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2-(Pyrazol-4-yl)-1,3-oxaselenolanes from Pyrazole Carbaldehydes and 2-Selanyl-1-ethanol

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ABSTRACT: *Pyrazole carbaldehydes react with 2-selanyl-1-ethanol at room temperature in the presence of trimethylchlorosilane followed by treatment with triethyl amine to afford the corresponding 2-(pyrazol-4-yl)-1,3-oxaselenolanes. The structure of the novel compounds was confirmed by IR, ^{13}C, ^{1}H, ^{15}N, and ^{77}Se NMR spectroscopy.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–7, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21200

INTRODUCTION

Currently, an extremely limited number of 1,3-oxaselenolane derivatives is known. This is explained by the fact that their syntheses are laborious and multistage, the initial selenols being inaccessible and unstable compounds [1]. At the same time, similar to sulfur analogs, the five-membered oxaselenolane ring is present in nucleoside structures possessing antiviral activity against hepatitis B and HIV infection, thus representing considerable interest for synthesis [2–11].

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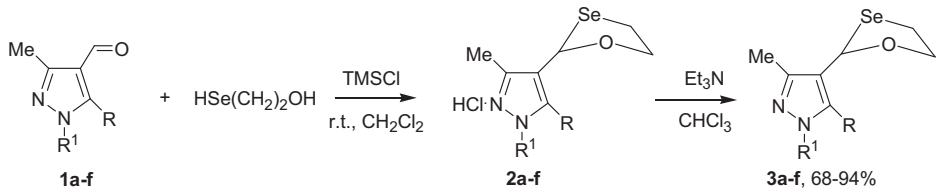
Urgency of such research is due to the pyrazole carbaldehydes (unlike aromatic aldehydes) react with selenoethanol analog, mercaptoethanol, in the presence of trimethylchlorosilane (Me_3SiCl) in quite different fashion delivering, even with an equimolar amount of mercaptoethanol, mainly open-chained S,S-acetals of pyrazole carbaldehydes [12] or pyrazolyloxadithiocanes [13]. Only under specially found conditions, individual 2-(pyrazol-4-yl)-1,3-oxathiolanes are formed in quantitative yields [12].

While the reaction of nitrobenzaldehydes with an equimolar amount of 2-mercaptoethanol without heating in the presence of Me_3SiCl furnishes aryl-1,3-oxathiolanes with good selectivity, the formylpyrazoles react with 2-mercaptoethanol under similar conditions to give mainly open-chained bis(2-hydroxyethyl)dithioacetals. Noteworthy, when twofold molar excess of 2-mercaptoethanol is employed, bis(2-hydroxyethyl)dithioacetals are formed almost quantitatively.

In continuation of the systematic investigations of the thio- and a selenoacetalyzation of hetarylcarbaldehydes in the presence of alkylchlorosilanes, we have studied the reactions of pyrazole aldehydes with 2-selanyl-1-ethanol.

RESULTS AND DISCUSSION

In the present work, we have found that unlike 2-mercaptoethanol, 2-selenoetanol reacts with



R = Me, R^1= Bn (**a**), Me (**b**), Pr(**c**), *i*-Pr (**d**), Allyl (**e**); R = Cl, R^1= Ph (**f**)

SCHEME 1 Synthesis of 2-(pyrazol-4-yl)-1,3-oxaselenanes **3a–f**.

pyrazole aldehydes in a different manner. The reaction is implemented with equimolar amounts of reagents in four- to sixfold excess trimethylchlorosilane in the CH_2Cl_2 solution at room temperature for 1 h (under the conditions of predominant formation of open-chained bis(2-hydroxyethyl) dithioacetals [12]) to exclusively deliver 2-(pirazol-4-yl)-1, 3-oxaselenolane hydrochlorides **2a–f** in high yields (Scheme 1).

The synthesized hydrochlorides **2a–f** are unstable and upon storage in air or during the treatment with solvents and admixtures of water undergo hydrolysis to give the initial aldehydes and other unidentified compounds, probably, products of 2-selanyl-1-ethanol oxidation.

The treatment of compounds **2a–f** with a triethylamine solution in chloroform leads to hardly accessible 1,3-oxaselenolanes in 68–94% yields.

In contrast to the initially formed hydrochlorides, 1,3-oxaselenolanes **3a–f** are stable and do not undergo the ring opening with the formation of the starting aldehydes under the action of water.

