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Stereoselective Organoselenium-Induced Cyclization of N-Allyl Acethydrazides to 1,3,4-Oxadiazines or N-Acetyl Pyrazolidines

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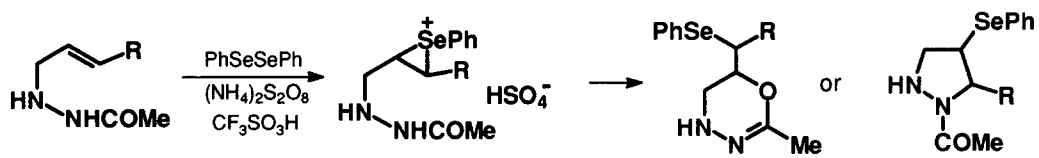
Abstract: N-Allyl acethydrazides easily give rise to organoselenium-induced cyclization reactions to afford phenylseleno substituted 5,6-dihydro-4*H*-1,3,4-oxadiazines or N-acetyl pyrazolidines as the kinetically or the thermodynamically controlled products, respectively.

Selenium-induced cyclization of alkenes containing internal nucleophiles continues to attract the attention of several research groups since it represents an efficient synthesis of a wide variety of heterocyclic compounds. Alkenols, alkenoic acids and alkenyl nitrones easily afford cyclic ethers,[1-3] lactones[1-3] or tetrahydro-1,2-oxazines,[4] respectively, by the formation of a carbon-oxygen bond. Nitrogen heterocycles can be similarly prepared by the formation of a carbon-nitrogen bond. N-protected primary alkenyl amines give the desired ring-closure reaction products[5-7] and alkenyl imines cleanly undergo selenium-induced cyclizations to afford cyclic iminium compounds.[8-10] Several new cyclization reactions leading to nitrogen heterocycles have been recently reported.[11-17] Interesting competitive cyclization reactions have been recently observed in those cases in which the nitrogen atom is incorporated in a functional group containing other nucleophilic atoms. Thus, as the result of the formation of a carbon-oxygen or a carbon-nitrogen bond, respectively, cyclic N-hydroxy imidates or N-hydroxy γ-lactams were obtained from alkenyl hydroxamic acids[18] and 1,4,2-dioxazines or N-acyl isoxazolidines were formed from O-allyl hydroxamic acids.[19] Similarly, alkenyl oximes gave rise to dihydro-1,2-oxazines and/or to cyclic nitrones.[17] It is noteworthy that in these cases the course of the cyclization reaction can be governed by working under conditions of kinetic or thermodynamic control. We now report that the cyclization of N-allyl acethydrazides **1** (Scheme 1), promoted by phenylselenenyl sulfate ($PhSeOSO_3H$), represents a new example of these competitive processes. In fact, depending on the nature of the substituent R and/or on the experimental conditions employed, the seleniranium intermediate **2** can be trapped by the oxygen atom of the carbonyl group or by the nitrogen atom to give the six-membered 5,6-dihydro-4*H*-1,3,4-oxadiazines **3** or the five-membered N-acetyl pyrazolidines **4**, respectively.

