

A Facile CAN-Mediated Synthesis of Selenocyanates from Arylalkenes and Heteroarenes

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Keywords: Aryl alkenes / Cerium / Heteroarenes / Selenium

Selenocyanation of styrenes and indoles mediated by cerium(IV) ammonium nitrate (CAN) afforded the corresponding selenocyanates in moderate to good yields.

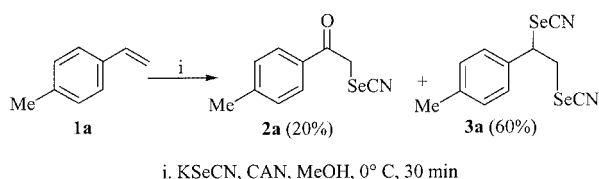
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Introduction

Carbon–carbon and carbon–heteroatom bond-forming reactions mediated by cerium(IV) ammonium nitrate have attracted recent attention. Investigations in our laboratory and elsewhere have expanded the scope of these reactions.^[1–5] Recently, we have reported the synthesis in high yield of bis(thiocyanates) and oxo thiocyanates from arylalkenes,^[6,7] and a very efficient thiocyanation of electron-rich aromatic and heteroaromatic systems.^[8] Impressed by the efficiency of the reaction, and in view of the importance of selenocyanates,^[9] we thought it logical to explore the possibility of CAN-mediated selenocyanation reactions. The preliminary results of our efforts in this direction involving arylalkenes and electron-rich aromatic systems are reported here. It is noteworthy that, although the alkoxyselenocyanation^[10,11] and haloselenocyanation^[11,12] of alkenes have been reported, the synthesis of bis(selenocyanates)^[13] and oxo selenocyanates^[14] has received very little attention.

Results and Discussion

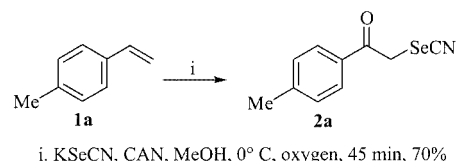
In the initial experiment, a solution of 4-methylstyrene and potassium selenocyanate in methanol afforded the products **2a**^[14,15] and **3a** on treatment with a methanolic solution of CAN (Scheme 1).



Scheme 1

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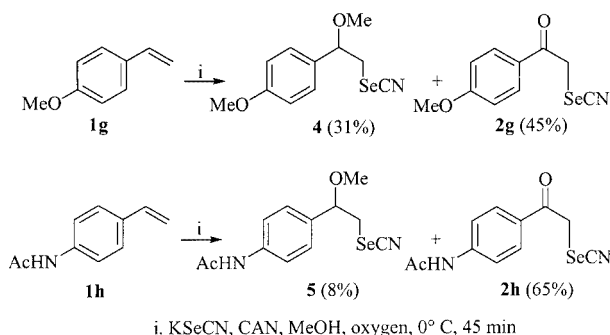
In the belief that the oxo selenocyanate was formed by the trapping of oxygen by the initially formed benzylic radical, followed by further transformation of the peroxy intermediate, the above experiment was performed under oxygen to afford the phenacyl selenocyanate exclusively^[14] (Scheme 2). Similar results were obtained with other styrenes, and these are shown in Table 1. 4-Methoxystyrene and 4-acetamidostyrene underwent the reaction to afford products as shown in Scheme 3.



Scheme 2

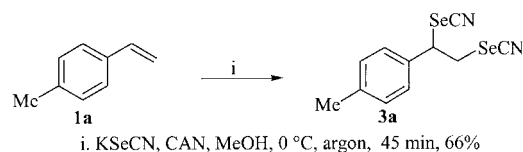
Table 1. Synthesis of oxo selenocyanates

Entry	Substrate	Product	Yield (%)
1	styrene (1b)	2b ^{[14][15]}	71
2	4-chlorostyrene (1c)	2c	68
3	2-chlorostyrene (1d)	2d	54
4	1-vinylnaphthalene (1e)	2e	55
5	2-vinylnaphthalene (1f)	2f	54



Scheme 3

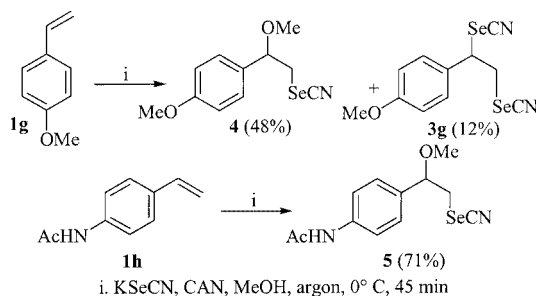
In view of the above results, it was reasonable to assume that experimentation under an oxygen-free gas would afford bis(selenocyanates) only. In the event, when a deoxygenated solution of **1a** and potassium selenocyanate in methanol was exposed to CAN solution under argon, the bis(selenocyanate) **3a** was formed exclusively (Scheme 4). The reaction was also found to be general in this case, and the results are shown in Table 2. With 4-methoxystyrene and 4-acetamidostyrene, the reaction proceeded as shown in Scheme 5.



