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SYNTHESIS OF 1,3-SELENAZETIDINES AND 4*H*-1,3,5-OXADIAZINES USING ACYL ISOSELENOCYANATES

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Abstract – Reactions of acyl isoselenocyanates with carbodiimides afforded 1,3-selenazetidines as major product and 4-selnoxo-3,4-dihydro-2*H*-1,3,5-oxadiazine as minor product, respectively.

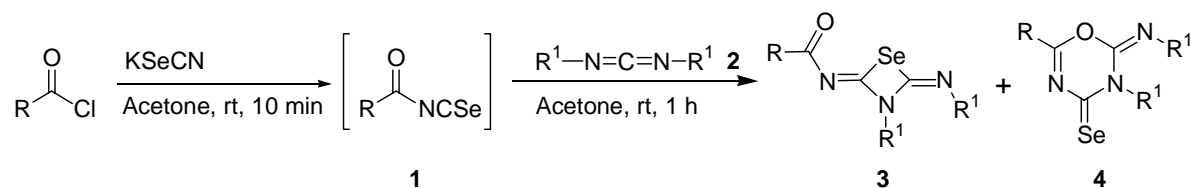
INTRODUCTION

Syntheses of selenium-nitrogen containing five-membered ring and six-membered ring heterocycles such as 1,3-selenazoles and 1,3-selenazines have been extensively studied, not only because of strong interest in these compounds as synthetic tools¹ but also as a result of their biological activities.² In contrast, there are little reports of selenium containing four-membered ring heterocycles.³ Many reports on the synthesis of the heterocycles use selenoamide or selenourea as the starting material.⁴ In contrast, the chemistry of heterocycles using isoselenocyanates has been limited. Recently, heterocycles such as 1,3-selenazolidines and perhydro-1,3-selenazines, 2-phenyl-6*H*-[5,1,3]benzoselenadiazocines, 1*H*-5-selena-1,3,6-triazaaceanthrylene, pyrido[1,2-*a*]pyrazines and 1,3-selenazoles have been synthesized by reactions using alkyl isoselenocyanates.⁵ Herein, we describe the preparation of four-membered ring 1,3-selenazetidines using acyl isoselenocyanates.

RESULTS AND DISCUSSION

Acyl isoselenocyanates (**1**) were prepared as intermediate by reactions of acyl chloride with KSeCN.⁶ Reactions of five kinds of the acyl isoselenocyanates (**1**) with three kinds of carbodiimides (**2**) were carried out at room temperature for 1 h. The reactions afforded 2-acylimino-4-imino-1,3-selenazetidines

(**3**) as major products, formal [2+2] cycloadducts, and 4-imino-2*H*-1,3,5-oxadiazine-2-selones (**4**) as minor ones, formal [4+2] cycloadducts, respectively (Scheme 1).⁷



SCHEME 1

Table 1. Preparation of 2-acylimino-4-imino-1,3-selenazetidines (**3**) and 4-imino-4-seleoxo-3,4-dihydro-2*H*-1,3,5-oxadiazines (**4**)

Entry	R	R ¹	Yield (%)	
			3	4
1	<i>t</i> -(CH ₃) ₃ C	(CH ₃) ₂ CH	78 (3a)	0 (4a)
2	<i>p</i> -ClC ₆ H ₄	(CH ₃) ₂ CH	38 (3b)	trace (4b)
3	<i>p</i> -CH ₃ OC ₆ H ₄	(CH ₃) ₂ CH	81 (3c)	11 (4c)
4	C ₆ H ₅	(CH ₃) ₂ CH	62 (3d)	9 (4d)
5	<i>p</i> -CH ₃ C ₆ H ₄	(CH ₃) ₂ CH	86 (3e)	10 (4e)
6	<i>p</i> -CH ₃ C ₆ H ₄	Cyclo-C ₆ H ₁₁	72 (3f)	8 (4f)
7	<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	0	0

