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Synthesis of 3,3-disubstituted oxindoles by organoselenium-induced radical cyclizations of *N*-arylacrylamides

Abstract: A simple and practical approach to oxindole derivatives *via* organoselenium-induced radical cyclizations of *N*-arylacrylamides has been developed. This method provides a convenient access to a variety of selenium-containing oxindoles in good to excellent yields under relatively mild reaction conditions. As one of its notable features, the radical process allows for the direct formation of a Se-C bond and the construction of a oxindole ring in one reaction.

Keywords: alkenes; cyclization; organoselenium; oxindole; radical cyclization.

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Introduction

The prevalence of the oxindole ring system that represents a key structural component in natural products and pharmaceutical chemistry is well-established [1, 2]. Moreover, functionalized oxindoles have also found wide utility as versatile starting materials for the synthesis of a broad range of heterocyclic compounds. Accordingly, the search for sustainable and more efficient methods for the preparation of oxindoles is of constant interest [3, 4]. Among many different approaches to 3,3′-disubstituted oxindoles, radical-mediated cyclization of *N*-arylacrylamides has received much attention because of the potential application of the products of such reactions in pharmaceutical research. A wide range of function groups including trifluoromethyl [5], azide [6], diphenylphosphine oxide [7], carbonyl [8], nitro [9], substituted alkyl [10], trifluoromethylthio [11], sulfonyl [12], and aryl [13] have been introduced into oxindole frameworks through the radical cyclization strategy. To the best of our knowledge, a similar protocol using organoselenium derivatives as selenyl radicals is not well-documented.

The development of C-Se bond formation has emerged as a significant field of research in organic chemistry on account of organoselenium compounds as synthetic intermediates and discovery of their useful biological activities [14]. Thus, extensive studies have been focused on development of new synthetic strategies to introduce a selenium moiety into chemical structures [15]. The incorporation of selenium atom or selenium-containing functional groups can effectively modify the reactivity and physical, pharmacological, and toxicological properties of parent molecules. The methods used for incorporation of an organoselenium moiety into the organic structures are based on the use of electrophile [16], nucleophile [17, 18], or radical selenium species [19]. However, reports on the direct selenium-carbocyclization of *N*-arylacrylamides *via* a radical pathway to prepare selenium-containing oxindoles are quite rare. Following our research on the synthesis of oxindoles from arylacrylamides [20, 21], herein we wish to report an efficient tandem selenium-carbocyclization of arylacrylamides with *N*-(phenylseleno) phthalimide (N-PSP). The one-pot reactions generated the corresponding selenium-containing oxindoles in good yields.

These studies were initiated by screening for the optimal conditions for the selenium-carbocyclization of *N*-arylacrylamide **1a**. When the reaction was carried out in the presence of $K_2S_2O_8$ (1.5 equiv) and diphenyl diselenide (0.5 equiv) in CH_3CN at 70°C for 2 h, the desired oxindole **2a** was obtained in 35% isolated yield. In the absence of $K_2S_2O_8$, no reaction occurred. Using $(NH_4)_2S_2O_8$ instead of $K_2S_2O_8$ led to the increased yield of 44%. Changing the solvent to THF or DCE afforded only a trace amount of **2a**. The yield was further improved to 67% when the reaction was conducted in DMSO. Screening of the selenium reagents showed that the use of N-PSP gave better results than diphenyl diselenide.

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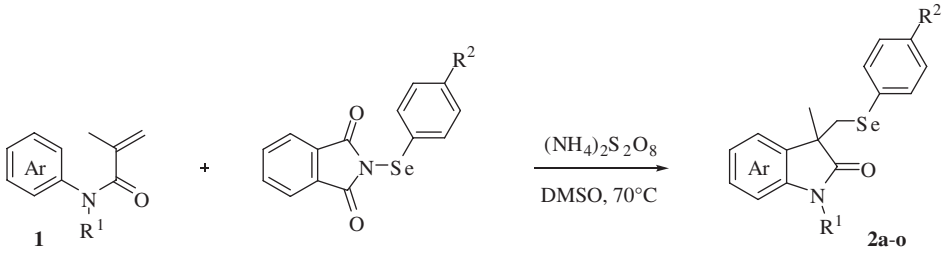