The application of 2 molar excess of the selenoalcohol in the reaction do not lead to the formation of open-chained bis(2-hydroxyethyl)diselenoacetals of pyrazole carbaldehydes, unlike similar interaction of formylpyrazoles with 2-mercaptoethanol under similar conditions [12]. As a result, a hard-to-separate mixture containing pyrazolyloxaselenolanes **3a–f**, selenoethanol (thin-layer chromatography (TLC)) and unidentified products has been obtained.

Such difference in behavior of selenoethanol and mercaptoethanol in the reaction with formylpyrazoles is likely due to the steric effect originated owing to the presence of bulkier selenium atom in the selenoalcohol in comparison with mercaptoethanol sulfur atom. Despite the complementarity of the carbaldehyde group in 4-formylpyrazoles to the mercaptoalcohol, the chalcogenol fragment mentioned by us earlier, in this case, the steric hindrance is, apparently, a decisive factor ensuring the formation of only Se,O-cycle of 1,3-oxaselenolanes. Obviously, the difference in the reactions of selenoethanol and mercaptoethanol with formylpyrazoles is also owing to the formation of thermodynamically more steady structure, i.e., pyrazolyloxaselenolane.

The synthesized pyrazolyloxaselenolanes **3a–f** are white fine-crystalline substances, well soluble in the majority of organic solvents. The structure of compounds **3a–f** has been proved using ^{1}H, ^{13}C, ^{77}Se, and ^{15}N NMR technique. The composition of the products is confirmed by the data of element analysis.

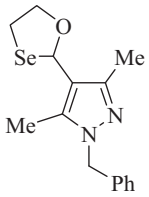
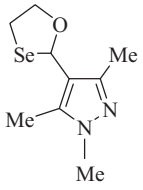
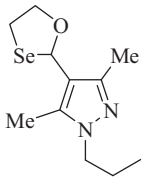
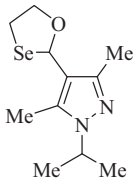
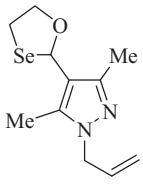
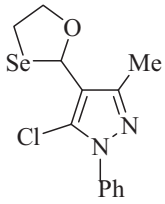
In the ^{1}H NMR spectra, 1,3-oxaselenolanes fragment of compounds **2a, 3a–f** is present as a five-membered cycle with nonequivalent diastereotopic protons of $SeCH_2$ (^2J = 9.1–10.8 Hz and vicinal ^3J = 5.3–6.2 Hz and ^3J = 0.9–1.7 Hz) and OCH_2 groups with heminal ^2J = 9.2–10.2 Hz and vicinal ^3J = 5.3–11.0 Hz and ^3J = 0.9–1.7 Hz spin–spin coupling constants. The structure of the compounds synthesized is also supported by the presence of satellite signals of protons and carbons adjacent to selenium atom, which are caused by the spin–spin interaction with magnetically active selenium isotope ^{77}Se. For instance, a proton signal of the OCHSe moiety in oxaselenolanes **2a, 3a–f** appears as a singlet at 6.17–6.37 ppm with a characteristic constant $^2J_{H–Se}$ = 14.4–14.9 Hz, $^1J_{C–Se}$ = 53.4–57.9 Hz.

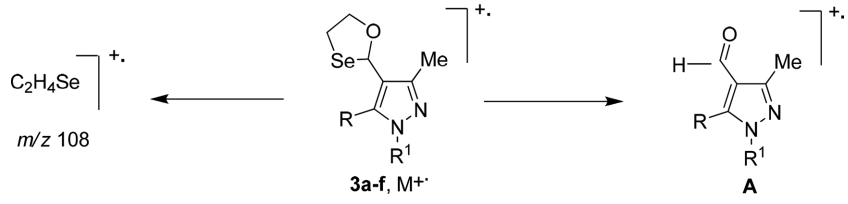
In the ^{77}Se NMR spectra of compounds **2a, 3a–f**, the signal of selenium atom is present in the region of 305.4–337.2 ppm.

In the ^{15}N NMR spectra, signals of the pyridine and pyrrole nitrogen atoms are detected.