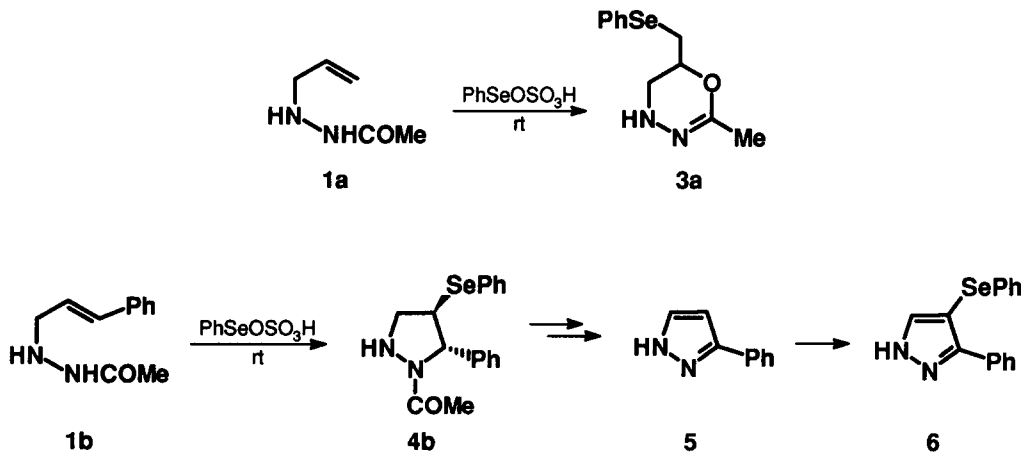
Scheme 1



1 **2** **3** **4**

The products necessary for the present investigation were easily obtained by allylation of acethydrazide. These were added, at room temperature or at -30 °C, to the solution of phenylselenenyl sulfate produced by oxidation of diphenyl diselenide with ammonium persulfate in the presence of trifluoromethanesulfonic acid in acetonitrile.[17] From the reaction carried out at room temperature the allyl acethydrazide **1a** gave the 1,3,4-oxadiazine **3a** in 57% yield (Scheme 2) whereas the cinnamyl acethydrazide **1b** gave the N-acetyl pyrazolidine **4b** in 95% yield. The low yields of **3a** are due to its partial decomposition during column chromatography. Compound **4b** was obtained as a single stereoisomer indicating that the cyclization process is a stereospecific *trans* addition. Together with **4b** a second product was isolated in very small amounts. This was identified as the 3-phenylpyrazole **5** which very likely originates from the persulfate promoted oxidative elimination of the phenylseleno group[20] followed by deacylation. In a parallel experiment the selenide **4b** was treated with an excess of ammonium persulfate in acetonitrile. Under these conditions the presence of the 3-phenylpyrazole **5** was indicated by TLC and GC-MS but the product could not be isolated because it gave rise to a rapid electrophilic aromatic phenylselenenylation reaction[21] to afford the 3-phenyl-4-(phenylseleno)pyrazole **6** (82%). A quantitative conversion of **4b** into **5** was obtained by oxidation with hydrogen peroxide in methanol. The same results were obtained when the reactions of **1a** and **1b** were carried out at -30 °C or at 50 °C. Thus, in these cases the nature of the reaction products is governed only by the structure of the starting allyl acethydrazides. In both cases the cyclization is completely regioselective and takes place with a Markovnikov orientation. The cyclizations of **1a** to the corresponding N-acetyl pyrazolidine and of **1b** to the 1,3,4-oxadiazine do not compete since they would require an *anti*-Markovnikov orientation.

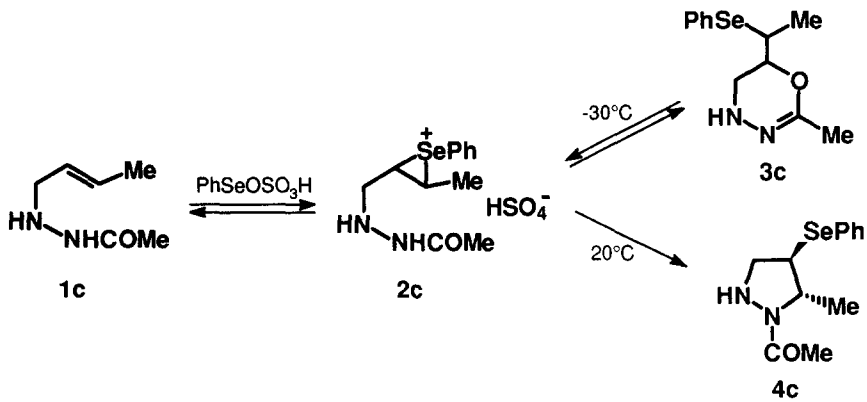
Scheme 2



The results described above suggest that competitive cyclizations could be observed only with substrates in which the regioselectivity of the addition does not play a very important role. This should occur starting from acethydrazides **1** in which R is an alkyl group. Indeed, this was confirmed by the results obtained with the methyl derivative **1c**. When the reaction of **1c** with phenylselenenyl sulfate (Scheme 3) was carried out at room temperature the only product obtained (62% yield) was the N-acetyl pyrazolidine **4c**. On the contrary,