2a: Ar = Ph; R^1 = Me; R^2 = H
2b: Ar = Ph; R^1 = Et; R^2 = H
2c: Ar = Ph; R^1 = ^{i}Pr; R^2 = H
2d: Ar = Ph; R^1 = ^{n}Bu; R^2 = H
2e: Ar = 4-MeC_6H_4; R^1 = Me; R^2 = H
2f: Ar = 4-MeOC_6H_4; R^1 = Me; R^2 = H
2g: Ar = 4-FC_6H_4; R^1 = Me; R^2 = H
2h: Ar = 4-ClC_6H_4; R^1 = Me; R^2 = H
2i: Ar = 4-BrC_6H_4; R^1 = Me; R^2 = H
2j: Ar = 4-$CF_3C_6H_4$; R^1 = Me; R^2 = H
2k: Ar = 2-MeC_6H_4; R^1 = Me; R^2 = H
2l: Ar = 3,5-*di*-MeC_6H_3; R^1 = Me; R^2 = H
2m: Ar = Ph; R^1 = Et; R^2 = Me
2n: Ar = Ph; R^1 = Et; R^2 = OMe
2o: Ar = Ph; R^1 = Et; R^2 = Cl

Scheme 1

With the optimized reaction conditions in hand, we probed the reaction of a variety of *N*-arylacrylamides with N-PSP (Scheme 1). It was found that *N*-alkyl-substituted substrates, such as **1a–d** are reactive. Subsequently, the effect of substituents at the *N*-aryl moiety was examined. Both electron-donating and electron-withdrawing groups located in the *para* or *ortho* position of the aromatic ring were found to be tolerated in this reaction, furnishing the corresponding oxindoles **2e–k** in moderate to good yields. Moreover, 3,5-disubstituted *N*-arylacrylamide **1s** was also transformed into the desired product **2s** in 62% yield. The procedure seems sensitive to steric effects. Generally, substitutents in the *para* position on benzene are well tolerated. By contrast, the presence of *ortho* substituents on benzene reduces the yields. Finally, a variety of substituted N-PSP substrates reacted with *N*-arylacrylamide **1b** smoothly to generate the desired products **2m–o**.

Conclusion

A facile synthesis of 3,3-disubstituted oxindoles is reported. The reaction tolerates a wide range of functional groups.

Experimental

Solvents were purified or dried in a standard manner. Reactions were monitored by TLC on silica gel plates (GF254). ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were measured in $CDCl_3$ with TMS as an internal standard.

General procedure for the synthesis of selenium-containing oxindoles 2a–o

A solution of *N*-arylacrylamide **1** (0.3 mmol), N-PSP (0.36 mmol), and $(NH_4)_2S_2O_8$ (0.45 mmol) in 3.0 mL of DMSO was stirred at 70°C for 2 h under nitrogen atmosphere. After complete consumption of the starting material, as monitored by TLC, the mixture was quenched with 5 mL of water, extracted with EtOAc (3 × 10 mL), dried over $MgSO_4$, and concentrated. The residues were purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1 v/v) to afford product **2**.

1,3-Dimethyl-3-[(phenylseleno)methyl]indolin-2-one (2a): Yield 75%; yellow solid; mp 87–89°C; ^{1}H NMR ($CDCl_3$): δ 7.32–7.35 (m, 4H), 7.21–7.25 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.37 (d, *J* = 10.0 Hz, 1H), 3.32 (d, *J* = 10.0 Hz, 1H), 3.24 (s, 3H), 1.47 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 179.0, 143.6, 134.0, 133.5, 130.9, 129.3, 128.9, 127.3, 126.6, 122.4, 109.1, 49.3, 35.9, 26.3, 23.6; EI-MS: *m/z* 331 (M^+). Anal. Calcd for $C_{17}H_{17}NOSe$: C, 61.82; H, 5.19; N, 4.24. Found: C, 62.12; H, 4.95; N, 4.16.