We have studied the mass spectra of compounds **3a–f** (Table 1). Upon electron ionization, 1,3-oxaselenolanes **3a–f** generate unstable molecular ions, unlike the corresponding pyrazole-substituted 1,3-oxathiolanes, which under the close conditions give a stable molecular ions ($I_{rel.}$, 18–60%) [14]. At the same time, the main direction of decomposition of the molecular ions is similar both for sulfur- and selenium-containing pyrazoles and involves the cleavage of saturated heterocycle to produce the radical cation of the corresponding carbaldehyde (Scheme 2, ion **A**). Further decomposition of the

TABLE 1 Full Mass Spectrums of Electronic Ionization 2-(Pyrazol-4-yl)-1,3-oxaselenolanes **3a–f** *m/z* (Intensity, Rated Rather Maximum Peak)

Compound	*Structure*	*m/z ($I_{rel.}$,%), ^{80}Se, ^{35}Cl*
3a		322(<1) $[M]^{+\cdot}$, 215 (11), 214 (80), 213 (45), 200 (4), 199 (37), 186 (3), 185 (15), 171 (6), 158 (3), 144 (3), 137 (6), 123 (6), 122 (3), 108 (2), 106 (1), 104 (4), 92 (8), 91 (100), 82 (2), 77 (2), 65 (20), 51 (3).
3b		246 (<1) $[M]^{+\cdot}$, 218 (2), 216 (1), 139 (5), 138 (52), 137 (100), 110 (2), 109 (3), 108 (9), 107 (3), 106 (7), 105 (2), 104 (2), 82 (2), 80 (2), 66 (3), 65 (3), 56 (6).
3c		274 (<1) $[M]^{+\cdot}$, 246 (4), 244 (2), 167 (8), 166 (58), 165 (10), 151 (15), 138 (18), 137 (100), 125 (5), 124 (48), 123 (98), 110 (4), 109 (3), 108 (16), 107 (3), 106 (7), 105 (3), 104 (5), 82 (19), 80 (6), 69 (2), 68 (3), 67 (6), 66 (4), 65 (5), 56 (8).
3d		274 (<1) $[M]^{+\cdot}$, 246 (3), 244 (1), 167 (5), 166 (51), 165 (5), 151 (41), 125 (5), 124 (36), 123 (100), 110 (1), 108 (11), 107 (2), 106 (3), 104 (2), 86 (3), 84 (4), 80 (1), 67 (5).
3e		272 (<1) $[M]^{+\cdot}$, 244 (3), 242 (1), 165 (11), 164 (84), 163 (100), 149 (11), 137 (17), 135 (12), 123 (31), 122 (6), 121 (8), 120 (3), 110 (3), 109 (4), 108 (16), 107 (5), 106 (10), 105 (4), 104 (3), 95 (4), 94 (9), 93 (3), 86 (5), 84 (9), 82 (10), 81 (5), 80 (7), 79 (2), 68 (4), 67 (6), 66 (5), 65 (7), 56 (4), 55 (4), 54 (2).
3f		328(<1) $[M]^{+\cdot}$, 302 (1), 300 (5), 298 (2), 222 (30), 221 (43), 220 (85), 219 (100), 155 (9), 153 (3), 143 (3), 110 (3), 108 (10), 106 (5), 105 (3), 104 (7), 77 (34), 65 (4), 51 (18).



SCHEME 2 Pyrazolyl-substituted 1,3-oxaselenolanes **3a–f** under the electron ionization (EI).

radical cation **A** has been discussed previously [14]. As expected, in the mass spectrum of compound **3a**, the most intensive peak is assigned to the benzyl moiety with *m/z* 91 [15, 16].

It should be noted that the elimination of oxygen-containing fragments from the molecular ion of 1,3-oxaselenolane does not occur. Instead, the mass spectra of compounds **3a–f** show a weak intensity peak of the $[M - C_2H_4]^{+\cdot}$ ion. All mass spectral characteristics of compounds **3a–f** are given in Table 1.

Thus, the nature of chalcogene in a five-membered saturated heterocycle essentially affects stability of the molecular ion but does not influence the character of fragmentation.

CONCLUSIONS

In conclusion, the reaction of a series of 4-formylpyrazoles, bearing diverse substituents at the N-1 atom, with selenoethanol has been studied for the first time. It is revealed that in the presence of Me_3SiCl, the reaction is carried out without heating to chemoselectively afford hitherto unknown heterocyclic derivatives, 2-(pyrazol-4-yl)-1,3-oxaselenolane hydrochlorides, which are readily transformed into the corresponding stable free bases.