when the same reaction was carried out at -30 °C the product obtained in 78% yield was the 1,3,4-oxadiazine **3c**. In this case, if the reaction mixture is left to reach room temperature before the work up, the initially formed 1,3,4-oxadiazine **3c** is completely converted into the N-acetyl pyrazolidine **4c**. Moreover, **4c** was also obtained when the isolated **3c** was treated with trifluoromethanesulfonic acid at room temperature. Both **3c** and **4c** were obtained as single stereoisomers indicating that both types of cyclizations are sterospecific processes.

Scheme 3



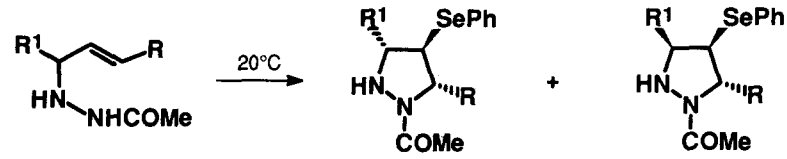
As indicated in Scheme 3 these results can be explained assuming that in the selenium-induced ring-closure reactions of the N-allyl acethydrazide **1c** product formation can be either kinetically or thermodynamically controlled. The trapping of the seleniranium intermediate **2c** by the oxygen atom, leading to the 1,3,4-oxadiazine **3c**, is faster than the trapping by the nitrogen atom, which leads to the N-acetyl pyrazolidine **4c**. However, under the experimental conditions employed, the formation of the 1,3,4-oxadiazine is reversible. It is thus possible to direct the reaction towards one or the other of the two types of products using appropriate reaction conditions. Very likely similar results can be observed with other allyl acethydrazides provided the substituent R is an alkyl group. The above described reactivity of the N-allyl acethydrazides **1** is similar to that observed with the O-allyl hydroxamic acids.[19]

In order to gain information about the diastereoselectivity of these cyclization reactions, some experiments were then carried out with the substrates **7a-d**. These reactions were carried out at room temperature so that only the five-membered N-acetyl pyrazolidines **8** and **9** could be formed by cyclization. The results obtained are collected in Scheme 4.

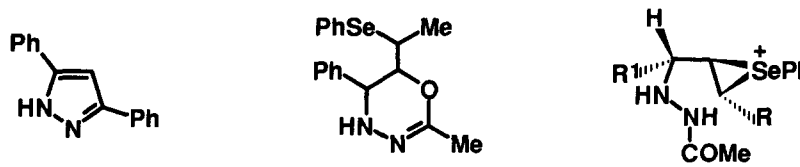
Structural assignments were effected by ^{1}H and ^{13}C NMR spectra and were based on the results of differential NOE experiments. In agreement with the results described above, it was observed that the ring-closure reaction is a *trans* stereospecific process in every case. From the reaction of **7a** a single stereoisomer was obtained. This was identified as compound **8a** in which the PhSe is *trans* in respect to the phenyl group in position 3. A second product was isolated in considerable amounts (24%). This was the 3,5-diphenyl pyrazole **10** which very likely originates through the same reaction sequence proposed above for compound **5**. The reaction of **7b** was not completely stereoselective, the two stereoisomers **8b** and **9b** being formed in a 6:1 ratio.[22] Finally, the N-allyl acethydrazides **7c** and **7d** gave exclusively the stereoisomers **8c** and **8d** with no trace of the isomeric compounds **9**. From the reaction mixture of **7c** a 10% of the six-membered 1,3,4-

oxadiazine **11** was isolated. This compound also consisted of a single stereoisomer. This high, and in most cases complete, diastereoselectivity observed in the conversions of compounds **7a-d** into the products **8a-d** can be rationalized assuming that the formation of the seleniranium ion **12** has considerable steric demands and that therefore the approach of the electrophilic phenylselenenylating species to the carbon-carbon double bond preferentially occurs away from the substituent R^1.

