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Selenium-containing heterocycles from isoselenocyanates: synthesis of 2-methylidene-1,3-selenazolidine derivatives

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Abstract–A convenient and unequivocal synthesis of the title compounds from isoselenocyanates, malononitrile or 2-cyanoacetate, and 1,2-dibromoethane or α-halogenated carboxylic acid derivatives is reported. The proposed reaction mechanism involves *in situ* cyclization of different halogenated compounds with an intermediate keten-*N,Se*-acetal, generated by the base promoted nucleophilic addition of the acidic cyanomethylenes to aliphatic and aromatic isoselenocyanates. Chemical and spectroscopic evidence for the structures of the new compounds is presented.

1. Introduction

The explosive growth of the interest in organoselenium chemistry over the past twenty-five years can be attributed to the specific properties of organic selenium compounds, which fit into the requirements of modern organic synthesis. Most of them are well adapted to chemo-, regio-, and stereoselective

Keywords: Isoselenocyanates; Selenaheterocycles; 1,3-Selenazolidines.

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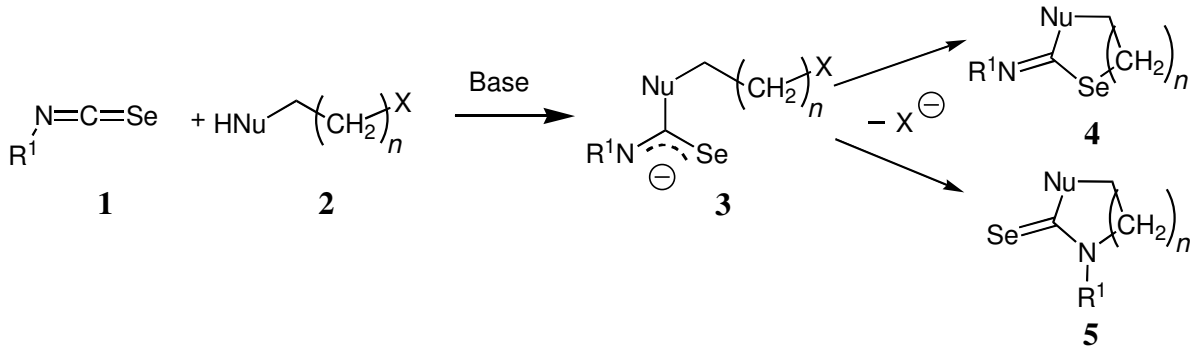
reactions.[2] In particular, selenium-containing heterocyclic compounds have been well recognized not only because of their remarkable reactivities and chemical properties,[3] but also because of their diverse pharmaceutical applications.[4] For this reason we are interested in the use of isoselenocyanates **1** in heterocyclic synthesis.[5] They are useful starting materials, since they are easy to prepare[6] and are safe to handle and store. In addition, they typically react under mild conditions, which are compatible with the low stability of substrates and products in the preparation of complex molecules.

Several reviews[7] have described the preparation and pharmaceutical potential of 1,3-selenazoles.[8] They have been studied in diverse areas of interest, for example as antitumor[9] and antiradiation agents,[10] enzyme inhibitors,[11] antifilarial[12] and antiviral compounds,[13] delivery agents,[14] and prodrugs of selenocysteine,[15] and are also well recognized in the chemistry of dyes.[16]

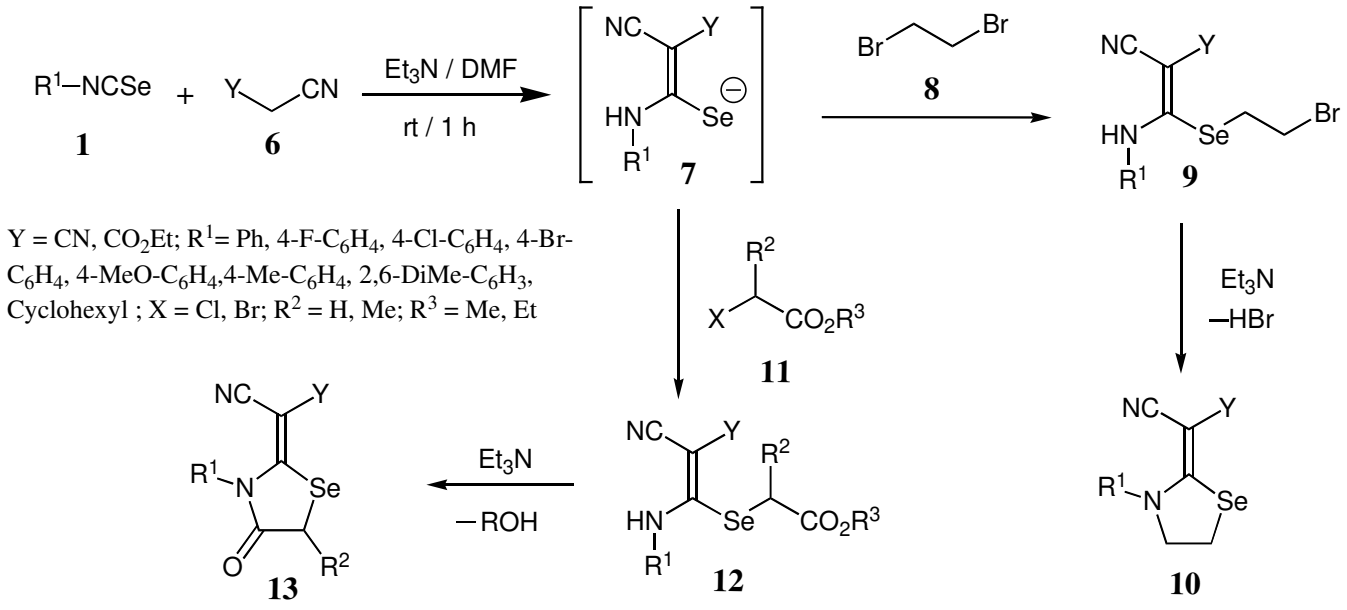
For the reaction of isoselenocyanates with nucleophiles it is known that nitrogen, oxygen, sulfur, and selenium nucleophiles add to the central carbon atom,[17] whereas phosphorus nucleophiles attack either the central carbon atom or the selenium atom.[18] Although only a few examples of the reaction of isoselenocyanates with carbon nucleophiles have been described, it was recently reported that suitable carbanions and isoselenocyanates can produce selenium-containing compounds.[19] To the best of our knowledge, only one paper describes such a reaction being used for the synthesis of 1,3-selenazoles.[20] On the other hand, 1,3-selenazolidinones have been prepared from different starting materials, such as isothiocyanates,[21] selenazadienes,[22] and widely from selenoureas,[23] but never with isoselenocyanates. For this reason, we have investigated the use of isoselenocyanates **1**, which are conveniently prepared by *Barton*'s procedure,[6] as building blocks in the synthesis of selenaheterocycles and heterocyclic selones.[24-35] For example, it has been shown that the reactions of bifunctional nucleophiles **2** with **1** yield five to seven-membered heterocycles of type **4** and **5** (Scheme 1). A likely intermediate is the adduct **3**, which undergoes the ring closure by nucleophilic substitution of the leaving group X either by the Se or the N-atom. As a continuation of previous work, we decided to investigate the addition of carbon nucleophiles with **1** and to trap the intermediate by a suitably substituted electrophilic reagent.



Scheme 1.

2. Results and discussion

After several unsuccessful attempts at reactions of isoselenocyanates with *β*-diketons like acetylacetone and dibenzoylmethane, we were successful by using cyanomethylene derivatives. Malononitrile and ethyl cyanoacetate react at room temperature with aryl and alkyl isoselenocyanates in the presence of a base to afford an intermediate keten-*N,Se*-acetal **7**, which subsequently can react with different halogenated compounds (Scheme 2).