EXPERIMENTAL

General

^1H, ^{13}C, ^{77}Se, and ^{15}N NMR spectra were recorded on a Bruker DRX-400 instrument (Bruker BioSpin, Rheinstetten, Germany) (^1H, 400.13; ^{13}C, 100.62; ^{77}Se, 76.31; and ^{15}N, 40.56 MHz, respectively) in the $CDCl_3$ solution using TMS (^1H, ^{13}C), Me_2Se (^{77}Se), and CH_3NO_2 (^{15}N) as internal standards. The couplings are given in hertz. IR spectra were measured on a Bruker Vertex 70 spectrometer (Eftlinger, Germany) in KBr pellets or in thin layer. Mass spectra of electron ionization were obtained on a Agilent 5975C instrument (Agilent Technologies, Santa Clara, CA).

The samples were introduced via an Agilent 6890N chromatograph and separated on a chromatographic column HP-5MS (30 m × 0.25 mm × 0.25 μm, mode linear programming column temperature from 60°C to 190°C at 5°C/min). Helium was used as a gas carrier.

The reaction course and purity of the compounds obtained were monitored using a TLC technique on Silica gel 60 F_{254} Merk, and diethyl ether:methanol = 98:2 was used as eluent. Commercial solvents were removed by distillation.

A method for the preparation of 2-selanyl-1-ethanol was proposed and successfully realized by researchers of laboratory of sulfur chemistry at the A.E. Favorsky Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia [17]. Pyrazole carbaldehyde **1f** was used as commercial product (Sigma-Aldrich Corporate, St. Louis, MO). 1,3,5-Trialkylsubstituted 4-formylpyrazoles **1a–e** were synthesized by the modified protocol of Vilsmeir–Haack formylation of the corresponding 1,3,5-trialkylpyrazoles. The comparison with literature data [13, 18, 19] showed that the increase in the reaction time to 8 h at 130–137°C allowed increasing the conversion of trialkylpyrazoles up to 100% and synthesizing the target products with 98% purity.

*1-Allyl-3,5-dimethylpyrazole carbaldehyde (**1e**).* To DMF (10.96 g, 150 mmol), $POCl_3$ (22.99 g, 150 mmol) was added. Then, the mixture obtained was added to 1-allyl-3,5-dimethylpyrazole (13.62 g, 100 mmol). The reaction mixture was heated to 130–137°C and stirred for 8 h. After the reaction completion, the mixture was poured into water, pH of the solution reached neutral values with Na_2CO_3, the reaction product was extracted with ethyl acetate, dried over $MgSO_4$, the solution was evaporated, and the residue was distilled in a vacuum. Yield 10.18 g (62%), boiling point (bp) 136–145°C (10 mm Hg). ^1H NMR δ (ppm): 2.32 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.57 (d, 2H, CH_2), 4.99 (d, J = 17.15, 1H, =CH_2), 5.17 (d, J = 10.24, 1H, =CH_2), 5.87 (m, 1H, =CH), 9.78 (s, 1H, C(O)H). ^{13}C NMR δ (ppm): 9.03 (CH_3), 11.57 (CH_3), 50.39 (CH_2), 116.33 (C^2), 116.89 (CH_2=), 131.33 (CH=), 142.92 (C^3), 149.50 (C^1), 182.97 (C(O)H). Anal. calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.88; H, 7.36; N, 17.03.

Pyrazole carbaldehydes **1a–d** were obtained analogously.

*1-Benzyl-3,5-dimethylpyrazole carbaldehyde (**1a**).* Yield 64%, melting point (mp) 66–68°C, (lit [18]: yield 60.7%, mp 73–74°C).

*1,3,5-Trimethylpyrazole carbaldehyde (**1b**).* Yield 61%, bp 114–116°C (5 mm Hg), (lit [18]: yield 62%, mp 84°C; lit [19]: yield 59%, bp 130°C, (5 mm Hg), mp 80–83°C).

*1-Propyl-3,5-dimethylpyrazole carbaldehyde (**1c**).* Yield 62%, bp 110–112°C (2 mm Hg) (lit [19]: yield 86%, bp 125°C (5 mm Hg)).

*1-i-Propyl-3,5-dimethylpyrazole carbaldehyde (**1d**).* Yield 64%, mp 115–116°C (in literature [12, 14, 20–22] the yields and physical–chemical constants of carbaldehydes **1a–e** were not given).

Pyrazoles involved in formylation were synthesized by the protocol used for the preparation of linearly bonded pyrazoles [13].

