiazole (4g)

White solid, mp 42-44 °C; ^{1}H NMR: δ = 8.10-8.04 (m, 2H), 7.21-7.16 (m, 2H), 6.78-6.72 (m, 1H), 6.61-5.97 (m, 2H); ^{13}C NMR = 174.5, 167.7, 164.5 (*J* = 249.4 Hz), 129.3 (*J* = 8.6 Hz), 129.0, 122.6 (*J* = 3.2 Hz), 120.4, 115.5 (*J* = 22.2 Hz); IR (KBr): ν_{max} = 3061, 2926, 1917, 1610, 1472, 1422, 1215, 965, 846, 790, 516 cm^{-1}; EI-MS: *m/z* (%) = 190 (M^+); Anal. Calcd for $C_{10}H_7FN_2O$: C, 63.16; H, 3.71; N, 14.73. Found: C, 63.23; H, 3.80; N, 14.79.

3-Benzyl-5-vinyl-1,2,4-oxadiazole (4h)

Oil; ^{1}H NMR: δ = 7.38-7.36 (m, 2H), 7.27-7.25 (m, 3H), 6.69-6.61 (m, 2H), 5.95-5.87 (m, 1H), 4.20 (s, 2H); ^{13}C NMR = 173.9, 167.8, 132.9, 128.6, 128.4, 127.1, 125.3, 120.2, 31.5; IR (neat): ν_{max} = 3035, 2925, 1567, 1528, 1496, 1031, 980, 945, 730, 696 cm^{-1}; EI-MS: *m/z* (%) = 186 (M^+); Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 71.02; H, 5.51; N, 15.10.

3-(*i*-Propyl)-5-vinyl-1,2,4-oxadiazole (4i)

Oil; ^{1}H NMR: δ = 6.65-6.58 (m, 1H), 6.23-6.08 (m, 1H), 5.87-5.75 (m, 1H), 3.12-3.05 (m, 1H), 1.33 (s, 3H),

1.31 (s, 3H); ^{13}C NMR = 175.1, 167.8, 125.0, 120.2, 26.2, 19.8; IR (neat): ν_{max} = 2978, 2938, 2879, 1645, 1565, 1385, 1370, 1012, 980, 943 cm^{-1}; EI-MS: *m/z* (%) = 138 (M^+); Anal. Calcd for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.28. Found: C, 60.91; H, 7.41; N, 20.35.

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