Scheme 4

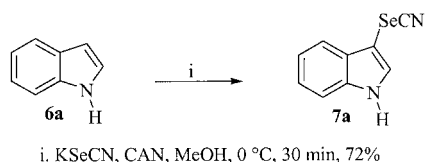
Table 2. Synthesis of bis(selenocyanates)

Entry	Substrate	Product	Yield (%)
1	styrene (1b)	3b ^[11,12]	67
2	4-chlorostyrene (1c)	3c	52
3	2-chlorostyrene (1d)	3d	46
4	1-vinylnaphthalene (1e)	3e	65
5	2-vinylnaphthalene (1f)	3f	55



Scheme 5

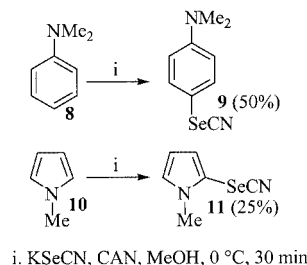
As a logical extension of this work, we investigated treatment of indole with potassium selenocyanate and CAN in methanol at 0 °C, and the 3-(selenocyanato)indole^[16] was obtained as the only isolable product (Scheme 6). Similar results were also obtained with other indoles (Table 3). CAN-mediated selenocyanation was observed with *N,N*-dimethylaniline and 1-methylpyrrole also, albeit in lower yields (Scheme 7).^[16d,17]



Scheme 6

Table 3. Selenocyanation of indoles

Entry	Substrate	Product	Yield (%)
1	2-methylindole (6b)	7b ^[16b,16c]	80
2	1-methylindole (6c)	7c ^[16b,16c]	70
3	2-phenylindole (6d)	7d	73



Scheme 7

Conclusion

In conclusion, we have devised an efficient method for the synthesis of bis(selenocyanates) and oxo selenocyanates. In addition, we have found that CAN-mediated selenocyanation of electron-rich systems such as indoles and dimethylaniline occurs efficiently.

Experimental Section

General: Melting points: MELTEMP II apparatus. IR: Nicolet Impact FT-IR and Bomem MB Series FT-IR. NMR: Bruker 300 MHz FT-NMR [¹H NMR (300 MHz; CDCl₃/CCl₄, 3:1, v/v); TMS as internal standard]. ¹³C NMR (75 MHz; CDCl₃/CCl₄, 3:1, v/v); CDCl₃ as internal standard. Elemental analyses: Perkin–Elmer 2400 CHNS Analyzer.

Typical Experimental Procedure and Data for 2a: A methanolic (10 mL) solution of CAN (1.26 g, 2.3 mmol) was added dropwise, at 0 °C under oxygen and with stirring, to a methanolic (5 mL) solution of 4-methylstyrene (118 mg, 1.0 mmol) and potassium selenocyanate (216 mg, 1.5 mmol). Stirring was continued for 45 min. On completion of the reaction, the mixture was extracted with dichloromethane, and the extract was dried and concentrated. The crude residue, after purification by silica gel column chromatography with hexane/ethyl acetate mixture (95:5) as eluent, afforded **2a** (166 mg, 70%) as a colorless solid.

Compound 2a: Recrystallised from hexane/dichloromethane, m.p. 131–133 °C. IR (KBr): $\tilde{\nu}_{\max}$ = 2987, 2150, 1657, 1607, 1569, 1382, 1294, 1176, 1003, 801, 741 cm^{−1}. ¹H NMR: δ = 7.84 (d, *J* = 8.1 Hz, 2 H, ArH), 7.31 (d, *J* = 8.0 Hz, 2 H, ArH), 4.92 (s, 2 H, CH₂SeCN), 2.47 (s, 3 H, CH₃) ppm. ¹³C NMR: δ = 22.0, 38.7, 101.8, 128.9, 129.9, 131.5, 146.1, 192.6 ppm. C₁₀H₉NOSe (238.14): calcd. C 50.43, H 3.81, N 5.88; found C 50.92, H 3.66, N 5.86.