1-Allyl-3,5-dimethylpyrazole. A mixture of KOH (11.20 g, 200 mmol) and DMSO (10 mL) was stirred for 10 min, and then 3,5-dimethylpyrazole (9.61 g, 100 mmol) was added and the mixture was stirred for 20 min at 20–22°C. Next, allyl bromide (14.52 g, 120 mmol) was added slowly keeping the temperature not above 30°C, and the mixture was stirred at 20–22°C for 3 h. The reaction mixture was poured into water (100 mL). 1-Allyl-3,5-dimethylpyrazole was extracted with diethyl ether, dried over $MgSO_4$, the solution was evaporated, and the residue was distilled in vacuum. Yield 11.45 g (84%), bp 86–92°C (15 mm Hg) (lit [23]: yield 48%, bp 187–190°C (746 mm Hg)). ^{1}H NMR δ (ppm): 2.10 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 4.50 (d, 2H, CH_2), 4.92 (d, J = 17.15, 1H, =CH_2), 5.10 (d, J = 10.24, 1H, =CH_2), 5.62 (s, 1H, H-4), 5.87 (m, 1H, =CH). Anal calcd for $C_8H_{12}N_2$: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.49; H, 8.89; N, 20.54 (in the work [23], it was reported on synthesis of 1-allyl-3,5-dimethylpyrazole, but the yield and constants were not given).

1,3,5-Trimethylpyrazole was prepared in 89% yield, bp 60–66°C (10 mm Hg) (lit [24]: yield 79%, bp 165–167°C (741 mm Hg)).

1-Benzyl-3,5-dimethylpyrazole was prepared in 88% yield, bp 191–193°C (20 mm Hg) (lit [24]: yield 33–67%, bp 154–156°C (18 mm Hg)).

1-Propyl-3,5-dimethylpyrazole was prepared in 85% yield, bp 151–156°C (20 mm Hg) (lit [25]: yield 80%, bp 62°C (3 mm Hg)).

1-i-Propyl-3,5-dimethylpyrazole was prepared in 83% yield, bp 95–98°C (8 mm Hg) (in the work [25], it was reported on synthesis of 1-*i*-propyl-3,5-dimethylpyrazole, but the yield and constants were not given).

*1-Benzyl-3,5-dimethyl-4-(1,3-oxaselenolan-2-yl)-1H-pyrazole hydrochloride (***2a***).* To a solution of formylpyrazole **1a** (0.214 g, 1 mmol) in CH_2Cl_2 (2 mL), a solution of 2-selanyl-1-ethanol (0.125 g, 1 mmol) in CH_2Cl_2 (1 mL) was added upon stirring and bubbling of argon at room temperature. The reaction proceeded with self-heating for 2 h. Then, the solvent, excess Me_3SiCl, and the formed hexamethyldisiloxane were removed under reduced pressure to give hydrochloride **2a** as light-yellowish flakes spreading in air, yield 0.346 g (98%). IR (neat, ν, cm^{-1}): 2746–2140 br (NH^+). ^{1}H NMR δ (ppm): 2.35 (s, 3H, Me-5), 2.50 (s, 3H, Me-3), 3.33 (ddd, ^2J = 9.1, ^3J = 6.2, ^3J = 11.2, 1H, $SeCH_2$), 3.41 (dd, ^2J = 9.1, ^3J = 5.3, 1H, $SeCH_2$), 3.69 (ddd, ^2J = 9.8, ^3J = 5.3, ^3J = 11.2, 1H, OCH_2), 4.70 (dd, ^2J = 9.8, ^3J = 6.2, 1H, OCH_2), 5.65 (s, 2H, NCH_2), 6.17 (s, 1H, SeCHO), 7.31–7.43 (m, 5H, Ph). ^{13}C NMR δ (ppm): 10.03 (Me-5), 10.10 (Me-3), 30.15 ($^1J_{C-Se}$ = 62.7 Hz, $SeCH_2$), 51.77 (NCH_2), 71.48 ($^1J_{C-Se}$ = 57.9 Hz, SeCHO), 73.34 (OCH_2), 117.08 (C-4), 127.85 (C*m*), 128.82 (C*p*), 129.03 (C*o*), 132.39 (C*i*), 142.24 (C-5), 143.05 (C-3). ^{15}N NMR δ (ppm): –183.5 (N-1), –168.6 (N-2). ^{77}Se NMR δ (ppm): 337.2. Anal. calcd for $C_{15}H_{18}N_2OSe{\cdot}HCl$: C, 50.36; H, 5.35; Cl, 9.91; N, 7.83; Se, 22.07. Found: C, 50.65; H, 5.31; Cl, 9.96; N, 7.88; Se, 21.95. By taking into account instability, the synthesized hydrochlorides **2b–f** were converted to free bases **3b–f** without isolating.