Scheme 4



7	8	9
a : R = R^1 = Ph	71%	
b : R = Ph, R^1 = Me	82%	14%
c : R = Me, R^1 = Ph	45%	
d : R = R^1 = Me	60%	



10 (24%) **11** (10%) **12**

The presently described stereoselective phenylselenium-induced cyclization reactions of allyl acethydrazides to the six-membered 5,6-dihydro-4*H*-1,3,4-oxadiazines or to the five-membered N-acetyl pyrazolidines represent a new example of the competitive processes which can take place starting from alkenes containing an internal ambident nucleophile. The structure of the substituents linked to the carbon-carbon double bond is the most important factor which governs the regiochemistry of the process and hence the nature of the cyclization products. Only in those cases in which the regioselectivity does not play a very important role the cyclization can be governed so that the products deriving from the kinetic or the thermodynamic control can be obtained. A further interesting aspect of these cyclization reactions is that in most cases they are completely diastereoselective. Finally, the reactions reported in this paper can also have considerable synthetic interest since they represent a convenient way to obtain either pyrazolidine or 1,3,4-oxadiazine derivatives.[23]

EXPERIMENTAL

Melting points were determined on a capillary melting point apparatus and are uncorrected. GLC analyses and MS spectra were carried out with an HP 5890 gaschromatograph (dimethyl silicone column,

12.5 m) equipped with an HP 5971 Mass Selective Detector; for the ions containing selenium only the pick arising from the selenium-80 isotope is given. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; $CDCl_3$ was used as solvent and TMS as standard. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer and were in good agreement with the calculated values. All new compounds were fully characterized by MS, ^1H, and ^{13}C NMR spectroscopy.

Synthesis of N-Allyl Acethydrazides. The allyl halides were commercially available or were prepared from the corresponding alcohols by treatment with $SOCl_2$.[24] The alkylation of acethydrazide was effected according to a slight modification of the general procedure reported in the literature.[25] The appropriate allyl halide (1 mmol) in EtOH (10 mL) was added to acethydrazide (8 mmol) in EtOH (15 mL) and the mixture was stirred at room temperature for 1-3 h. EtOH was evaporated under reduced pressure and water and CH_2Cl_2 were added to the residue. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The products were purified by silica gel column chromatography. Physical and spectral data are reported below.

1-Acetyl-2-allylhydrazide (1a): mp 40-42 °C (43%); ^1H NMR δ 8.9 (br s, 1 H), 5.85 (ddt, 1 H, *J* = 6.1, 10.4, 16.4 Hz), 5.35-5.08 (m, 2 H), 4.8 (br s, 1 H), 3.42 (d, 2 H, *J* = 6.1 Hz), 1.97 (s, 3 H); ^{13}C NMR δ 169.2, 134.0, 117.2, 54.0, 20.4. MS *m/z* (relative intensity) 114 (M^+, 6), 86 (4), 72 (54), 60 (50), 56 (100), 45 (19), 43 (78). Anal. Calcd for $C_5H_{10}N_2O$: C, 52.61; H, 8.83; N, 24.54. Found: C, 52.70; H, 8.76; N, 24.47.

1-Acetyl-2-cinnamylhydrazide (1b): mp 90-91 °C (64%); ^1H NMR δ 8.1 (br s, 1 H), 7.38-7.12 (m, 5 H), 6.52 (d, 1 H, *J* = 15.9 Hz), 6.2 (dt, 1 H, *J* = 6.5, 15.9 Hz), 4.7 (br s, 1 H), 3.57 (d, 2 H, *J* = 6.5 Hz), 1.9 (s, 3 H); ^{13}C NMR δ 169.5, 136.7, 133.0, 128.3, 127.4, 126.2, 125.5, 53.8, 20.8. MS *m/z* (relative intensity) 190 (M^+, 1), 147 (2), 130 (63), 117 (100), 91 (19), 43 (13). Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.47; H, 7.52; N, 14.65.