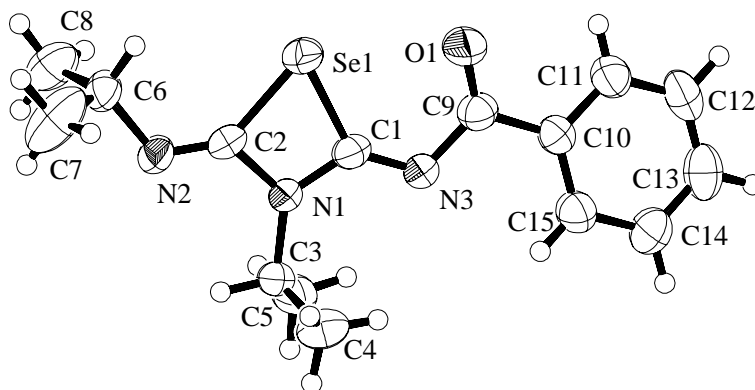


Figure 1. X-Ray crystal structure of 3-isopropyl-2-isopropylimino-4-*p*-toluoylimino-1,3-selenazetidone (**3e**) (ORTEP drawing).

Various kinds of reactions were carried out (Table 1). Reactions with diphenyl carbodiimide did not proceed (Table 1, entry 7). The structure of **3e** was elucidated by studies of IR, MS, ¹H-, ¹³C-, ⁷⁷Se-NMR, COSY, HMQC and HMBC data and X-Ray analysis. The structures of products (**3a-3f**) were determined by comparing the spectral data with those of **3e**. The X-Ray crystal structure of 3-isopropyl-2-isopropylimino-4-*p*-toluoylimino-1,3-selenazetidone (**3e**) was studied.⁸ An ORTEP drawing, depicted in Figure 1, shows the crystal structure of the **3e**. The bond angle of the selenium atom C1-Se1-C2 in **3e** was 67.2(17)°, consistent with the previously reported value of 2,4-diimino-1,3-selenazetidone and selenetane.³ The selenazetidone ring is planar and both imino groups

of **3e** are (*Z*)-configured. Furthermore, the arrangement of Se1, C1, N1, C2, N2, N3 and C3 atoms is co-planar (dihedral angle: C(2)-Se(1)-C(1)-N(1) $-1.1(2)^\circ$, N(3)-C(1)-N(1)-C(2) $-177.5(4)^\circ$, Se(1)-C(1)-N(1)-C(3) $-177.0(3)^\circ$, C(1)-N(1)-C(2)-N(2) $178.0(4)^\circ$ and C(3)-N(1)-C(2)-Se(1) $177.1(3)^\circ$). There are only two additional examples of the synthesis of 1,3-selenazetidine in the literature.^{3a,9} One example is synthesis of 4-benzimino-3-phenyl-1,3-selenazetidine-2-thione by reaction of *N,N*-disubstituted selenourea, PhNHC(:Se)NHC(O)Ph with thiophosgene in acetone.¹⁰ Another example is preparation of 2,4-diimino-1,3-selenazetidines by the reactions of alkyl isoselenocyanates with carbodiimides.^{3a} Latter reactions were carried out at reflux for 12 hours in hexane,^{3a} while the present reaction could proceed at room temperature for 1 hour in acetone under milder conditions to afford 2-acylimino-4-imino-1,3-selenazetidines (**3**) in high yields.

Thus, four-membered ring heterocycles have been prepared using isoselenocyanates. The use of the isoselenocyanates is one of the most efficient methods for the synthesis of heterocyclic compounds.

EXPERIMENTAL

General

The ⁷⁷Se chemical shifts were expressed in ppm deshielded with respect to neat Me₂Se in CDCl₃ or DMSO. ¹J(⁷⁷Se-¹H) values are observed as ⁷⁷Se satellites of the ¹H NMR spectra.

Synthesis of 3-isopropyl-2-isopropylimino-4-pivaloylimino-1,3-selenazetidine (3a). Potassium selenocyanate (0.28 g, 2.0 mmol) in acetone solution (5 mL) was dropwise added to the pivaloyl chloride (0.12 mL, 1.0 mmol) in acetone (5 mL). The reaction mixture was stirred for 10 min under argon atmosphere. To the reaction mixture, *N,N*-isopropylcarbodiimide (0.15 mL, 1.0 mmol) was added then stirred at room temperature for 1 h. The mixture was extracted with diethyl ether and washed with water, and the organic layer was separated, dried over Na₂SO₄, and evaporated. The residue was subjected to flash column chromatography on silica gel using hexane:Et₂O (1:50) as the eluent, giving **3a** (0.25 g, 78%) as yellow liquid.