*General Method for the Synthesis of 2-(Pyrazol-4-yl)-1,3-oxaselenolanes (***3a–f***)*

To hydrochlorides **2a–f**, obtained by the above protocol from pyrazole carbaldehydes **1a–f** (1 mmol), a solution of Et_3N (1 mmol, 0.101 g) in $CHCl_3$ (2 mL) was added. The product formed was purified by column chromatography using silica gel (diethyl ether:methanol = 98:2). The target 1,3-oxaselenolanes **3a–f** were isolated as white crystals.

*1-Benzyl-3,5-dimethyl-4-(1,3-oxaselenolan-2-yl)-1H-pyrazole (***3a***).* Yield 0.267 g (83%), mp 63–65°C. IR (KBr, ν, cm^{-1}): 2923, 2858, 1568, 1495, 1434, 1261, 1190, 1177, 1057, 964, 852, 794, 758, 699, 650, 632, 597, 575.^{1}H NMR δ (ppm): 2.15 (s, 3H, Me-5), 2.27 (s 3H, Me-3), 3.33 (ddd, ^2J = 9.1, ^3J = 5.9, ^3J = 10.4, 1H, $SeCH_2$), 3.36 (ddd, ^2J = 9.1, ^3J = 5.6, ^3J = 1.6, 1H, $SeCH_2$), 3.67 (ddd, ^2J = 10.2, ^3J = 10.4, ^3J = 5.6 Hz, 1H, OCH_2), 4.65 (ddd, ^2J = 10.2, ^3J = 5.9, ^3J = 1.6 Hz, 1H, OCH_2), 5.18 (s, 2H, NCH_2), 6.27 (s, $^2J_{H,Se}$ = 14.4, 1H, SeCHO), 7.06 (m, 2H, H*o*), 7.23 (m, 1H, H*p*), 7.28 (m, 2H, H*m*).^{13}C NMR δ (ppm): 10.26 (Me-5), 12.55 (Me-3), 29.94 ($^1J_{C-Se}$ = 63.5, $SeCH_2$) 52.72 (NCH_2), 73.03 (OCH_2), 75.30 (SeCHO), 113.84 (C-4), 126.69 (C*m*), 127.53 (C*p*), 128.73 (C*o*), 136.91 (C*i*), 137.85 (C-5), 146.50 (C-3). ^{15}N NMR δ (ppm): –192.1 (N-1), –98.2 (N-2). ^{77}Se NMR δ (ppm): 310.1. Anal. calcd for $C_{15}H_{18}N_2OSe$: C, 56.08; H, 5.65; N, 8.72; Se, 24.58. Found: C, 55.88; H, 5.64; N, 8.68; Se, 24.90.

*1,3,5-Ttrimethyl-4-(1,3-oxaselenolan-2-yl)-1H-pyrazole (***3b***).* Yield 0.191 g (78%), mp 70–72°C. IR (KBr, ν, cm^{-1}): 2920, 2857, 1567, 1435, 1380, 1264, 1180, 1055, 993, 965, 860, 838, 794, 710, 659, 632, 514. ^{1}H NMR δ (ppm): 2.23 (s, 3H, Me-3), 2.24 (s, (3H, Me-5), 3.36 (dd, ^2J = 9.2, ^3J = 6.0, 1H, $SeCH_2$), 3.38 (ddd, ^2J = 9.2, ^3J = 5.6, ^3J = 1.5, 1H, $SeCH_2$), 3.67 (s, 3H, NMe), 3.70 (dd, ^2J = 9.7, ^3J = 5.6, 1H,

OCH_2), 4.67 (ddd, ^2J = 9.7, ^3J = 6.0, ^3J = 1.5, 1H, OCH_2), 6.27 (s, $^2J_{H,Se}$ = 14.4, 1H, SeCHO). ^{13}C NMR δ (ppm): 10.15 (Me-5), 12.25 (Me-3), 29.84 ($^1J_{C-Se}$ = 64.0, $SeCH_2$), 35.64 (MeN), 72.96 (OCH_2), 75.35 ($^1J_{C-Se}$ = 53.5, SeCHO), 113.26 (C-4), 137.73 (C-5), 145.85 (C-3). ^{15}N NMR δ (ppm): –202.0 (N-1), –99.6 (N-2). ^{77}Se NMR δ (ppm): 305.4. Anal. calcd for $C_9H_{14}N_2OSe$: C, 44.09; H, 5.76; N, 11.43; Se, 32.20. Found: C, 43.87; H, 5.72; N, 11.37; Se, 32.36.