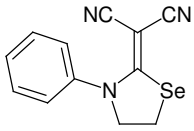
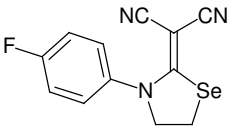
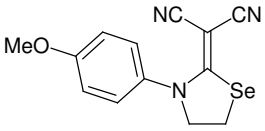
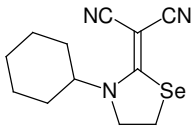
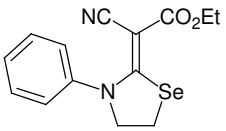


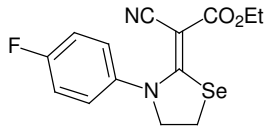
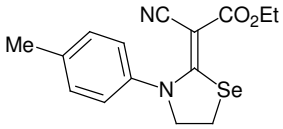
Scheme 2.

For example, the carbanion obtained from malononitrile (**6a**) and triethylamine in DMF added to isoselenocyanates **1** to give an intermediate of type **7**. The latter reacted with 1,2-dibromoethane (**8**) to give another intermediate **9**, which cyclized to yield 1,3-selenazolidine derivatives of type **10**. After stirring for four hours, the reaction mixture was evaporated to dryness and the residue was purified by column chromatography on silica gel and recrystallization from ethyl acetate (Table 1). Similar reactions were performed starting with ethyl cyanoacetate (**6b**). It is worth mentioning that only one isomer was obtained in the case of the cyanoacetates **10e-g** (Table 1).

The structures of the products were established on the basis of their spectroscopic data and, in the cases of **10a** and **10c**, by X-ray crystallography (Figure 1). The 2-(1,3-selenazolidin-2-ylidene)malononitriles **10a-d** show two different CN absorptions in the IR spectra (KBr; ca. 2203 and 2190 cm^{-1}) and ^{13}C NMR spectra (DMSO; ca. 112 and 118 ppm). For the 2-cyano-2-(1,3-selenazolidin-2-yliden)acetates **10e-g**, the CN absorption appears at ca. 2195 cm^{-1} and 114 ppm.

Table 1. Preparation of 1,3-selenazolidines **10** from isoselenocyanates **1**

Entry	R^1	Y	1,3-Selenazolidines **10**	Yield (%)
a	Phenyl	CN		62
b	4-F-C_6H_4	CN		54
c	4-MeO-C_6H_4	CN		61
d	Cyclohexyl	CN		42
e	Phenyl	CO_2Et		31

f	4-F-C_6H_4	CO_2Et		36
g	4-Me-C_6H_4	CO_2Et		31

In the crystal structure of **10a**, the two CH_2 groups in the five-membered ring are disordered over two approximately equally occupied positions, which result from alternate half-chair puckering of the ring conformation. The two cyano groups are coplanar with the atoms Se(1),C(2),N(3), and C(6), but the bond angles at the dicyanomethylidene C-atom are significantly different: whereas the angles C(2)-C(6)-C(7) and C(7)-C(6)-C(8) are small (118.2(1) and 115.7(1)°, resp.), the angle C(2)-C(6)-C(8) is widened (126.1(2)°), i.e. the CN group is tilted away from the phenyl residue. In turn, the latter is twisted out of the plane above mentioned by ca. 86°. Furthermore, the CN group pointing toward the phenyl residue is slightly bent away from the phenyl ring (N(8)-C(8)-C(6) = 175.2(2)°) whereas the other one is linear (N(7)-C(7)-C(6) = 179.3(2)°. In the case of **10c**, the five-membered ring has a half-chair conformation twisted on C(4)-C(5). The other structure parameters of **10c** are very similar to those of **10a**.

a) b)

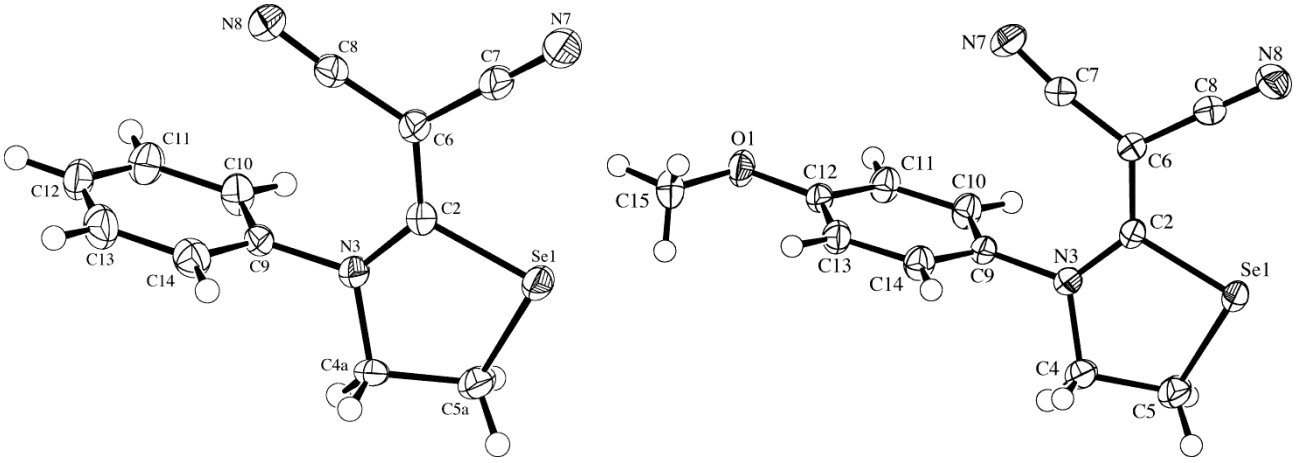
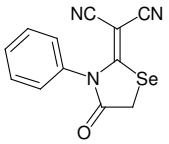
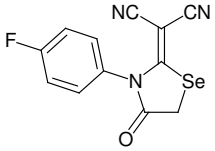
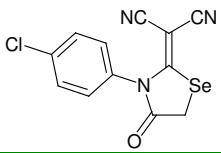


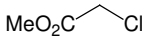
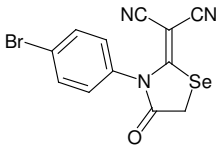
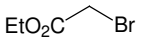
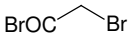
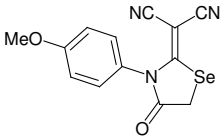
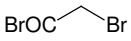
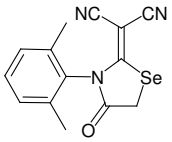
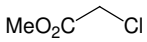
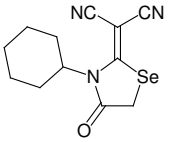
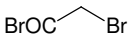
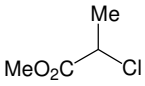
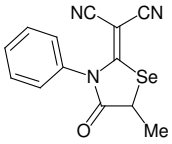
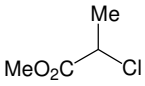
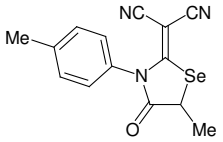
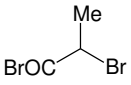
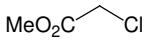
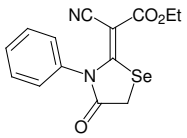
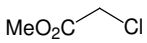
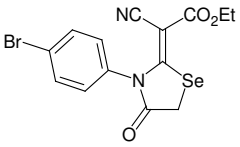
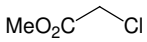
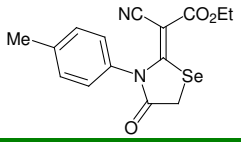
Figure 1. ORTEP plot[36] of the molecular structure of a) the major conformation of **10a** and b) of **10c** (arbitrary numbering of atoms; 50% probability ellipsoids).