Compound 2c: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 141–143 °C. IR (KBr): $\tilde{\nu}_{\max}$ = 2921, 2155, 1657, 1595, 1483, 1297, 1185, 1091, 998, 817 cm^{−1}. ¹H NMR: δ = 7.91 (d, ArH, *J* = 8.4 Hz, 2 H), 7.51 (d, ArH, *J* = 8.4 Hz, 2 H), 4.89 (s, 2 H, CH₂SeCN) ppm. ¹³C NMR: δ = 38.1, 101.4, 129.7, 130.2,

132.3, 141.8, 192.0 ppm. $C_9H_6ClNOSe$ (258.56): calcd. C 41.81, H 2.34, N 5.42; found C 41.88, H 2.61, N 5.39.

Compound 2d: Colorless liquid. IR (neat): $\tilde{\nu}_{max}$ = 2996, 2934, 2155, 1670, 1589, 1564, 1477, 1427, 1384, 1290, 1178, 1060, 991, 755 cm^{-1} . 1H NMR: δ = 7.78 (d, 2 H, ArH, J = 7.7 Hz, 2 H), 7.56–7.51 (m, 2 H, ArH), 7.44–7.40 (m, 1 H, ArH), 4.91 (s, 2 H, CH_2SeCN) ppm. ^{13}C NMR: δ = 40.2, 101.3, 127.3, 127.6, 130.8, 131.0, 133.9, 138.8, 194.1 ppm.

Compound 2e: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 110–112 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3046, 2921, 2149, 1640, 1564, 1508, 1377, 1290, 1253, 1209, 1166, 948, 799, 761 cm^{-1} . 1H NMR: δ = 8.85 (d, J = 8.5 Hz, 1 H, ArH), 8.11 (d, J = 8.2 Hz, 1 H, ArH), 8.05 (d, J = 7.2 Hz, 1 H, ArH), 7.90 (d, J = 8.0 Hz, 1 H, ArH), 7.68–7.51 (m, 3 H, ArH), 5.08 (s, 2 H, CH_2SeCN) ppm. ^{13}C NMR: δ = 40.7, 101.5, 124.1, 125.7, 127.0, 128.6, 129.2, 130.3, 130.5, 130.7, 134.0, 135.4, 195.2 ppm. $C_{13}H_9NOSe$ (274.18): calcd. C 56.95, H 3.31, N 5.11; found C 56.72, H 3.19, N 4.90.

Compound 2f: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 129–131 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2996, 2946, 2149, 1651, 1626, 1465, 1371, 1297, 1163, 1122, 998, 848, 811, 736 cm^{-1} . 1H NMR: δ = 8.47 (s, 1 H, ArH), 7.99–7.88 (m, 4 H, ArH), 7.69–7.58 (m, 2 H, ArH), 5.07 (s, 2 H, CH_2SeCN) ppm. ^{13}C NMR: δ = 38.4, 101.5, 123.3, 127.3, 127.9, 129.1, 129.4, 129.6, 131.1, 132.2, 136.1, 192.7 ppm. $C_{13}H_9NOSe$ (274.18): calcd. C 56.95, H 3.31, N 5.11; found C 57.17, H 3.46, N 5.09.

Compound 4: Colorless, viscous liquid. IR (neat): $\tilde{\nu}_{max}$ = 3002, 2934, 2834, 2149, 1608, 1508, 1458, 1247, 1172, 1097, 1023, 960, 823, 637, 562 cm^{-1} . 1H NMR: δ = 7.22 (d, J = 8.6 Hz, 2 H, ArH), 6.89 (d, J = 8.6 Hz, 2 H, ArH), 4.40 (dd, J = 4.0, J = 9.6 Hz, 2 H, $CHOCH_3$), 3.80 (s, 3 H, OCH_3), 3.43–3.26 (m, 2 H, CH_2SeCN), 3.22 (s, 3 H, OCH_3) ppm. ^{13}C NMR: δ = 36.0, 55.0, 56.7, 81.4, 102.0, 114.1, 127.6, 130.5, 159.8 ppm.