*3,5-Dimethyl-4-(1,3-oxaselenolan-2-yl)-1-propyl-1H-pyrazole (***3c***).* Yield 0.153 g (56%), mp 55–56°C. IR (KBr, ν, cm^{-1}): 2960, 2862, 1565, 1458, 1430, 1379, 1267, 1205, 1175, 1052, 995, 963, 924, 859, 832, 795, 707, 648. ^{1}H NMR δ (ppm): 0.91 (t, ^3J = 7.5, 3H, *Me*CH_2CH_2), 1.78 (sextet, ^3J = 7.5, 2H, Me*CH_2*CH_2), 2.23 (s, 3H, Me-3), 2.24 (s (3H, Me-5), 3.37 (ddd, ^2J = 9.2, ^3J = 6.0, ^3J = 5.8, 1H, $SeCH_2$), 3.39 (ddd, ^2J = 9.2, ^3J = 11.0, ^3J = 1.5, 1H, SeCH), 3.69 (ddd, ^2J = 10.0, ^3J = 11.0, ^3J = 5.8, 1H, OCH_2), 3.89 (m (2H, CH_2N), 4.67 (ddd, ^2J = 10.0, ^3J = 5.8, ^3J = 1.5, 1H, OCH_2), 6.28 (s, $^2J_{H,Se}$ = 14.8, 1H, SeCHO).^{13}C NMR δ (ppm): 10.18 (Me-5), 12.46 (Me-3), 11.23 (*Me*CH_2CH_2), 23.64 (Me*CH_2*CH_2), 29.94 ($^1J_{C-Se}$ = 63.5 Hz, $SeCH_2$), 50.33 (CH_2N), 73.00 (OCH_2), 75.49 ($^1J_{C-Se}$ = 53.4 Hz, SeCHO), 112.86 (C-4); 137.26 (C-5), 145.98 (C-3).^{15}N NMR δ (ppm): –189.9 (N-1), –100.8 (N-2). ^{77}Se NMR δ (ppm): 308.4. Anal. calcd for $C_{11}H_{18}N_2OSe$: C, 48.35; H, 6.64; N, 10.25; Se, 28.90. Found: C, 48.60; H, 6.61; N, 10.30; Se, 28.77.

*1-Isopropyl-3,5-dimethyl-4-(1,3-oxaselenolan-2-yl)-1H-pyrazole (***3d***).* Yield 0.239 g (88%), mp 75–77°C. IR (KBr, ν, cm^{-1}): 2977, 2856, 1569, 1491, 1437, 1261, 1177, 1056, 988, 963, 921, 850, 795, 652, 602. ^{1}H NMR δ (ppm): 1.43 (d, ^3J = 6.6, 6H, Me_2CH), 2.25 (s, 3H, Me-5), 2,26 (s, 3H, Me-3), 3.36 (ddd, ^2J = 9.2, ^3J = 5.9, ^3J = 9.9, 1H, $SeCH_2$), 3.40 (ddd, ^2J = 9.2 Hz, ^3J = 5.6 Hz, ^3J = 0.9 Hz, 1H, $SeCH_2$). 3.70 (ddd, ^2J = 10.2, ^3J = 9.9, ^3J = 5.6, 1H, OCH_2), 4.34 (m, ^3J = 6.6, 1H, Me_2CH-N), 4.67 (ddd, ^2J = 10.2, ^3J = 5.9, ^3J = 0.9, 1H, OCH_2), 6.29 (s, $^2J_{H,Se}$ = 14.4, 1H, SeCHO). ^{13}C NMR δ (ppm): 10.09 (Me-5), 12.67 (Me-3), 22.47 (Me_2CH), 29.94 ($^1J_{C-Se}$ = 62.7, $SeCH_2$), 73.01 (OCH_2), 75.69 (SeCHO), 49.32 (Me_2*CH*-N), 115.18 (C-4), 136.43 (C-3), 145.93 (C-5). ^{15}N NMR δ (ppm): –178.9 (N-1), –107.5 (N-2). ^{77}Se NMR δ (ppm): 305.7. Anal. calcd for $C_{11}H_{18}N_2OSe$: C, 48.35; H, 6.64; N, 10.25; Se, 28.90. Found: C, 48.58; H, 6.62; N, 10.31; Se, 28.74.