3-Isopropyl-2-isopropylimino-4-pivaloylimino-1,3-selenazetidine (3a)

IR (neat): 1678, 1587 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.21 (d, 6H, *J* = 6.3 Hz), 1.22 (s, 9H), 1.48 (d, 6H, *J* = 6.9 Hz), 3.09 (7th, 1H, *J* = 6.3 Hz), 4.29 (7th, 1H, *J* = 6.9 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 20.2, 24.1, 26.7, 41.8, 49.0, 57.8, 139.5, 156.9, 190.2; ⁷⁷Se NMR (75 MHz, CDCl₃): δ 752.7; MS (EI): *m/z* = 317 [M]⁺; *Anal.* Calcd for C₁₃H₂₃N₃OSe: C, 49.36; H, 7.33; N, 13.28. Found: C, 49.45; H, 7.14; N, 13.31.

2-*p*-Chlorobenzoylimino-3-isopropyl-4-isopropylimino-1,3-selenazetidine (3b)

mp 72.0-74.7 °C; IR (KBr): 1652, 1579, 1284 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.23 (d, 6H, $J = 6.3$ Hz), 1.55 (d, 6H, $J = 6.9$ Hz), 3.14 (7th, 1H, $J = 6.3$ Hz), 4.43 (7th, 1H, $J = 6.9$ Hz), 7.43 (d, 2H, $J = 8.6$ Hz), 8.20 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 20.4, 24.1, 49.5, 57.9, 128.6, 131.3, 133.7, 138.7, 139.5, 159.6, 174.7; ^{77}Se NMR (75 MHz, CDCl_3): δ 756.2; MS (EI): $m/z = 371$ $[\text{M}]^+$; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{OClSe}$: C, 48.60; H, 4.89; N, 11.33. Found: C, 48.60; H, 5.04; N, 11.18.

4-*p*-Anisoylimino-3-isopropyl-2-isopropylimino-1,3-selenazetidine (3c)

mp 72.1 -74.7 °C; IR (KBr): 1655, 1584, 1287 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.23 (d, 6H, $J = 6.3$ Hz), 1.56 (d, 6H, $J = 6.3$ Hz), 3.13 (7th, 1H, $J = 6.3$ Hz), 3.86 (s, 3H), 4.41 (7th, 1H, $J = 6.9$ Hz), 6.95 (d, 2H, $J = 9.2$ Hz), 8.23 (d, 2H, $J = 9.2$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 20.3, 24.1, 49.3, 55.4, 57.9, 113.6, 128.0, 132.1, 139.6, 158.0, 163.8, 174.9; ^{77}Se NMR (75 MHz, CDCl_3): δ 751.8; MS (EI): $m/z = 367$ $[\text{M}]^+$; Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2\text{Se}$: C, 52.46; H, 5.78; N, 11.47. Found: C, 52.35; H, 5.79; N, 11.25.

3-Isopropyl-2-isopropylimino-6-*p*-methoxyphenyl-4-selenoxo-3,4-dihydro-2*H*-1,3,5-oxadiazine (4c)

mp 104.9-106.8 °C; IR (KBr): 1706, 1596, 1511, 1248 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.23 (d, 6H, $J = 6.3$ Hz), 1.58 (d, 6H, $J = 6.3$ Hz), 3.90 (s, 3H), 4.10 (7th, 1H, $J = 6.3$ Hz), 6.02 (7th, 1H, $J = 6.9$ Hz), 6.98 (d, 2H, $J = 8.6$ Hz), 8.17 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 18.3, 23.6, 46.6, 55.6, 58.5, 114.6, 119.7, 131.4, 131.9, 151.1, 165.0, 189.8; MS (EI): $m/z = 367$ $[\text{M}]^+$; Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2\text{Se}$: C, 52.46; H, 5.78; N, 11.47. Found: C, 52.43; H, 5.53; N, 11.51.