1-Ethyl-3-methyl-3-[(phenylseleno)methyl]indolin-2-one (2b): Yield 80%; yellow solid; mp 75–76°C; ^{1}H NMR ($CDCl_3$): δ 7.31–7.33 (m, 2H), 7.23–7.26 (m, 1H), 7.09–7.18 (m, 4H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 3.82–3.89 (m, 1H), 3.68–3.75 (m, 1H), 3.41 (d, *J* = 10.0 Hz, 1H), 3.31 (d, *J* = 10.0 Hz, 1H), 1.45 (s, 3H), 1.29 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 178.9, 142.5, 133.4, 132.9, 130.4, 128.9, 128.2, 127.0, 123.2, 122.3, 108.2, 48.9, 36.1, 34.8, 23.7,12.8; EI-MS: *m/z* 345 (M^+). Anal. Calcd for $C_{18}H_{19}NOSe$: C, 62.79; H, 5.56; N, 4.07. Found: C, 63.05; H, 5.13; N, 4.14.

1-Isopropyl-3-methyl-3-[(phenylseleno)methyl]indolin-2-one (2c): Yield 77%; yellow oil; ^{1}H NMR ($CDCl_3$): δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.14–7.26 (m, 4H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 4.72 (m, 1H), 3.43 (d, *J* = 11.2 Hz, 1H), 3.32 (d, *J* = 11.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.47 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 179.0, 142.1, 133.4, 133.1, 130.5, 128.8, 127.9, 127.0, 123.2, 121.9, 109.9, 48.6, 43.9, 36.5, 23.8, 19.6, 19.5; EI-MS: *m/z* 359 (M^+). Anal. Calcd for $C_{19}H_{21}NOSe$: C, 63.68; H, 5.91; N, 3.91. Found: C, 63.79; H, 5.60; N, 3.80.

1-Butyl-3-methyl-3-[(phenylseleno)methyl]indolin-2-one (2d): Yield 78%; yellow oil; ^{1}H NMR ($CDCl_3$): δ 7.34–7.37 (m, 2H), 7.26–7.29 (m, 1H), 7.13–7.22 (m, 4H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 3.78–3.84 (m, 1H), 3.67–3.73 (m, 1H), 3.45 (d, *J* = 10.0 Hz, 1H), 3.34 (d, *J* = 10.0 Hz, 1H), 1.69–1.75 (m, 2H), 1.48 (s, 3H), 1.43–1.47 (m, 2H), 0.98 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 179.2, 142.9, 133.3, 132.9, 130.4, 128.9, 128.2, 127.0, 123.2, 122.2, 108.4, 48.9, 39.9, 36.0, 19.6, 23.9, 20.3, 19.6, 13.8; EI-MS: *m/z* 373 (M^+). Anal. Calcd for $C_{20}H_{23}NOSe$: C, 64.51; H, 6.23; N, 3.76. Found: C, 64.89; H, 5.86; N, 3.65.

1,3,5-Trimethyl-3-[(phenylseleno)methyl]indolin-2-one (2e): Yield 84%; yellow solid; mp 103–105°C; ^{1}H NMR ($CDCl_3$): δ 7.28 (d, *J* = 7.6 Hz, 2H), 7.11–7.17 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.35 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 10.0 Hz, 1H), 3.21 (s, 3H), 2.21 (s, 3H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 179.3, 141.0, 133.6, 132.6, 131.9, 130.2, 128.7, 128.4, 127.0, 124.0, 107.8, 49.2, 36.1, 26.3, 23.7, 21.1; EI-MS: *m/z* 345 (M^+). Anal. Calcd for $C_{18}H_{19}NOSe$: C, 62.79; H, 5.56; N, 4.07. Found: C, 62.65; H, 5.23; N, 4.01.

1,3-Dimethyl-3-[(phenylseleno)methyl]indolin-2-one (2f): Yield 83%; yellow solid; mp 126–127°C; ^{1}H NMR ($CDCl_3$): δ 7.29–7.30 (m, 2H), 7.12–7.17 (m, 3H), 6.74–6.78 (m, 2H), 6.67–6.674 (m, 1H), 3.68 (s, 3H), 3.35 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 10.0 Hz, 1H), 3.20 (s, 3H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 178.9, 155.9, 136.9, 133.9, 133.5, 130.2, 128.8, 127.1, 112.6, 110.4, 108.4, 55.7, 49.6, 36.1, 26.4, 23.7; EI-MS: *m/z* 361 (M^+). Anal. Calcd for $C_{18}H_{19}NO_2Se$: C, 60.00; H, 5.32; N, 3.89. Found: C, 60.32; H, 5.01; N, 3.76.