1-Acetyl-2-(2-buten-1-yl)hydrazide (1c): mp 54-56 °C (60%); ^1H NMR δ 8.6 (br s, 1 H), 5.78-5.42 (m, 2 H), 4.65 (br s, 1 H), 3.4 (d, 2 H, *J* = 6.2 Hz), 2.0 (s, 3 H), 1.73 (dd, 3 H, *J* = 1.1, 6.0 Hz); ^{13}C NMR δ 169.2, 129.1, 126.5, 53.5, 20.5, 17.3. MS *m/z* (relative intensity) 128 (M^+, 2), 113 (1), 86 (9), 71 (21), 70 (100), 60 (56), 55 (92), 43 (65). Anal. Calcd for $C_6H_{12}N_2O$: C, 56.23; H, 9.44; N, 21.86. Found: C, 56.12; H, 9.38; N, 21.94.

1-Acetyl-2-(1-phenyl)cinnamylhydrazide (7a): oil (42%); ^1H NMR δ 7.5-7.1 (m, 11 H), 6.61 (d, 1 H, *J* = 15.9 Hz), 6.28 (dd, 1 H, *J* = 7.8, 15.9 Hz), 5.0 (br s, 1 H), 4.71 (d, 1 H, *J* = 7.8 Hz), 1.8 (s, 3 H); ^{13}C NMR δ 169.5, 140.5, 136.5, 132.2, 129.6, 128.6, 128.4, 127.6, 126.4, 66.8, 20.8. Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.73; H, 6.78; N, 10.54.

1-Acetyl-2-(1-methyl)cinnamylhydrazide (7b): mp 92-93 °C (30%); ^1H NMR δ 7.95 (br s, 1 H), 7.38-7.12 (m, 5 H), 6.47 (d, 1 H, *J* = 15.9 Hz), 6.06 (dd, 1 H, *J* = 7.9, 15.9 Hz), 4.7 (br s, 1 H), 3.65 (dq, 1 H, *J* = 6.4, 7.9 Hz), 1.88 (s, 3 H), 1.21 (d, 3 H, *J* = 6.4 Hz); ^{13}C NMR δ 169.3, 136.7, 131.5, 131.3, 128.4, 127.4, 126.2, 58.1, 20.8, 19.1. MS *m/z* (relative intensity) 204 (M^+, 1), 161 (1), 144 (9), 131 (100), 116 (9), 91 (27), 77 (4), 43 (4). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.89; N, 13.71. Found: C, 70.65; H, 7.82; N, 13.80.

1-Acetyl-2-(1-phenyl-2-buten-1-yl)hydrazide (7c): oil (30%); ^1H NMR δ 7.7 (br s, 1 H), 7.4-7.2 (m, 5 H), 5.73 (dq, 1 H, *J* = 6.2, 15.2 Hz), 5.58 (ddq, 1 H, *J* = 1.0, 7.3, 15.2 Hz), 4.9 (br s, 1 H), 4.49 (d, 1 H, *J* = 7.3 Hz), 1.85 (s, 3 H), 1.68 (dd, 3 H, *J* = 1.0, 6.2 Hz); ^{13}C NMR δ 169.3, 141.2, 131.3, 128.3, 127.5, 127.3, 66.7,

20.7, 17.6. MS *m/z* (relative intensity) 204 (M^+, 1), 144 (5), 131 (100), 116 (19), 91 (56), 77 (8), 43 (9). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.89; N, 13.71. Found: C, 70.59; H, 7.94; N, 13.66.

1-Acetyl-2-(3-penten-2-yl)hydrazide (7d): mp 53-56 °C (30%); ^1H NMR δ 7.27 (br s, 1 H), 5.7-5.5 (m, 1 H), 5.4-5.2 (m, 1 H), 4.0 (br s, 1 H), 3.55-3.38 (m, 1 H), 1.97 (s, 3 H), 1.68 (dd, 3 H, J = 1.1, 6.4 Hz), 1.1 (d, 3 H, J = 6.4 Hz); ^{13}C NMR δ 169.0, 132.7, 126.7, 57.5, 20.5, 18.8, 17.2. Anal. Calcd for $C_7H_{14}N_2O$: C, 59.13; H, 9.92; N, 19.70. Found: C, 59.19; H, 9.84; N, 19.81.