Compound 2g: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 115–117 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2966, 2940, 2846, 2149, 1645, 1595, 1570, 1421, 1297, 1259, 1172, 1023, 991, 817 cm^{-1} . 1H NMR: δ = 7.91 (d, J = 8.8 Hz, 2 H, ArH), 6.96 (d, J = 8.8 Hz, 2 H, ArH), 4.90 (s, 2 H, CH_2SeCN), 3.90 (s, 3 H, OCH_3) ppm. ^{13}C NMR: δ = 38.4, 55.5, 101.7, 114.2, 126.8, 131.0, 164.7, 191.1 ppm. $C_{10}H_9NO_2Se$ (254.14): calcd. C 47.26, H 3.57, N 5.51; found C 47.28, H 3.55, N 5.34.

Compound 5: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 108–110 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3295, 3257, 2940, 2834, 2149, 1664, 1602, 1558, 1408, 1321, 1265, 1085, 948, 830, 749, 730, 606 cm^{-1} . 1H NMR: δ = 8.73 (s, 1 H, NH), 7.54–7.23 (m, 4 H, ArH), 4.42 (dd, J = 4.0, J = 9.2 Hz, 1 H, $CHOCH_3$), 3.41–3.28 (m, 2 H, CH_2SeCN), 3.25 (s, 3 H, OCH_3), 2.17 (s, 3 H, $NHCOCH_3$). ^{13}C NMR: δ = 24.5, 36.0, 57.1, 81.6, 102.1, 120.2, 127.2, 134.4, 138.5, 168.2 ppm.

Compound 2h: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 184–186 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3326, 3289, 2940, 2156, 1689, 1639, 1595, 1521, 1440, 1378, 1322, 1291, 1160, 1004, 811 cm^{-1} . 1H NMR: δ = 9.94 (s, 1 H, NH), 7.90 (d, J = 8.6 Hz, 2 H, ArH), 7.76 (d, J = 8.6 Hz, 2 H, ArH), 4.93 (s, 2 H, CH_2SeCN), 2.16 (s, 3 H, $NHCOCH_3$) ppm. ^{13}C NMR: δ = 24.3, 37.9, 102.0, 118.7, 128.3, 130.0, 145.1, 169.2, 191.6 ppm. $C_{11}H_{10}N_2O_2Se$ (281.17): calcd. C 46.99, H 3.58, N 9.96; found C 47.11, H 3.59, N 9.75.

Typical Experimental Procedure and Data for 3a: A methanolic (10 mL) solution of CAN (1.26 g, 2.3 mmol) was added dropwise, at 0

°C under argon and with stirring, to a methanolic (5 mL) solution of 4-methylstyrene (118 mg, 1.0 mmol) and potassium selenocyanate (288 mg, 2.0 mmol). Stirring was continued for 45 min. On completion of the reaction, the mixture was extracted with dichloromethane, and the extract was dried and concentrated. The crude residue, after purification by silica gel column chromatography with hexane/ethyl acetate mixture (90:10) as eluent, afforded **3a** (216 mg, 66%) as a colorless solid.

Compound 3a: Recrystallized from dichloromethane/hexane, m.p. 138–140 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3009, 2921, 2153, 1613, 1533, 1431, 1169, 1148, 899, 831, 724, 589, 528 cm^{-1} . 1H NMR: δ = 7.28–7.24 (m, 4 H, ArH), 4.97 (dd, J = 8.0 Hz and 11.7 Hz, 1 H, $CHSeCN$), 4.05–3.81 (m, 2 H, CH_2SeCN), 2.38 (s, 3 H, CH_3) ppm. ^{13}C NMR: δ = 21.3, 33.8, 48.0, 99.5, 100.8, 127.4, 130.5, 131.5, 140.5 ppm. $C_{11}H_{10}N_2Se_2$ (328.13): calcd. C 40.26, H 3.07, N 8.54; found C 40.77, H 3.15, N 8.05.

Compound 3c: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 136–138 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2921, 2143, 1589, 1489, 1421, 1222, 1141, 1091, 1010, 886, 823, 774, 718, 662, 574 cm^{-1} . 1H NMR: δ = 7.43 (d, J = 8.4 Hz, 2 H, ArH), 7.33 (d, J = 8.4 Hz, 2 H, ArH), 4.92 (dd, J = 5.0, J = 11.6 Hz, 2 H, $CHSeCN$), 4.06–3.74 (m, 2 H, CH_2SeCN) ppm. ^{13}C NMR: δ = 33.4, 47.2, 99.1, 100.1, 128.8, 130.1, 133.6, 136.4 ppm. $C_{10}H_7ClN_2Se_2$ (348.55): calcd. C 34.46, H 2.02, N 8.04; found C 34.80, H 2.11, N 7.83.