5-Fluoro-1,3-dimethyl-3-[(phenylseleno)methyl]indolin-2-one (2g): Yield 65%; yellow solid; mp 105–106°C; ^{1}H NMR ($CDCl_3$): δ 7.29–7.33 (m, 2H), 7.17–7.22 (m, 3H), 6.96–6.97 (m, 1H), 6.77–6.83 (m, 2H), 3.36 (d, *J* = 10.0 Hz, 1H), 3.32 (d, *J* = 10.0 Hz, 1H), 3.24 (s, 3H), 1.46 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 178.9, 159.2 (d, *J* = 240.0 Hz), 139.3 (d, *J* = 1.3 Hz), 134.3 (d, *J* = 8.1 Hz), 133.6, 129.8, 128.9, 127.3, 114.4 (d, *J* = 22.4 Hz), 111.4 (d, *J* = 25.1 Hz),108.4 (d, *J* = 8.0 Hz), 48.7, 35.8, 26.4, 23.6; EI-MS: *m/z* 349 (M^+). Anal. Calcd for $C_{17}H_{16}FNOSe$: C, 58.63; H, 4.63; N, 4.02; Found: C. 58.80; H. 4.86; N. 4.15.

5-Chloro-1,3-dimethyl-3-[(phenylseleno)methyl]indolin-2-one (2h): Yield 70%. yellow solid; mp 98–100°C; ^{1}H NMR ($CDCl_3$): δ 7.29–7.31 (m, 3H), 7.21–7.24 (m, 2H), 7.16–7.19 (m, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.33 (d, *J* = 1.6 Hz, 2H), 3.24 (s, 3H), 1.46 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 178.8, 141.9, 134.3, 133.7, 129.7, 128.9, 128.1, 127.9, 127.4, 123.8, 108.9, 49.6, 35.7, 26.4, 23.7; EI-MS: *m/z* 365 (M^+). Anal. Calcd for $C_{17}H_{16}ClNOSe$: C, 55.98; H, 4.42; N, 3.65. Found: C, 55.63; H, 4.17; N, 3.60.

5-Bromo-1,3-dimethyl-3-((phenylseleno)methyl)indolin-2-one (2i): Yield, 65%; yellow solid; mp 113–115°C; ^{1}H NMR ($CDCl_3$): δ 7.37–7.39 (m, 1H), 7.29–7.30 (m, 2H), 7.18–7.23 (m, 3H), 7.12 (d, *J* = 2.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 2H), 3.23 (s, 3H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 178.7, 142.5, 134.6, 133.7, 131.0, 129.6, 128.9, 127.5, 126.5, 115.2, 109.4, 49.6, 36.7, 26.4, 23.7; EI-MS: *m/z* 409 (M^+). Anal. Calcd for $C_{17}H_{16}BrNOSe$: C, 49.90; H, 3.94; N, 3.42; found: C, 50.13; H, 4.10; N, 3.35.

5-(Trifluoromethyl)-1,3-dimethyl-3-[(phenylseleno)methyl]indolin-2-one (2j): Yield 63%; yellow solid; mp 119–121°C; ^{1}H NMR ($CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.32–7.38 (m, 3 H), 7.15–7.23 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.35 (d, *J* = 10.2 Hz, 1H), 3.32 (d, *J* = 10.2 Hz, 1H), 3.22 (s, 3H), 1.48 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 179.7, 146.2, 134.1, 133.6, 129.9, 128.6, 127.4 (q, *J* = 269.6 Hz), 127.1, 125.6 (q, *J* = 4.6 Hz), 124.4 (q, *J* = 31.8 Hz), 120.5 (q, *J* = 3.6 Hz), 107.8, 49.5, 36.3, 26.5, 23.7; EI-MS: *m/z* 399 (M^+). Anal. Calcd for $C_{18}H_{16}F_3NOSe$: C, 54.28; H, 4.05; N, 3.52. Found: C, 53.97; H, 4.30; N, 3.78.

1,3,7-Trimethyl-3-((phenylseleno)methyl)indolin-2-one (2k): Yield, 45%; yellow oil; ^{1}H NMR ($CDCl_3$): δ 7.30–7.37 (m, 3H), 7.15–7.24 (m, 2H), 6.90–6.96 (m, 1H), 6.81 (d, *J* = 6.4 Hz, 2H), 3.36 (d, *J* = 9.2 Hz, 1H), 3.30 (d, *J* = 9.2 Hz, 1H), 3.24 (s, 3H), 2.39 (s, 3H), 1.46 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 180.6, 141.5, 134.0, 133.4, 131.5, 130.1, 129.0, 127.3, 121.9, 121.3, 119.0, 49.4, 36.2, 26.5, 23.8, 23.2; EI-MS: *m/z* 345 (M^+). Anal. Calcd for $C_{18}H_{19}NOSe$: C, 62.79; H, 5.56; N, 4.07. Found: C, 62.54; H, 5.88; N, 4.15.