The analogous reaction of **1**, **6a**, and methyl 2-chloroacetate (**11a**) gave the 2-(4-oxo-1,3-selenazolidin-2-ylidene)malononitriles of type **13** (Scheme 2, Table 2). We propose that **12** is the intermediate, which is the product of the reaction of the initially formed **7** with the halogenated compound. A subsequent condensation by elimination of methanol then yields **13**. In the case of **13a** and**13d**, the same products were obtained in increased yield by using ethyl bromoacetate (**11b**). Furthermore, the reaction with methyl 2-chloropropionate **11c** led to the 5-methyl derivatives **13h** and **13i** (Table 2).

As in the case of the malononitriles **10a**-**d**, the 4-oxo derivatives of type **13** show two CN absorptions in the IR (ca. 2220 and 2210 cm^{-1}) and in the ^{13}C NMR spectrum (ca. 110 and 115 ppm). In addition, the CO group appears at 1733-1743 cm^{-1} and 160-173 ppm. The structure of **13a** was established by X-ray crystallography (Figure 2). Although the compound is achiral, it has crystallized in a polar space group and the absolute structure has been determined by the diffraction experiment. The five-membered ring is almost planar, but is puckered slightly towards an envelope conformation where atom C(5) lies 0.149(2) Å from the mean plane defined by the other four ring atoms. The adjacent atoms O(4) and C(9), as well as the dicyanomethylidene group, are also lying in this ring plane. The phenyl group is oriented almost orthogonal to the above defined heterocyclic ring plane (dihedral angle ca. 86°). The other structure parameters are very similar to those of **10a** and **10c**.

Table 2. Preparation of 1,3-selenazolidin-4-ones **13** from isoselenocyanates **1**

Entry	R^1	Acetate	1,3-Selenazolidin-4-ones **13**	Yield (%)
a	Phenyl	MeO_2C–CH(Cl) **11a**		74
		EtO_2C–CH(Br) **11b**		81
		BrOC–CH(Br) **14a**		85
b	4-F-C_6H_4	BrOC–CH(Br) **14a**		83
c	4-Cl-C_6H_4	MeO_2C–CH(Cl) **11a**		68

d	4-Br-C_6H_4		**11a**		87
			**11b**		95
e	4-MeO-C_6H_4		**14a**		74
f	2,6-DiMe-C_6H_3		**14a**		83
g	Cyclohexyl		**11a**		34
			**14a**		33
h	Phenyl		**11c**		63
i	4-Me-C_6H_4		**11c**		89
			**14b**		63
k	Phenyl		**11a**		64
l	4-Br-C_6H_4		**11a**		86
m	4-Me-C_6H_4		**11a**		78

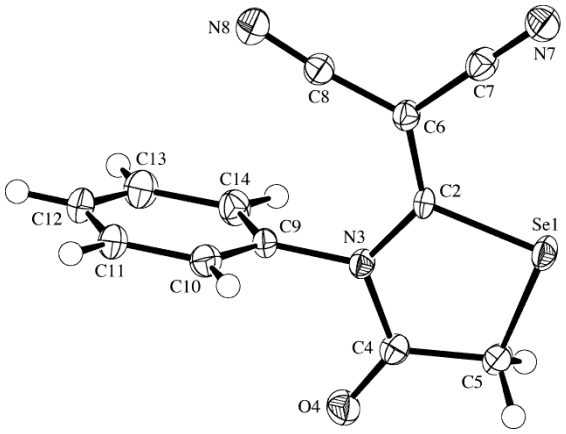


Figure 2. ORTEP plot[36] of the molecular structure of **13a** (arbitrary numbering of atoms; 50% probability ellipsoids).

The corresponding ethyl 2-cyano-2-(4-oxo-1,3-selenazolidin-2-yliden)acetates **13k**-**m** were prepared in a similar manner from **1**, **6b**, and **11a** (Scheme 2, Table 2). Again, only one isomer was obtained (TLC, NMR). In the case of **13k**, the molecular structure was established by X-ray crystallography (Figure 3). The exocyclic C,C-double bond is (*Z*)-configured, i.e., the sterically more demanding ester group is pointing away from the N-phenyl group. There are two symmetrically-independent molecules in the asymmetric unit. One of these molecules (A) has disorder in the terminal ethyl group of the ester substituent, with the major conformation being present in ca. 58% of the molecules. Molecules A and B have almost identical conformations with the only significant conformational difference being a small rotation in the orientation of the terminal ethyl group. The five-membered heterocyclic rings deviate only slightly from perfect planarity with the maximum deviation from the mean plane of the ring in molecule B being 0.032(2) Å for atom C(22). The ring in molecule A has a flattened envelope conformation puckered on atom Se(1), where Se(1) lies 0.204(1) Å from the mean plane defined by the other four ring atoms.

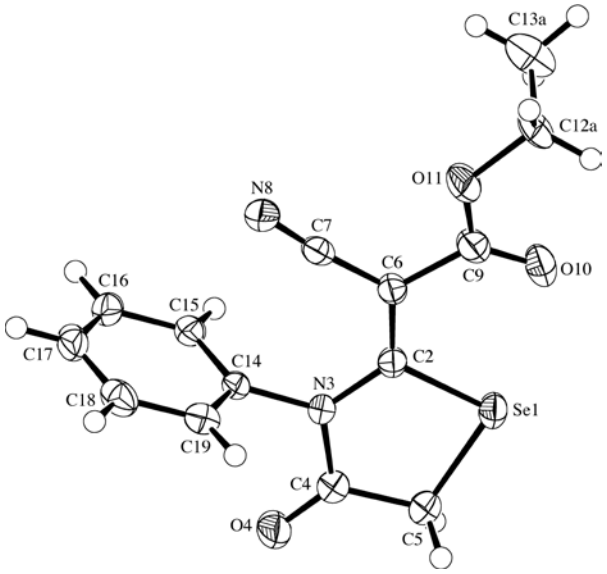


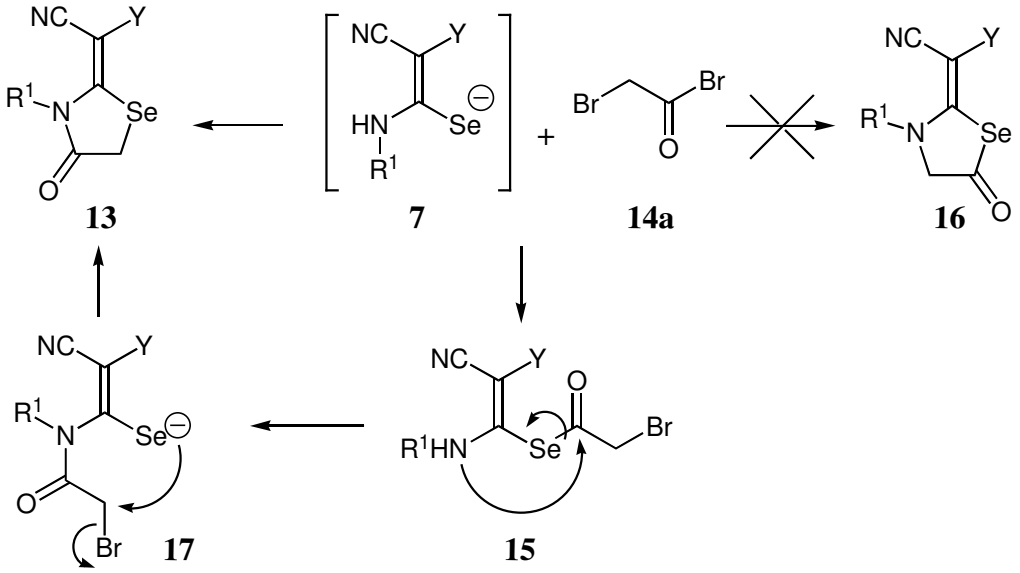
Figure 3. ORTEP plot[36] of the molecular structure of the major conformation of molecule A of **13k** (arbitrary numbering of atoms; 50% probability ellipsoids).