*1-Allyl-3,5-dimethyl-4-(1,3-oxaselenolan-2-yl)-1H-pyrazole (***3e***).* Yield 0.205 g (76%), mp 59–61°C. IR (KBr, ν, cm^{-1}): 3076, 2976, 2857, 1643, 1571, 1475, 1432, 1265, 1190, 1175, 1052, 993, 963, 906, 858, 794, 723, 650. ^{1}H NMR δ (ppm): 2.23 (s, 3H, Me-5), 2.25 (s, 3H, Me-3), 3.37 (ddd, ^2J = 10.8, ^3J = 5.5, ^3J = 11.0, 1H, $SeCH_2$), 3.40 (ddd, ^2J = 10.8, ^3J = 5.5, ^3J = 1.7, 1H, $SeCH_2$), 3.70 (ddd, ^2J = 9.2, ^3J = 11.0, ^3J = 5.5, 1H, OCH_2), 4.60 (d, ^3J = 5.3, (2H, CH_2N), 4.68 (ddd, ^2J = 9.2, ^3J = 5.5, ^3J = 1.7, 1H, OCH_2), 5.00 (ddt, *J*trans = 17.1, ^4J = 1.5, ^2J = 1.2, 1H, CH_2=), 5.18 (ddt, J_{cis} = 10.3, ^2J = 1.2, ^4J = 1.2, 1H, CH_2=), 5.91 (ddt, J_{trans} = 17.1, J_{cis} = 10.3, ^3J = 5.3, 1H, CH=). 6.28 (s, $^2J_{H,Se}$ = 14.6, 1H, SeCHO). ^{13}C NMR δ (ppm): 10.02 (Me-5), 12.40 (Me-3), 29.85 ($SeCH_2$), 51.49 (NCH_2), 72.99 (OCH_2), 75.35 (SeCHO), 113.54 (C-4), 117.07 (=CH_2), 132.97 (=CH), 137.70 (C-5), 145.93 (C-3). ^{15}N NMR δ (ppm): –193.6 (N-1), –99.8 (N-2). ^{77}Se NMR δ (ppm): 311.3. Anal. calcd for $C_{11}H_{16}N_2OSe$: C, 48.71; H, 5.25; N, 10.33; Se, 29.11. Found: C, 48.95; H, 5.28; N 10.38; Se 29.25.

*5-Chloro-3-methyl-4-(1,3-oxaselenolan-2-yl)-1-phenyl-1H-pyrazole (***3f***).* Yield 0.306 g (94%), mp 82–83°C. IR (KBr, ν, cm^{-1}): 2964, 2864, 1597, 1560, 1501, 1415, 1381, 1332, 1264, 1180, 1055, 1003, 989, 966, 809, 770, 763. ^{1}H NMR δ (ppm): 2.40 (s, 3H, Me-3), 3.40 (ddd, ^2J = 9.3, ^3J = 5.8, ^3J = 10.8, 1H, $SeCH_2$), 3.43 (ddd, ^2J = 9.3, ^3J = 5.6, ^3J = 1.0, 1H, $SeCH_2$), 3.77 (ddd, ^2J = 9.4, ^3J = 10.8, ^3J = 5.6, 1H, OCH_2), 4.75 (ddd, ^2J = 9.4, ^3J = 5.8, ^3J = 1.0 Hz, 1H, OCH), 6.37 (s, $^2J_{H,Se}$ = 14.9, 1H, SeCHO), 7.39 (m, 1H, H*p*), 7.47 (m, 2H, H*m*), 7.51 (m, 2H, H*o*). ^{13}C NMR δ (ppm): 13.64 (Me-3), 30.11 ($^1J_{C-Se}$ = 61.9 Hz, $SeCH_2$), 73.62 (OCH_2), 73.57 ($^1J_{C-Se}$ = 55.5 Hz, SeCHO), 104.28 (C-5), 115.18 (C-4), 125.12 (C*o*), 128.26 (C*p*), 129.09 (C*m*), 138.22 (C*i*), 149.43(C-3). ^{15}N NMR δ (ppm): –187.6 (N-1), –92.2 (N-2). ^{77}Se NMR δ (ppm): 317.5. Anal. calcd for $C_{13}H_{13}ClN_2OSe$: C, 47.65; H, 4.00; Cl, 10.82; N, 8.55; Se, 24.10. Found: C, 47.89; H, 4.04; Cl, 10.85; N, 8.59; Se, 24.23.

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