Cyclization of N-Allyl Acethydrazides. General Procedure. A solution of diphenyl diselenide (1 mmol), ammonium persulfate (1.2 mmol) and trifluoromethanesulfonic acid (2.2 mmol) in acetonitrile (10 mL) was stirred for 15 min at room temperature. The N-allyl acethydrazides (1 mmol) were added at room temperature or at -30 °C as reported above. The progress of the reaction was monitored by TLC and GC-MS. Reaction times ranged from 30 min to 1 h. The reaction mixture was poured into a 10% aqueous solution of Na_2CO_3 and extracted with methylene chloride. The organic layer was dried (Na_2SO_4), evaporated and the residue was chromatographed through a silica gel column. Reaction yields are indicated above. Compounds **5** and **10** have physical and spectral data identical to those reported in the literature.[26] Physical and spectral data of the other compounds are reported below.

2-Methyl-6-(phenylseleno)methyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (3a): oil; ^1H NMR δ 7.6-7.48 (m, 2 H), 7.3-7.27 (m, 3 H), 4.42 (dddd, 1 H, J = 3.1, 5.3, 6.1, 8.2 Hz), 3.21 (dd, 1 H, J = 3.1, 11.4 Hz), 3.15 (dd, 1 H, J = 5.3, 12.8 Hz), 3.02 (dd, 1 H, J = 8.2, 12.8 Hz), 2.9 (dd, 1 H, J = 6.1, 11.4 Hz), 1.8 (s, 3 H); ^{13}C NMR δ 147.9, 132.8, 129.7, 129.2, 127.1, 74.6, 44.6, 29.6, 19.0. MS *m/z* (relative intensity) 270 (M^+, 53), 234 (22), 184 (18), 157 (34), 154 (51), 113 (78), 104 (15), 95 (24), 91 (26), 78 (27), 77 (36), 71 (55), 69 (51), 43 (100). Anal. Calcd for $C_{11}H_{14}N_2OSe$: C, 49.08; H, 5.24; N, 10.41. Found: C, 49.16; H, 5.13; N, 10.61.

2-Methyl-6-[1-(phenylseleno)ethyl]-5,6-dihydro-4*H*-1,3,4-oxadiazine (3c): oil; ^1H NMR δ 7.6-7.5 (m, 2 H), 7.3-7.2 (m, 3 H), 4.7 (br s, 1 H), 4.3 (ddd, 1 H, J = 3.1, 7.2, 7.8 Hz), 3.4 (quint, 1 H, J = 7.1 Hz), 3.3 (dd, 1 H, J = 3.1, 11.4 Hz), 3.0 (dd, 1 H, J = 7.0, 11.4 Hz), 1.81 (s, 3 H), 1.49 (d, 3 H, J = 7.1 Hz); ^{13}C NMR δ 147.9, 135.0, 128.9, 128.1, 127.7, 78.7, 44.2, 40.4, 18.8, 17.7. MS *m/z* (relative intensity) 284 (M^+, 37), 241 (22), 198 (9), 172 (9), 158 (19), 127 (25), 83 (70), 55 (100), 43 (55), 42 (13). Anal. Calcd for $C_{12}H_{16}N_2OSe$: C, 50.89; H, 5.69; N, 9.89. Found: C, 50.76; H, 5.80; N, 9.84.

1-Acetyl-4-(phenylseleno)-5-phenylpyrazolidine (4b): oil; ^1H NMR δ 7.58-7.45 (m, 2 H), 7.4-7.1 (m, 8 H), 5.14 (d, 1 H, J = 6.2 Hz), 4.55 (br s, 1 H), 3.64 (dt, 1 H, J = 6.2, 8.0 Hz), 3.45 (dd, 1 H, J = 6.2, 12.0 Hz), 2.96 (dd, 1 H, J = 8.0, 12.0 Hz), 2.2 (s, 3 H); ^{13}C NMR δ 171.5, 140.5, 135.1, 129.3, 128.6, 128.3, 127.4, 125.6, 65.6, 54.9, 49.7, 21.4. MS *m/z* (relative intensity) 346 (M^+, 13), 304 (1), 260 (3), 189 (2), 180 (5), 145 (38), 117 (100), 91 (11), 43 (13). Anal. Calcd for $C_{17}H_{18}N_2OSe$: C, 59.13; H, 5.25; N, 8.11. Found: C, 59.06; H, 5.33; N, 8.16.