Treatment of the intermediates **7** with bromoacetyl bromide (**14a**) led to a surprising result. As the reaction between thioureas and acyl halides is known to give S-acylated isothioureas,[37] we expected that **7** and **14a** would give **15** by the reaction of the more nucleophilic Se-atom with the more electrophilic acyl C-atom (Scheme 3). Under the basic reaction conditions, the subsequent cyclization via nucleophilic substitution of bromide by the N-atom could lead to the 5-oxo-1,3-selenazolidine derivatives **16**, which are isomers of **13**. *Mohareb*,[38] *Bukowski*,[39] and more recently *Metwally* and coworkers,[40] described analogous reactions with isothiocyanates, which led to 1,3-thiazolidin-5-ones. On the other hand, *Koketsu et al.*[41] reported the synthesis of 1,3-selenazolidine-4-ones from selenourea and α-haloacyl halides. Although NMR analysis should differentiate clearly between the two isomeric structures, some doubts about the structures remain.

The reaction of **1a** with **6a** and **14a** under the usual conditions led to a single product in 85% yield, which was identified as **13a** by direct comparison with the product obtained from the reaction with **11a**. Analogously, only one product was formed in all the other reactions of **1** with **6a**,**b** and **14a**. By comparison of their ^{1}H and ^{13}C NMR spectra with those of **13a**, we attributed the structures **13b**, **13e**, **13f**, and **13g** to these products (Table 2). Furthermore, the product **13g** obtained from cyclohexyl isoselenocyanate, malononitrile (**6a**), and 2-bromoacetyl bromide (**14a**) was in all respects identical with

13g formed in the reaction with methyl 2-chloroacetate. With 4-methylphenyl isoselenocyanate, **6a**, and 2-bromopropanoyl bromide (**14b**), **13i** was obtained in 63% yield (Table 2).

The unexpected formation of the 4-oxo-1,3-selenazolidine derivatives **13** in the reactions with 2-bromoacetyl bromide **14a** can be explained by the reaction mechanism shown in Scheme 4. The intermediate **15**, which is formed by the nucleophilic substitution of the acyl bromide of **14a** by the Se-atom of **7** undergoes a base catalyzed 1,3-acyl shift to give the rearranged intermediate **17**. Similar S → N migrations of the acetyl group are known and have been studied in depth kinetically[42] and described recently by *Pihlaja* and coworkers.[43] Finally, the Se-atom attacks the α-carbon atom of the amide group and forms the 1,3-selenazolidinone ring by displacing the bromide ion to give **13**.



Scheme 3.

Another goal of the present study was the synthesis of analogous 1,3-selenazolidin-4,5-diones. In the first instance, we tried to trap **7** with oxalyl chloride, but we did not succeed in obtaining the dioxo derivatives. Furthermore, all attempts to use diethyl oxalate or the recently described ethyl 2-chloro-oxoacetate[44] were also unsuccessful. In addition, the oxidation of **13a** by selenium dioxide[45] failed to give the corresponding 1,3-selenazolidine-4,5-dione.

3. Conclusion

In conclusion, we have shown that malononitrile (**6a**) and alkyl 2-cyanoacetates (**6b**,**c**) react with isoselenocyanates **1** in DMF in the presence of excess triethylamine to give intermediates **7**, which react with 1,2-dibromoethane or α-halogenated acyl derivatives to give 1,3-selenazolidines **10** and 1,3-selenazolidin-4-ones **13**, respectively, in moderate to good yields. This one-pot reaction offers a convenient access to these selenium-containing five-membered heterocycles by starting with isoselenocyanates **1** as building blocks.

4. Experimental Part

4.1. General

Thin layer chromatography (TLC): silica gel 60 F_{254} plates (0.25 mm; Merck). Column chromatography (CC): silica gel 60 (0.040-0.063 mm; Merck). Mp: Büchi B-540 apparatus in capillary tubes; uncorrected. IR Spectra: Perkin–Elmer-1600 FT-IR spectrophotometer; in KBr; absorptions in cm^{-1}. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75.5 MHz) Spectra: Bruker ARX-300 instrument; in (D_6)DMSO unless otherwise stated; chemical shifts (δ) in ppm; couplig constants *J* in Hz. CI-MS: Finnigan SSQ-700 or MAT-90 instrument; NH_3 as carrier gas.

Starting materials. Malononitrile (**6a**) and all halogenated compounds are commercially available (Fluka). Isoselenocyanates (**1**) were prepared according to Barton's procedure[6] by starting from formamides. Formanilide and N-cyclohexylformamide were purchased (Fluka and Aldrich), *N*-(4-chlorophenyl)-, *N*-(4-bromophenyl)-, *N*-(4-fluorophenyl)-, and *N*-(4-methoxyphenyl)formamide were prepared from the respective anilines and 95% formic acid (ref.[46]). The solution was heated to reflux for 30 min and then evaporated to dryness *in vacuo*. The residue was dissolved in ether and washed with diluted acetic acid (5%), water, and aqueous $NaHCO_3$ (5%). The aqueous layer was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and evaporated under reduced pressure. The crude products were purified by recrystallization in water.

General Procedure for the preparation of 1,3-selenazolidine derivatives. A 25 mL round-bottom flask equipped with a magnetic stirrer and condenser was charged with a solution of malononitrile (**6a**; 73 mg,

1.1 mmol) in DMF (10 mL). Triethylamine (0.15 mL, 1.1 mmol) was added and the mixture was stirred for 30 min at rt. Isoselenocyanate (**1**; 1.1 mmol) was added and the mixture was stirred for 1 h at rt. Then, the α-halogenated compound (1.1 mmol) was added dropwise and the mixture was stirred for 4 h before being evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (100/0 to 50/50) as eluant and recrystallized from ethyl acetate.

4.2. Preparation of 2-methylene-1,3-selenazolidines 10

4.2.1. 2-(3-Phenyl-1,3-selenazolidin-2-ylidene)malononitrile (**10a**). Yield: 187 mg (62%). Yellowish crystals. Mp 295–297 °C. IR: 2935w, 2205s, 2191s, 1594w, 1527s, 1492m, 1453w, 1432w, 1388m, 1310m, 1238w, 1220w, 1064w, 1057w, 759w, 691m. ^{1}H-NMR: 3.49 (t, J = 7.1, CH_2), 4.46 (t, J = 7.1, CH_2), 7.31 (d-like, J = 8.2, 2 arom. H), 7.46–7.51 (m, 3 arom. H). ^{13}C-NMR: 22.2 (CH_2), 51.8 ($C(CN)_2$), 64.6 (CH_2), 112.0 (CN), 117.7 (CN), 126.4 (2 CH), 129.8 (CH), 129.9 (2 CH), 138.9 (C_{ar}), 171.9 (CNSe). ESI-MS: 298 (100, $[M(^{80}Se)+Na]^+$), 276 (22, $[M(^{80}Se)+1]^+$). Anal. calcd for $C_{12}H_9N_3Se$ (274.19): C 52.57, H 3.31, N 15.33; found: C 52.54, H 3.49, N 15.41.
Suitable crystals for the X-ray crystal structure determination were grown from CH_2Cl_2 by slow evaporation of the solvent.