2-Benzoylimino-3-isopropyl-4-isopropylimino-1,3-selenazetidine (3d)

mp 70.0 -71.0 °C; IR (KBr): 1655, 1578, 1282 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.24 (d, 6H, $J = 6.3$ Hz), 1.56 (d, 6H, $J = 6.9$ Hz), 3.14 (7th, 1H, $J = 6.3$ Hz), 4.43 (7th, 1H, $J = 6.9$ Hz), 7.43-7.50 (m, 2H), 7.55-7.60 (m, 1H), 8.24-8.29 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 20.4, 24.1, 49.4, 57.9, 128.3, 129.9, 133.2, 135.2, 139.1, 158.9, 175.7; ^{77}Se NMR (75 MHz, CDCl_3): δ 754.4; MS (EI): $m/z = 337$ $[\text{M}]^+$; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{OSe}$: C, 53.57; H, 5.69; N, 12.50. Found: C, 53.48; H, 5.84; N, 12.40.

3-Isopropyl-2-isopropylimino-4-selenoxo-6-phenyl-3,4-dihydro-2*H*-1,3,5-oxadiazine (4d)

mp 112.0-133.5 °C; IR (KBr): 1702, 1602, 1334 cm^{-1} ; ^1H NMR (500 MHz, Acetone- d_6): δ 1.12 (d, 6H, $J = 6.3$ Hz), 1.45 (d, 6H, $J = 6.9$ Hz), 4.10 (7th, 1H, $J = 6.3$ Hz), 5.92 (7th, 1H, $J = 6.9$ Hz), 7.47 (t, 2H, $J = 8.0$ Hz), 7.67 (t, 1H, $J = 8.0$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, Acetone- d_6): δ 18.4, 24.0, 47.2, 58.9, 129.4, 130.0, 130.1, 131.2, 135.3, 151.6, 190.4; MS (EI): $m/z = 337$ $[\text{M}]^+$; HRMS: $m/z = 337.0693$, calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{OSe}$, found 337.0678.

3-Isopropyl-2-isopropylimino-4-*p*-tolylimino-1,3-selenazetidine (3e)

A crystal data of **3e**. $\text{C}_{15}\text{H}_{19}\text{N}_3\text{OSe}$, FW = 336.29, Crystal system Monoclinic, Space group $P2_1/n$, $a = 11.223(7)$ Å, $b = 11.479(7)$ Å, $c = 12.564(8)$ Å, $\beta = 94.647(8)^\circ$, $Z = 4$, $\rho_{\text{calcd}} = 1.385$ g/cm^3 , Limiting

indices -14 *h* 14, -13 *k* 14, -10 *l* 16, Reflections collected 13051, Independent reflections 3683, Goodness-of-fit on F^2 1.202, Final *R* indices [$I > 2\sigma(I)$] $RI = 0.0768$, $wR2 = 0.1057$, *R* indices (all data) $RI = 0.1260$, $wR2 = 0.1173$. Selected bond lengths [Å] and angles [°] for **3e**. Se(1)-C(1) 1.931(4), Se(1)-C(2) 1.976(4), C(1)-N(3) 1.278(5), C(1)-N(1) 1.356(5), N(1)-C(2) 1.406(5), N(1)-C(3) 1.473(5), C(2)-N(2) 1.237(5), C(3)-C(4) 1.509(5), C(3)-C(5) 1.512(5), N(2)-C(6) 1.476(5), C(6)-C(8) 1.495(6), C(6)-C(7) 1.501(6), N(3)-C(9) 1.407(5), C(9)-O(1) 1.216(4), C(9)-C(10) 1.494(6), C(10)-C(15) 1.375(5), C(10)-C(11) 1.387(5), C(11)-C(12) 1.370(6), C(12)-C(13) 1.367(6), C(13)-C(14) 1.376(6), C(14)-C(15) 1.396(6), C(1)-Se(1)-C(2) 67.2(17), N(3)-C(1)-N(1) 128.8(4), N(3)-C(1)-Se(1) 134.5(3), N(1)-C(1)-Se(1) 96.7(3), N(2)-C(2)-Se(1) 139.9(3) N(1)-C(2)-Se(1) 93.0(3) for all data.⁸