1-Acetyl-4-(phenylseleno)-5-methylpyrazolidine (4c): oil; ^1H NMR δ 7.6-7.5 (m, 2 H), 7.35-7.2 (m, 3 H), 4.53 (br s, 1 H), 4.11 (quint, 1 H, J = 6.2 Hz), 3.45-3.25 (m, 2 H), 2.92-2.72 (m, 1 H), 2.11 (s, 3 H), 1.32 (d, 3 H, J = 6.2 Hz); ^{13}C NMR δ 170.8, 134.8, 129.1, 128.0, 127.6, 58.6, 54.3, 48.2, 21.4, 18.9. MS *m/z* (relative intensity) 284 (M^+, 31), 241 (16), 198 (7), 172 (11), 158 (13), 117 (4), 83 (100), 78 (11), 77 (8), 55 (28), 43 (25). Anal. Calcd for $C_{12}H_{16}N_2OSe$: C, 50.89; H, 5.69; N, 9.89. Found: C, 50.81; H, 5.74; N, 9.77.

3-Phenyl-4-(phenylseleno)pyrazole (6): mp 95-97 °C; ^1H NMR δ 13.1 (br s, 1 H), 7.78-7.6 (m, 2 H), 7.65 (s, 1 H), 7.4-7.25 (m, 3 H), 7.25-7.08 (m, 5 H); ^{13}C NMR δ 149.5, 142.7, 133.3, 130.3, 129.1, 128.7, 128.4,

128.0, 125.9, 99.0. MS *m/z* (relative intensity) 300 (M^+, 42), 220 (100), 169 (15), 116 (13), 104 (14), 89 (13), 77 (28), 51 (19). Anal. Calcd for $C_{15}H_{12}N_2Se$: C, 60.21; H, 4.04; N, 9.36. Found: C, 60.16; H, 4.12; N, 9.48.

1-Acetyl-3,5-diphenyl-4-(phenylseleno)pyrazolidine (8a): mp 96-98 °C; ^1H NMR δ 7.48-7.02 (m, 15 H), 5.42 (d, 1 H, *J* = 7.6 Hz), 4.66 (d, 1 H, *J* = 12.7 Hz), 4.15 (dd, 1 H, *J* = 9.7, 12.7 Hz), 3.67 (dd, 1 H, *J* = 7.6, 9.7 Hz), 2.21 (s, 3 H); ^{13}C NMR δ 172.3, 140.6, 136.0, 135.0, 129.0, 128.8, 128.5, 127.6, 126.6, 125.8, 70.7, 67.6, 56.2, 21.3. Anal. Calcd for $C_{23}H_{22}N_2OSe$: C, 65.56; H, 5.26; N, 6.65. Found: C, 65.46; H, 5.34; N, 6.72.

1-Acetyl-3-methyl-4-(phenylseleno)-5-phenylpyrazolidine (8b):[22] ^1H NMR δ 7.5-7.41 (m, 2 H), 7.4-7.1 (m, 8 H), 5.14 (d, 1 H, *J* = 7.7 Hz), 4.15 (d, 1 H, *J* = 12.1 Hz), 3.08 (ddq, 1 H, *J* = 6.0, 9.9, 12.1 Hz), 2.97 (dd, 1 H, *J* = 7.7, 9.9 Hz), 2.13 (s, 3 H), 1.16 (d, 3 H, *J* = 6.0 Hz); ^{13}C NMR δ 171.9, 140.7, 135.6, 129.1, 128.5, 128.3, 127.2, 126.7, 125.7, 67.2, 62.4, 57.8, 21.2, 14.7. MS *m/z* (relative intensity) 360 (M^+, 36), 317 (2), 260 (29), 180 (14), 159 (49), 131 (100), 91 (20), 77 (7), 43 (6). Anal. Calcd for $C_{18}H_{20}N_2OSe$: C, 60.17; H, 5.61; N, 7.80. Found: C, 60.28; H, 5.52; N, 7.92. **(9b):** ^1H NMR (C_6D_6) δ 7.38-6.8 (m, 10 H), 5.21 (d, 1 H, *J* = 8.2 Hz), 4.2 (br s, 1 H), 3.42 (dd, 1 H, *J* = 5.9, 8.2 Hz), 3.05 (quint, 1 H, *J* = 6.6 Hz), 2.10 (s, 3 H), 1.0 (d, 3 H, *J* = 6.7 Hz). ^{13}C NMR (C_6D_6) δ 185.0, 141.4, 136.8, 129.1, 127.6, 126.8, 125.5, 65.6, 57.9, 57.1, 21.5, 15.4.