4.2.2. 2-[3-(4-Fluorophenyl)-1,3-selenazolidin-2-ylidene]malononitrile (**10b**). Yield: 174 mg (54%). White crystals. Mp 193–195 °C. IR: 2985w, 2202s, 2191s, 1535s, 1505s, 1453w, 1394w, 1319w, 1236w, 1214m, 1054w, 846w. ^{1}H-NMR: 3.54 (t, J = 7.1, CH_2), 4.42 (t, J = 7.1, CH_2), 7.27 (t-like, $J \approx$ 8.9, 2 arom. H), 7.50 (dd-like, $J \approx$ 9.0, 4.9, 2 arom. H). ^{13}C-NMR: 23.6 (CH_2), 51.1 ($C(CN)_2$), 65.5 (CH_2), 113.1 (CN), 117.4 (d, $^{2}J_{CF}$ = 22, 2 CH), 118.7 (CN), 129.7 (d, $^{3}J_{CF}$ = 9, 2 CH), 141.9 (C_{ar}), 167.4 (d, $^{1}J_{CF}$ = 248, CF), 173.7 (CNSe). CI-MS: 311 (100, $[M(^{80}Se)+NH_4]^+$), 294 (7, $[M(^{80}Se)+1]^+$).

4.2.3. 2-[3-(4-Methoxyphenyl)-1,3-selenazolidin-2-ylidene]malononitrile (**10c**). Yield: 205 mg (61%). Yellowish crystals. Mp 187–189 °C. IR: 2939w, 2839w, 2203s, 2190s, 1607w, 1587w, 1539s, 1509w, 1474m, 1443w, 1391s, 1319m, 1299m, 1246s, 1171w, 1109w, 1056w, 1026m, 985w, 864w, 831m, 803w. ^{1}H-NMR: 3.47 (t, J = 7.1, CH_2), 3.83 (s, CH_3), 4.40 (t, J = 7.1, CH_2), 6.96, 7.21 (AA'BB', $J_{AB} \approx$ 8.2, 4 arom. H). ^{13}C-NMR: 22.0 (CH_2), 51.2 ($C(CN)_2$), 55.5 (CH_3O), 64.8 (CH_2), 112.2 (CN), 115.0 (2 CH), 118.0 (CN), 127.8 (2 CH), 131.4 (C_{ar}), 160.5 (C_{ar}), 172.2 (CNSe). CI-MS: 323 (100,

[M(^{80}Se)+NH_4]$^+$), 306 (8, [M(^{80}Se)+1]$^+$). Anal. calcd for $C_{13}H_{11}N_3OSe$ (304.21): C 51.33, H 3.64, N 13.81; found: C 51.22, H 3.62, N 13.77.

Suitable crystals for the X-ray crystal structure determination were grown from CH_2Cl_2 by slow evaporation of the solvent.

4.2.4. 2-(3-Cyclohexyl-1,3-selenazolidin-2-ylidene)malononitrile (**10d**). Yield: 130 mg (42%). Yellowish crystals. Mp 187–189 °C. IR: 2937s, 2850m, 2202s, 2188s, 1527s, 1457m, 1396w, 1372m, 1350w, 1308w, 1241w, 1192w, 1124w, 1010w, 982w, 893w, 879w, 823w. ^{1}H-NMR: 1.40–1.52 (m, 4 H), 1.60–1.70 (m, 2 H), 1.75–1.98 (m, 4 H), 3.26 (t, J = 7.1, CH_2), 4.13 (t, J = 7.1, CH_2) 4.35–4.45 (m, CH). ^{13}C-NMR: 21.7 (CH_2), 24.8 (2 CH_2), 24.9 (CH_2), 31.4 (2 CH_2), 48.0 (C(CN)$_2$), 55.6 (CH), 59.4 (CH_2), 115.1 (CN), 118.3 (CN), 171.4 (CNSe). CI-MS: 299 (100, [M(^{80}Se)+NH_4]$^+$), 282 (7, [M(^{80}Se)+1]$^+$). Anal. calcd for $C_{12}H_{15}N_3Se$ (280.23): C 51.43, H 5.40, N 15.00; found: C 51.33, H 5.45, N 14.88.

4.2.5. Ethyl 2-cyano-2-(3-phenyl-1,3-selenazolidin-2-ylidene)acetate (**10e**). Yield: 110 mg (31%). Yellowish crystals. Mp 151–153 °C. IR: 2969w, 2195s, 1668s, 1595w, 1512s, 1458m, 1431w, 1392m, 1367w, 1283s, 1254w, 1187w, 1172m, 1023w, 921w, 763m, 695m. ^{1}H-NMR: 1.27 (t, J = 7.1, CH_3), 3.10 (t, J = 7.2, CH_2), 4.21 (q, J = 7.2, CH_2), 4.28 (t, J = 7.1, CH_2), 7.26 (d-like, $J \approx$ 8.2, 2 arom. H), 7.40–7.49 (m, 3 arom. H). ^{13}C-NMR: 14.3 (CH_3), 20.0 (CH_2), 61.1 (CH_2), 62.5 (CH_2), 73.3 (C(CN)), 114.6 (CN), 126.5 (2 CH), 128.9 (CH), 129.6 (2 CH), 141.3 (C_{ar}), 167.6 (CO_2), 171.6 (CNSe). CI-MS: 340 (100, [M(^{80}Se)+NH_4]$^+$), 323 (53, [M(^{80}Se)+1]$^+$). Anal. calcd for $C_{14}H_{14}N_2O_2Se$ (321.24): C 52.35, H 4.39, N 8.72; found: C 51.98, H 4.46, N 8.70.

4.2.6. Ethyl 2-cyano-2-[3-(4-fluorophenyl)-1,3-selenazolidin-2-ylidene]acetate (**10f**). Yield: 135 mg (36%). Yellowish crystals. Mp 162–164 °C. IR: 3048w, 2976m, 2878w, 2190s, 1671s, 1603m, 1510s, 1454s, 1432m, 1387s, 1365m, 1288s, 1234m, 1221m, 1191w, 1171w, 1117s, 1057w, 1029w, 995m, 918m, 845s, 767s, 735w, 717w. ^{1}H-NMR: 1.28 (t, J = 7.1, CH_3), 3.11 (t, J = 7.2, CH_2), 4.19–4.27 (m, 2 CH_2), 7.11–7.17 (m, 2 arom. H), 7.23–7.29 (m, 2 arom. H). ^{13}C-NMR: 14.3 (CH_3), 19.9 (CH_2), 61.2 (CH_2), 62.5 (CH_2), 73.1 (C(CN)), 114.5 (CN), 116.7 (d, $^2J_{CF}$ = 23, 2 CH), 128.4 (d, $^3J_{CF}$ = 9, 2 CH), 137.2 (C_{ar}), 163.4 (d, $^1J_{CF}$ = 256, CF), 167.5 (CO_2), 171.9 (CNSe). CI-MS: 358 (100, [M(^{80}Se)+NH_4]$^+$), 341 (33, [M(^{80}Se)+1]$^+$).