mp 78.6 -79.7 °C; IR (KBr): 1656, 1587, 1275 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.23 (d, 6H, $J = 6.3$ Hz), 1.56 (d, 6H, $J = .9$ Hz), 2.42 (s, 3H), 3.13 (7th, 1H, $J = 6.3$ Hz), 4.42 (7th, 1H, $J = 6.9$ Hz), 7.26 (d, 2H, $J = 8.0$ Hz), 8.15 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 20.4, 21.8, 24.1, 49.3, 57.9, 129.0, 130.0, 130.2, 130.6, 132.6, 139.4, 144.0, 158.5, 175.5; ^{77}Se NMR (75 MHz, CDCl_3): δ 753.2; MS (EI): $m/z = 351$ [M]⁺; *Anal.* Calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{OSe}$: C, 54.86; H, 6.04; N, 11.99. Found: C, 54.71; H, 6.09; N, 11.64.

3-Isopropyl-2-isopropylimino-4-selenoxo-6-*p*-tolyl-3,4-dihydro -2*H*-1,3,5-oxadiazine (4e)

mp 97.8 -99.2 °C; IR (KBr): 1698, 1598, 1329 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.23 (d, 6H, $J = 6.3$ Hz), 1.58 (d, 6H, $J = 6.9$ Hz), 2.42 (s, 3H), 4.11 (7th, 1H, $J = 6.3$ Hz), 6.00 (7th, 1H, $J = 6.9$ Hz), 7.29 (d, 2H, $J = 8.0$ Hz), 8.10 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 18.2, 22.0, 23.6, 46.6, 58.6, 125.0, 129.6, 129.8, 131.3, 146.0, 151.2, 189.7; MS (EI): $m/z = 351$ [M]⁺; HRMS: $m/z = 351.0850$, calcd. for $\text{C}_{16}\text{H}_{20}\text{N}_3\text{OSe}$, found 350.0805.

3-Cyclohexyl-2-cyclohexylimino-4-*p*-toluoylimino-1,3-selenazetidine (3f)

mp 107.6-109.9 °C; IR (KBr): 1652, 1579, 1281 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.19-1.40 (m, 6H), 1.43-1.56(m, 2H), 1.58-1.89 (m, 8H), 1.93-2.10 (m, 2H), 2.15-2.29 (m, 2H), 2.43 (s, 3H), 2.77-2.85 (m, 1H), 3.98-4.06 (m, 1H), 7.27(d, 2H, $J = 8.0$ Hz),), 8.15(d, 2H, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 21.8, 24.4, 25.2, 25.5, 25.7, 30.3, 34.1, 56.9, 65.3, 129.1, 130.0, 132.7, 139.3, 144.0, 158.9, 175.6; ^{77}Se NMR (75 MHz, CDCl_3): δ 750.6; MS (EI): $m/z = 431$ [M]⁺; *Anal.* Calcd for $\text{C}_{22}\text{H}_{29}\text{N}_3\text{OSe}$: C, 61.39; H, 6.79; N, 9.76. Found: C, 61.31; H, 6.73; N, 9.82.

3-Cyclohexyl-2-cyclohexylimino-4-selenoxo-6-*p*-tolyl-3,4-dihydro -2*H*-1,3,5-oxadiazine (4f)

mp 123.6-124.9 °C; IR (KBr): 1706, 1602 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.34-1.89 (m, 17H), 2.41 (s, 3H), 2.55-2.66 (m, 2H), 3.78-3.89 (m, 1H), 5.60-5.71 (m, 1H), 7.29 (d, 2H, $J = 8.0$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 22.0, 23.9, 25.4, 25.8, 26.1, 27.6, 33.4, 53.7, 66.8, 125.1,

129.6, 129.9, 131.5, 145.9, 151.3, 190.0; MS (EI): $m/z = 431 [M]^+$; HRMS: $m/z = 431.1476$, calcd. for $C_{22}H_{29}N_3OSe$, found 431.1403.

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