1-Acetyl-3-phenyl-4-(phenylseleno)-5-methylpyrazolidine (8c): oil; ^1H NMR δ 7.48-7.03 (m, 10 H), 4.55-4.3 (m, 2 H), 3.98 (dd, 1 H, *J* = 9.8, 12.4 Hz), 3.26 (dd, 1 H, *J* = 7.5, 9.8 Hz), 2.13 (s, 3 H), 1.38 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR δ 171.6, 136.0, 135.4, 129.1, 128.8, 128.6, 128.4, 127.4, 69.5, 61.0, 54.9, 21.5, 19.2. MS *m/z* (relative intensity) 360 (M^+, 15), 200 (18), 198 (92), 159 (84), 145 (21), 131 (100), 117 (15), 91 (46), 77 (20), 43 (20). Anal. Calcd for $C_{18}H_{20}N_2OSe$: C, 60.17; H, 5.61; N, 7.80: Found: C, 60.16; H, 5.68; N, 7.73.

1-Acetyl-3,5-dimethyl-4-(phenylseleno)pyrazolidine (8d): mp 51-52 °C; ^1H NMR δ 7.63-7.55 (m, 2 H), 7.38-7.21 (m, 3 H), 4.14 (dq, 1 H, *J* = 6.3, 7.9 Hz), 4.02 (br s, 1 H), 3.0-2.81 (m, 1 H), 2.62 (dd, 1 H, *J* = 8.1, 9.9 Hz), 2.08 (s, 3 H), 1.31 (d, 3 H, *J* = 6.3 Hz), 1.18 (d, 3 H, *J* = 6.2 Hz); ^{13}C NMR δ 171.2, 135.7, 129.1, 128.3, 127.1, 61.6, 60.8, 56.5, 21.2, 19.0, 15.0. MS *m/z* (relative intensity) 298 (M^+, 66), 255 (18), 198 (41), 196 (21), 183 (11), 157 (11), 125 (12), 117 (13), 97 (100), 85 (23), 83 (69), 69 (97), 43 (67), 41 (61). Anal. Calcd for $C_{13}H_{18}N_2OSe$: C, 52.53; H, 6.10; N, 9.42. Found: C, 52.61; H, 6.19; N, 9.31.

2-Methyl-5-phenyl-6-[1-(phenylseleno)ethyl]-5,6-dihydro-4*H*-1,3,4-oxadiazine (11): oil; ^1H NMR δ 7.4-7.1 (m, 10 H), 4.7 (br s, 1 H), 4.54 (dd, 1 H, *J* = 2.1, 8.1 Hz), 3.87 (d, 1 H, *J* = 8.1 Hz), 3.18 (dq, 1 H, *J* = 2.1, 7.1 Hz), 1.95 (s, 3 H), 1.37 (d, 3 H, *J* = 7.1 Hz); ^{13}C NMR δ 148.9, 134.3, 129.2, 129.0, 128.8, 128.7, 128.2, 127.5, 82.8, 57.1, 38.7, 18.7, 15.0. MS *m/z* (relative intensity) 360 (M^+, 15), 317 (2), 203 (23), 198 (52), 159 (22), 131 (100), 104 (35), 91 (21), 77 (19). Anal. Calcd for $C_{18}H_{20}N_2OSe$: C, 60.17; H, 5.61; N, 7.80. Found: C, 60.24; H, 5.55; N, 7.88.

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