4.2.7. Ethyl 2-cyano-2-[3-(4-methylphenyl)-1,3-selenazolidin-2-ylidene)acetate (**10g**). Yield: 115 mg (31%). Yellowish crystals. Mp 144–146 °C. IR: 2982w, 2918w, 2198s, 1669s, 1511s, 1392m, 1370w, 1287s, 1192w, 1170m, 1129s, 1058w, 1029w, 921w, 766m. ^{1}H-NMR: 1.27 (t, J = 7.1, CH_3), 2.39 (s, CH_3), 3.09 (t, J = 7.2, CH_2), 4.18–4.28 (m, 2 CH_2), 7.15, 7.25 (AA'BB', $J_{AB} \approx 8.1$, 4 arom. H). ^{13}C-NMR: 14.3 (CH_3), 19.9 (CH_2), 21.2 (CH_3), 61.1 (CH_2), 62.6 (CH_2), 73.1 (*C*(CN)), 114.6 (CN), 126.2 (2 CH), 130.2 (2 CH), 138.8 (C_{ar}), 139.0 (C_{ar}), 167.7 (CO_2), 171.6 (CNSe). CI-MS: 354 (100, [M(^{80}Se)+NH_4]$^+$), 337 (43, [M(^{80}Se)+1]$^+$). Anal. calcd for $C_{15}H_{16}N_2O_2Se$ (335.26): C 53.74, H 4.81, N 8.36; found: C 53.60, H 5.01, N 8.43.

4.3. Preparation of 2-methylene-1,3-selenazolidin-4-ones 13

4.3.1. 2-(4-Oxo-3-phenyl-1,3-selenazolidin-2-ylidene)malononitrile (**13a**). Yield: 235–270 mg (74–85%). Colorless crystals. Mp 265–267 °C. IR: 2985w, 2216s, 1733s, 1596w, 1522s, 1493m, 1368m, 1223s, 851w, 758w, 698m. ^{1}H-NMR: 4.39 (s, CH_2), 7.43 (d-like, $J \approx 7.9$, 2 arom. H), 7.50–7.60 (m, 3 arom. H). ^{13}C-NMR: 29.1 (CH_2), 56.7 (*C*$(CN)_2$), 110.1 (CN), 115.1 (CN), 128.9 (2 CH), 129.4 (2 CH), 130.8 (CH), 134.8 (C_{ar}), 173.3, 173.9 (CO, CNSe). CI-MS: 307 (100, [M(^{80}Se)+NH_4]$^+$); CI-MS (i-butane): 290 (100, [M(^{80}Se)+1]$^+$). Anal. calcd for $C_{12}H_7N_3OSe$ (288.16): C 50.02, H 2.45, N 14.58; found: C 49.98, H 2.60, N 14.34.

Suitable crystals for the X-ray crystal structure determination were grown from CH_2Cl_2 by slow evaporation of the solvent.

4.3.2. 2-[3-(4-Fluorophenyl)-4-oxo-1,3-selenazolidin-2-ylidene]malononitrile (**13b**). Yield: 280 mg (83%). Colorless crystals. M.p. 244–246 °C. IR: 2995w, 2982w, 2219s, 2210s, 1737s, 1600w, 1528s, 1516s, 1507s, 1373m, 1222s, 1208s, 1161w, 858w, 826w, 791w. ^{1}H-NMR: 4.65 (s, CH_2), 7.67 (t-like, $J \approx 9$, 2 arom. H), 7.49–7.59 (m, 2 arom. H). ^{13}C-NMR: 29.0 (CH_2), 56.7 (*C*$(CN)_2$), 110.2 (CN), 114.9 (CN), 116.4 (d, $^{2}J_{CF}$ = 23, 2 CH), 131.1 (C_{ar}), 131.5 (d, $^{3}J_{CF}$ = 9, 2 CH), 163.2 (d, $^{1}J_{CF}$ = 248, CF), 173.7, 173.9 (CO, CNSe). CI-MS: 325 (100, [M(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{12}H_6N_3OSeF$ (306.16): C 47.08, H 1.98, N 13.73; found: C 47.01, H 2.21, N 14.02.

4.3.3. 2-[3-(4-Chlorophenyl)-4-oxo-1,3-selenazolidin-2-ylidene]malononitrile (**13c**). Yield: 242 mg (68%). Colorless crystals. Mp 245–247 °C. IR: 2947w, 2223m, 2213m, 1733s, 1529s, 1485m, 1404w, 1370m, 1219s, 1172w, 1084w, 1015w, 845w, 813w, 722w. ^{1}H-NMR: 4.33 (s, CH_2), 7.45, 7.58 (AA'BB',

J_{AB} ≈ 8.7, 4 arom. H). ^{13}C-NMR: 29.1 (CH_2), 56.7 ($C(CN)_2$), 110.3 (CN), 114.9 (CN), 129.5 (2 CH), 131.0 (2 CH), 133.7 (C_{ar}), 135.5 (C_{ar}), 173.4, 173.8 (CO, CNSe). CI-MS: 341 (100, [M(^{80}Se, ^{35}Cl)+NH_4]$^+$). Anal. calcd for $C_{12}H_6N_3OSeCl$ (322.61): C 44.68, H 1.87, N 13.03; found: C 44.75, H 2.10, N 12.92.

4.3.4. 2-[3-(4-Bromophenyl)-4-oxo-1,3-selenazolidin-2-ylidene]malononitrile (**13d**). Yield: 351–383 mg (87–95%). Colorless crystals. Mp 247–249 °C. IR: 2947w, 2222s, 2211s, 1736s, 1585w, 1526s, 1481s, 1399w, 1371m, 1218s, 1171m, 1066w, 1012m, 842m, 809m, 711w. ^{1}H-NMR: 4.67 (s, CH_2), 7.71, 8.05 (AA'BB', J_{AB} ≈ 8.7, 4 arom. H). ^{13}C-NMR: 29.1 (CH_2), 56.8 ($C(CN)_2$), 110.3 (CN), 114.9 (CN), 129.5 (2 CH), 131.0 (2 CH), 133.7 (C_{ar}), 135.6 (C_{ar}), 173.4, 173.8 (CO, CNSe). CI-MS: 387 (79, [M(^{80}Se, ^{81}Br)+NH_4]$^+$), 385 (100, [M(^{80}Se, ^{79}Br)+NH_4]$^+$). Anal. calcd for $C_{12}H_6N_3OSeBr$ (367.07): C 39.27, H 1.65, N 11.45; found: C 39.44, H 1.86, N 11.49.

4.3.5. 2-[3-(4-Methoxyphenyl)-4-oxo-1,3-selenazolidin-2-ylidene]malononitrile (**13e**). Yield: 259 mg (74%). Orange crystals. Mp 193–195 °C. IR: 2945w, 2216m, 2210m, 1752m, 1606w, 1523s, 1508s, 1369m, 1303w, 1255m, 1212m, 1015w, 822w. ^{1}H-NMR: 3.83 (s, CH_3O), 4.38 (s, CH_2), 7.07, 7.35 (AA'BB', J_{AB} ≈ 8.0, 4 arom. H). ^{13}C-NMR: 28.9 (CH_2), 55.4 (CH_3), 56.6 ($C(CN)_2$), 110.2 (CN), 114.6 (2 CH), 115.1 (CN), 127.3 (C_{ar}), 130.2 (2 CH), 132.4 (C_{ar}), 160.8 (CO), 173.9 (CNSe). CI-MS: 337 (100, [M(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{13}H_9N_3O_2Se$ (318.20): C 49.07, H 2.85, N 13.21; found: C 48.84, H 3.01, N 13.57.

4.3.6. 2-[3-(2,6-Dimethylphenyl)-4-oxo-1,3-selenazolidin-2-ylidene]malononitrile (**13f**). Yield: 289 mg (83%). Colorless crystals. Mp 296–298 °C. IR: 3000w, 2944w, 2217s, 2206s, 1742s, 1517s, 1474m, 1392w, 1352s, 1217m, 1205s, 1183m, 1151m, 1035w, 837w, 785m, 736w. ^{1}H-NMR: 2.16 (s, 2 CH_3), 4.72 (s, CH_2), 7.28 (d, J = 7.8, 2 arom. H), 7.44 (t, J = 7.9, 1 arom. H). ^{13}C-NMR: 16.7 (2 CH_3), 28.7 (CH_2), 57.1 ($C(CN)_2$), 109.3 (CN), 114.7 (CN), 128.3 (2 CH), 130.9 (CH), 132.4 (C_{ar}), 136.5 (2 C_{ar}), 171.5, 173.3 (CO, CNSe). CI-MS: 335 (100, [M(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{14}H_{11}N_3OSe$ (316.22): C 53.18, H 3.51, N 13.29; found: C 53.18, H 3.58, N 13.03.