Compound 3d: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 96–98 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3071, 3021, 2143, 1589, 1570, 1471, 1440, 1340, 1278, 1228, 1191, 1147, 1122, 1029, 892, 755, 730 cm^{-1} . 1H NMR: δ = 7.51–7.40 (m, 4 H, ArH), 5.30 (dd, J = 6.5, J = 10.3 Hz, 2 H, $CHSeCN$), 4.05–3.98 (m, 2 H, CH_2SeCN) ppm. ^{13}C NMR: δ = 32.7, 44.5, 99.3, 100.0, 127.6, 128.0, 130.9, 131.0, 133.2, 134.2 ppm. $C_{10}H_7ClN_2Se_2$ (348.55): calcd. C 34.46, H 2.02, N 8.04; found C 34.64, H 1.95, N 7.77.

Compound 3e: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 108–110 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3058, 3008, 2149, 1602, 1539, 1508, 1434, 1396, 1209, 1128, 886, 805, 774 cm^{-1} . 1H NMR: δ = 8.08 (d, J = 8.1 Hz, 1 H, ArH), 7.93 (d, J = 7.6 Hz, 2 H, ArH), 7.70–7.65 (m, 1 H, ArH), 7.60 (d, J = 7.6 Hz, 1 H, ArH), 7.56–7.49 (m, 2 H, ArH), 5.84–5.79 (m, 1 H, $CHSeCN$), 4.21–4.18 (m, 2 H, CH_2SeCN) ppm. ^{13}C NMR: δ = 33.6, 48.4, 99.9, 100.9, 121.8, 124.5, 125.3, 126.8, 127.7, 129.6, 130.1, 130.4, 131.0, 134.2 ppm. $C_{14}H_{10}N_2Se_2$ (364.16): calcd. C 46.17, H 2.77, N 7.69; found C 46.67, H 2.46, N 7.66.

Compound 3f: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 141–143 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3064, 3008, 2149, 1620, 1595, 1502, 1427, 1365, 1265, 1147, 1128, 1054, 954, 892, 871, 742 cm^{-1} . 1H NMR: δ = 7.93–7.85 (m, 4 H, ArH), 7.57–7.42 (m, 3 H, ArH), 5.14 (dd, J = 4.8, J = 11.6 Hz, 2 H, $CHSeCN$), 4.16–3.93 (m, 2 H, CH_2SeCN) ppm. ^{13}C NMR: δ = 33.7, 48.4, 99.4, 100.6, 123.9, 127.3, 127.4, 127.6, 128.3, 130.1, 132.0, 133.2, 133.8 ppm. $C_{14}H_{10}N_2Se_2$ (364.16): calcd. C 46.17, H 2.77, N 7.69; found C 46.17, H 2.67, N 7.40.

Compound 3g: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 115–117 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3008, 2959, 2840, 2143, 1614, 1514, 1465, 1253, 1178, 1135, 1023, 892, 830, 724, 705 cm^{-1} . 1H NMR: δ = 7.30 (d, J = 8.5 Hz, 2 H, ArH), 6.93 (d, J = 8.5 Hz, 2 H, ArH), 5.00 (dd, J = 4.8, J = 11.7 Hz, 2 H, $CHSeCN$), 4.05–3.85 (m, 2 H, CH_2SeCN), 3.83 (s, 3 H, OCH_3) ppm. ^{13}C NMR: δ = 34.0, 48.1, 55.3, 99.5, 100.9, 115.1, 126.1, 128.9, 160.9 ppm.

Compound 7d: Colorless solid, recrystallized from hexane/dichloromethane, m.p. 170–172 °C. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3176, 3145, 3064, 2149, 1483, 1446, 1402, 1328, 1303, 1228, 1023, 742, 687 cm^{-1} . ^1H NMR: δ = 11.11 (s, 1 H, NH), 7.73–7.71 (m, 3 H, ArH), 7.50–7.42 (m, 4 H, ArH), 7.30–7.23 (m, 2 H, ArH) ppm. ^{13}C NMR: δ = 86.2, 101.9, 111.9, 119.4, 121.3, 123.2, 128.5, 128.9, 129.2, 130.6, 131.0, 136.3, 143 ppm. $\text{C}_{15}\text{H}_{10}\text{N}_2\text{Se}$ (297.21): calcd. C 60.62, H 3.39, N 9.43; found C 61.19, H 3.37, N 9.40.

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