1,3,4,6-Tetramethyl-3-[(phenylselanyl)methyl]indolin-2-one (2l): Yield 72%; yellow solid; mp 97–99°C; ^{1}H NMR ($CDCl_3$): δ 7.06–7.20 (m, 3H), 6.85–6.97 (m, 2H), 6.72 (s, 1H), 6.41 (s, 1H), 3.34 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 10.0 Hz, 1H), 3.20 (s, 3H), 2.46 (s, 3H), 2.25 (s, 3H), 1.50 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 180.0, 143.4, 137.1, 133.8, 133.6, 130.4, 129.0, 127.1, 126.9, 125.3, 106.9, 49.3, 36.1, 26.4, 123.5, 21.8, 21.6; EI-MS: *m/z* 359 (M^+). Anal. Calcd for $C_{19}H_{21}NOSe$: C, 63.68; H, 5.91; N, 3.91. Found: C, 63.35; H, 6.11; N, 4.02.

3-[(*p*-Tolylseleno)methyl]-1-ethyl-3-methylindolin-2-one (2m): Yield 76%; yellow solid; mp 93–94°C; ^{1}H NMR ($CDCl_3$): δ = 7.22–7.29 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.94–6.99 (m, 3H), 6.90 (d, *J* = 7.5 Hz, 1H), 3.85–3.90 (m, 1H), 3.71–3.76 (m, 1H), 3.40 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 10.0 Hz, 1H), 2.30 (s, 3H), 1.46 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 178.9, 142.5, 137.0, 133.0, 129.6, 128.1, 126.6, 123.2, 122.2, 108.2, 48.9, 36.4, 34.8, 23.7, 21.1, 12.8. 21.6; EI-MS: *m/z* 359 (M^+). Anal. Calcd for $C_{19}H_{21}NOSe$: C, 63.68; H, 5.91; N, 3.91. Found: C, 63.80; H. 5.69; N, 3.75.

3-[(4-Methoxyphenylseleno)methyl]-1-ethyl-3-methylindolin-2-one (2n): Yield 70%; yellow solid; mp 104–106°C; ^{1}H NMR ($CDCl_3$): δ 7.21–7.27 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.67–6.69 (m, 2H), 3.84–3.88 (m, 1H), 3.76 (s, 3H), 3.74–3.75 (m, 1H), 3.32 (d, *J* = 10.8 Hz, 1H), 3.22 (d, *J* = 10.8 Hz, 1H), 1.42 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 178.9, 159.2, 142.5, 135.9, 133.0, 128.1, 123.2, 122.2, 120.4, 114.5, 108.2, 55.3, 49.0, 37.0, 34.8, 23.8, 12.8; EI-MS: *m/z* 375 (M^+). Anal. Calcd for $C_{19}H_{21}NO_2Se$: C, 60.96; H, 5.65; N, 3.74. Found: C, 60.65; H, 5.47; N, 3.66.

3-[(4-Chlorophenylseleno)methyl]-1-ethyl-3-methylindolin-2-one (2o): Yield 64%; yellow solid; mp 107–109°C; ^{1}H NMR ($CDCl_3$): δ 7.21–7.28 (m, 3H), 7.05–7.11 (m, 3H), 6.88–6.95 (m, 2H), 3.84–3.89 (m, 1H), 3.71–3.73 (m, 1H), 3.38 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 10.0 Hz, 1H), 1.45 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 178.7, 142.5, 134.8, 133.3, 132.3, 128.9, 128.4, 128.3, 123.1, 122.3, 108.3, 48.9, 36.4, 34.8, 23.8, 12.8; EI-MS: *m/z* 379 (M^+). Anal. Calcd for $C_{18}H_{18}ClNOSe$: C, 57.08; H, 4.79; N, 3.70. Found: C, 57.30; H, 4.55; N, 3.79.

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