4.3.7. 2-(3-Cyclohexyl-4-oxo-1,3-selenazolidin-2-ylidene)malononitrile (**13g**). Yield: 107–110 mg (33–34%). Brownish crystals. Mp 123–125 °C. IR: 2996w, 2942s, 2855m, 2217m, 2206m, 1738s, 1701w, 1573m, 1507s, 1448m, 1400w, 1335m, 1254w, 1202m, 1193m, 1179m, 1141m, 1052w, 980w,

895w, 696m. ^{1}H-NMR: 1.23–1.54 (m, 4 H), 1.71–1.90 (m, 4 H), 2.27–2.40 (m, 2 H), 3.98 (s, CH_2), 4.51–4.61 (m, CH). ^{13}C-NMR: 24.4 (CH_2), 24.8 (2 CH_2), 28.7 (2 CH_2), 32.2 (CH), 59.4 (*C*$(CN)_2$), 61.7 (CH), 112.0 (CN), 114.3 (CN), 170.1 (CO), 173.5 (CNSe). CI-MS: 313 (100, [*M*(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{12}H_{13}N_3OSe$ (294.21): C 48.99, H 4.45, N 14.28; found: C 50.23, H 4.54, N 14.40.

4.3.8. 2-(5-Methyl-4-oxo-3-phenyl-1,3-selenazolidin-2-ylidene)malononitrile (**13h**). Yield: 210 mg (63%). White crystals. Mp 173–175 °C. IR: 2961w, 2217m, 2202m, 1735s, 1593w, 1518s, 1493m, 1363m, 1266w, 1222s, 1069w, 996w, 940w, 763w, 728w, 697w. ^{1}H-NMR: 1.94 (d, *J* = 7.3, CH_3), 4.55 (q, *J* = 7.3, CH), 7.26 (d, *J* = 8.1, 2 arom. H), 7.54–7.63 (m, 3 arom. H). ^{13}C-NMR: 19.4 (CH_3), 38.7 (CH), 61.6 (*C*$(CN)_2$), 109.3 (CN), 113.8 (CN), 128.6 (2 CH), 130.1 (CH), 131.6 (2 CH), 134.3 (C_{ar}), 167.4 (CO), 176.3 (CNSe). CI-MS: 321 (100, [*M*(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{13}H_9N_3OSe$ (302.19): C 51.67, H 3.00, N 13.91; found: C 51.50, H 4.10, N 14.15.

4.3.9. 2-[5-Methyl-3-(4-methylphenyl)-4-oxo-1,3-selenazolidin-2-ylidene)malononitrile (**13i**). Yield: 220–310 mg (63–89%). White crystals. Mp 223–225 °C. IR: 2933w, 2216m, 2208m, 1741s, 1521s, 1216s, 1160w, 1071w, 996w, 814w, 771w, 734w. ^{1}H-NMR: 1.92 (d, *J* = 7.3, CH_3), 2.44 (s, CH_3), 4.53 (q, *J* = 7.2, CH), 7.10, 7.35 (AA'BB', $J_{AB} \approx 8.1$, 4 arom. H). ^{13}C-NMR: 19.4 (CH_3), 21.4 (CH_3), 38.6 (CH), 61.6 (*C*$(CN)_2$), 109.3 (CN), 113.9 (CN), 128.2 (2 CH), 130.7 (2 CH), 131.6 (C_{ar}), 142.2 (C_{ar}), 167.5 (CO), 176.4 (CNSe). CI-MS: 335 (100, [*M*(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{14}H_{11}N_3OSe$ (316.22): C 53.18, H 3.51, N 13.29; found: C 53.31, H 43.59, N 13.30.

4.3.10. Ethyl 2-cyano-2-(4-oxo-3-phenyl-1,3-selenazolidin-2-ylidene)acetate (**13k**). Yield: 236 mg (64%). Brownish crystals. Mp 189–191 °C. IR: 2982w, 2936w, 2206s, 1739s, 1679s, 1595w, 1511s, 1496s, 1367w, 1355m, 1290s, 1210s, 1176s, 1167s, 1119s, 1016w, 846w, 768w, 696m. ^{1}H-NMR: 1.31 (t, *J* = 7.2, CH_3), 3.83 (s, CH_2), 4.29 (q, *J* = 7.1, CH_2O), 7.26 (d, *J* ≈ 8.2, 2 arom. H), 7.52–7.62 (m, 3 arom. H). ^{13}C-NMR: 14.1 (CH_3), 24.2 (CH_2), 62.2 (CH_2), 81.4 (*C*(CN)), 111.7 (CN), 128.7 (2 CH), 129.8 (2 CH), 131.0 (CH), 135.8 (C_{ar}), 166.4, 168.1 (CO, CO_2), 174.6 (CNSe). CI-MS: 354 (100, [*M*(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{14}H_{12}N_2O_3Se$ (335.22): C 50.16, H 3.61, N 8.36; found: C 50.01, H 3.93, N 8.04.

Suitable crystals for the X-ray crystal structure determination were grown from CH_2Cl_2 by slow evaporation of the solvent.

4.3.11. Ethyl 2-[3-(4-bromophenyl)-4-oxo-1,3-selenazolidin-2-ylidene]-2-cyanoacetate (**13l**). Yield: 392 mg (86%). Pale yellow crystals. Mp 191–193 °C. IR: 2984w, 2206s, 1743s, 1678s, 1509s, 1498s, 1486s, 1360m, 1292s, 1210m, 1176s, 1165s, 1129m, 1066w, 1013m, 845w, 834w, 821w, 770w, 714w. ^{1}H-NMR: 1.31 (t, J = 7.2, CH_3), 3.81 (s, CH_2), 4.29 (q, J = 7.1, CH_2O), 7.12, 7.67 (AA'BB', $J_{AB} \approx 8.3$, 4 arom. H). ^{13}C-NMR: 14.0 (CH_3), 24.1 (CH_2), 62.3 (CH_2), 81.6 (*C*(CN)), 111.9 (CN), 125.3 (C_{ar}), 130.3 (2 CH), 133.1 (2 CH), 134.7 (C_{ar}), 166.2, 167.4 (CO, CO_2), 174.3 (CNSe). CI-MS: 434 (80, [M(^{80}Se, ^{81}Br)+NH_4]$^+$), 432 (100, [M(^{80}Se, ^{79}Br)+NH_4]$^+$). Anal. calcd for $C_{14}H_{11}N_2O_3SeBr$ (414.12): C 40.60, H 2.68, N 6.76; found: C 40.71, H 2.91, N 6.68.

4.3.12. Ethyl 2-cyano-2-[4-oxo-3-(4-methylphenyl)-1,3-selenazolidin-2-ylidene)acetate (**13m**). Yield: 300 mg (78%). Pale yellow crystals. Mp 187–189 °C. IR: 2982w, 2930w, 2204s, 1740s, 1679s, 1505s, 1359m, 1291m, 1211s, 1180s, 1169s, 1117m, 1016w, 846w, 770w, 716w. ^{1}H-NMR: 1.30 (t, J = 7.2, CH_3), 2.44 (s, CH_3), 3.81 (s, CH_2), 4.28 (q, J = 7.1, CH_2O), 7.12, 7.33 (AA'BB', $J_{AB} \approx 8.3$, 4 arom. H). ^{13}C-NMR: 14.0 (CH_3), 21.4 (CH_3), 24.2 (CH_2), 62.2 (CH_2), 81.3 (*C*(CN)), 111.8 (CN), 128.4 (2 CH), 130.5 (2 CH), 133.1 (C_{ar}), 141.3 (C_{ar}), 166.5, 168.4 (CO, CO_2), 174.7 (CNSe). CI-MS: 368 (100, [M(^{80}Se)+NH_4]$^+$). Anal. calcd for $C_{15}H_{14}N_2O_3Se$ (349.25): C 51.59, H 4.04, N 8.02; found: C 52.06, H 4.38, N 7.94.

4.4. X-Ray crystal-structure determination of 10a, 10c, 13a, and 13k

All measurements were performed on a Nonius KappaCCD area-diffractometer[47] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. The data collection and refinement parameters are given below[48] and views of the molecules are shown in Figures 1–3. Data reduction was performed with HKL Denzo and Scalepack.[49] The intensities were corrected for Lorentz and polarization effects, and absorption corrections based on the multi-scan method[50] were applied. Equivalent reflections, other than the Friedel pairs in **13a**, were merged. The structures were solved by direct methods using SIR92,[51] which revealed the positions of all non-H-atoms. In the case of **10a**, the two CH_2 groups in the five-membered ring are disordered over two conformations. Two sets of positions were defined for the atoms of these groups and the site occupation factor of the major conformation refined to 0.51(1). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered C-atoms. In the case of **13k**, there are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules

were tested carefully for a relationship from a higher symmetry space group using the program PLATON,[52] but none could be found. The terminal ethyl group in one molecule is disordered over two conformations. Two sets of overlapping positions were defined for the atoms of this group and the site occupation factor of the major conformation of this group refined to 0.58(2). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered C-atoms, while neighboring atoms within and between each conformation of the disordered ethyl group were restrained to have similar atomic displacement parameters. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the methyl groups). The refinement of the structures was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied in the cases of **10c**, **13a**, and **13k**. In **10a** and in **10c**, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. Refinement of the absolute structure parameter[53] of **13a** yielded a value of –0.021(7), which confidently confirms that the refined coordinates represent the true absolute structure. Neutral atom scattering factors for non-H-atoms were taken from[54], and the scattering factors for H-atoms were taken from ref.[55] Anomalous dispersion effects were included in F_c;[56] the values for f' and f'' were those of ref.[57] The values of the mass attenuation coefficients are those of ref.[58] All calculations were performed using the *SHELXL97*[59] program.

Crystal data for **10a**: $C_{12}H_9N_3Se$, M = 274.12, pale-yellow, prism, crystal dimensions 0.07 × 0.12 × 0.20 mm, monoclinic, space group $P2_1/c$, Z = 4, reflections for cell determination 22243, 2θ range for cell determination 4 – 60°, a = 7.5986(1) Å, b = 16.6005(3) Å, c = 8.8620(1) Å, β = 94.199(1)°, V = 1114.86(3) Å^3, T = 160 K, D_X = 1.633 g·cm^{-3}, μ(MoK_α) = 3.339 mm^{-1}, scan type ϕ and ω, $2\theta_{(max)}$ = 60°, transmission factors (min; max) 0.542; 0.792, total reflections measured 33680, symmetry independent reflections 3253, reflections with $I > 2\sigma(I)$ 2814, reflections used in refinement 3252, parameters refined 164; restraints 3, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0267, $wR(F^2)$ [all data] = 0.0647 ($w = [\sigma^2(F_o^2)+(0.0275P)^2+0.5667P]^{-1}$, where $P = (F_o^2+2F_c^2)/3$), goodness of fit 1.058, final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min) = 0.41; –0.73 e Å^{-3}.

Crystal data for **10c**: $C_{13}H_{11}N_3OSe$, M = 304.15, pale-yellow, prism, crystal dimensions 0.10 × 0.23 × 0.28 mm, triclinic, space group $P\bar{1}$, Z = 2, reflections for cell determination 13000, 2θ range for cell determination 4 – 60°, a = 8.4715(2) Å, b = 8.6795(2) Å, c = 8.8012(2) Å, α = 98.756(2), β = 91.399(2)°, γ = 100.280(1), V = 628.44(3) Å^3, T = 160 K, D_X = 1.607 g·cm^{-3}, μ(MoK_α) = 2.976 mm^{-1}, scan type ϕ and ω, $2\theta_{(max)}$ = 60°, transmission factors (min; max) 0.489; 0.751, total reflections measured 18210, symmetry independent reflections 3671, reflections with $I > 2\sigma(I)$ 3252, reflections used in refinement 3670, parameters refined 165; $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0326, $wR(F^2)$ [all data] = 0.0838 ($w = [\sigma^2(F_o^2)+ (0.0458P)^2+0.1693P]^{-1}$, where $P = (F_o^2+2F_c^2)/3$), goodness of fit 1.058, secondary extinction coefficient 0.012(2), final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min) = 0.74; –0.95 e Å^{-3}.

Crystal data for **13a**: $C_{12}H_7N_3OSe$, M = 288.11, colorless, needle, crystal dimensions 0.10 × 0.10 × 0.28 mm, monoclinic, space group Cc, Z = 4, reflections for cell determination 9429, 2θ range for cell determination 4 – 60°, a =17.0737(4) Å, b = 9.5587(2) Å, c = 7.0931(2) Å, β = 104.623(1)°, V = 1120.11(5) Å^3, T = 160 K, D_X = 1.708 g·cm^{-3}, μ(MoK_α) = 3.335 mm^{-1}, scan type ϕ and ω, $2\theta_{(max)}$ = 60°, transmission factors (min; max) 0.508; 0.723, total reflections measured 14521, symmetry independent reflections 3197, reflections with $I > 2\sigma(I)$ 3084, reflections used in refinement 3197, parameters refined 155; restraints 2, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0236, $wR(F^2)$ [all data] = 0.0544 ($w = [\sigma^2(F_o^2)+ (0.0253P)^2+0.7032P]^{-1}$, where $P = (F_o^2+2F_c^2)/3$), goodness of fit 1.046, secondary extinction coefficient 0.0064(5), final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min) = 0.30; –0.46 e Å^{-3}.

Crystal data for **13k**: $C_{14}H_{12}N_2O_3Se$, M = 335.16, yellow, prism, crystal dimensions 0.10 × 0.22 × 0.25 mm, monoclinic, space group $P2_1/c$, Z = 8, reflections for cell determination 89915, 2θ range for cell determination 4 – 55°, a =9.6396(1) Å, b = 12.9321(2) Å, c = 21.8547(3) Å, β = 94.4025(8)°, V = 2716.37(6) Å^3, T = 160 K, D_X = 1.639 g·cm^{-3}, μ(MoK_α) = 2.771 mm^{-1}, scan type ϕ and ω, $2\theta_{(max)}$ = 55°, transmission factors (min; max) 0.590; 0.761, total reflections measured 55029, symmetry independent reflections 6222, reflections with $I > 2\sigma(I)$ 5276, reflections used in refinement 6222, parameters refined 384; restraints 39, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0305, $wR(F^2)$ [all data] = 0.0712 ($w = [\sigma^2(F_o^2)+$

$(0.0288P)^2+2.26P]^{-1}$, where $P = (F_o^2+2F_c^2)/3$), goodness of fit 1.046, secondary extinction coefficient 0.0012(2), final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min) = 0.60; –0.49 e Å^{-3}.

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