Synthesis of Selenium-Substituted Pyrroles and Pyrazol-3-ones

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Abstract: An approach to the synthesis of 4-(phenylseleno)pyrroles, 4-(phenylseleno)pyrazol-3-ones, and 4-(1,3-benzoselenazol-2-ylthio)pyrazol-3-ones is described. Their formation passes through hydrazonic intermediates obtained by the reaction between 1,2-diaza-1,3-butadienes and 1-(phenylseleno)ketones, phenylselenol, or 2-mercaptobenzoselenazole, respectively.

Key words: 1,2-diaza-1,3-butadienes, Michael additions, selenium, pyrroles, pyrazoles

Pyrroles are ubiquitous heterocycles as they occur in many naturally and biologically active compounds, such as porphyrins, phthalocyanines, alkaloids, and vitamin B_{12}.[1] Furthermore, a variety of synthetic pyrrolo derivatives are of pharmaceutical or phytopharmaceutical relevance.[1] Among these, heterosubstituted pyrroles represent an important subclass, both as synthons[2] and themselves as functionalized heterocycles. On the other hand, pyrazoles often recur in organic, biological, and medicinal chemistry, and they have been applied also in the analytical and agricultural fields.[3,4]

In recent years, Attanasi and co-workers have addressed their interest in developing new synthetic strategies to reach polyfunctionalized pyrroles[5,6] and pyrazoles,[5,7] starting from 1,2-diaza-1,3-butadienes and various nucleophiles.

At the same time, Tiecco and collaborators have turned their attention to the chemistry of organoselenium compounds.[8a–e] These compounds are useful and powerful reagents to effect nonconventional conversions of functional groups under mild reaction conditions.[8f–i]

Considering the actual growing interest on the biochemical and pharmacological properties of organoselenium compounds and their potential use as therapeutic and chemopreventive agents[9] we have designed a procedure to prepare Se-substituted pyrroles and pyrazol-3-ones,[10,11] starting from 1,2-diaza-1,3-butadienes and Se-containing nucleophiles.

The first experiments were carried out with 1,2-diaza-1,3-butadiene **1a** and 1-(phenylseleno)acetone[12] (**2a**) or 1-phenyl-2-(phenylseleno)ethanone[12] (**2b**) in the molar ratio of 1:1, in tetrahydrofuran at room temperature, with a catalytic amount of sodium hydride. The β-(phenylseleno)hydrazones **3a**,**b** were thus obtained (path a, Scheme 1, Table 1).[13] Under the same experimental conditions, compounds **1b**,**c** with **2a**,**b** gave complicated mixtures.

The same reaction between 1,2-diaza-1,3-butadienes **1a**,**b** and 1-(phenylseleno)ketones **2a**,**b** in the molar ratio of 2:1, with a stoichiometric amount of sodium hydride, directly produced 4-(phenylseleno)pyrroles **4a–c** in good yields.[14] Under these conditions, the concomitant formation of the 2-oxohydrazonic byproducts **5a**,**b** also occurred (path b, Scheme 1, Table 1).[14,15] All attempts to obtain pyrazoles **4** from hydrazones **3a**,**b** failed, probably because of the poor stability of compounds **3**.

In agreement with our previous findings,[5,6] the formation of hydrazones **3** is due to the preliminary 1,4-addition

Table 1 β-(Phenylseleno)hydrazones **3a**,**b**, 4-(Phenylseleno)pyrroles **4a–c**, and 2-Oxohydrazones **5a**,**b**

1	R^1	R^2	R^3	**2**	R^4	**3**[a]	Yield (%)[b]	Time (h)[c]	**4**[e]	Yield (%)[b]	Time (h)[c]	**5**	Yield (%)[b]
1a	Et	Me	NH_2	**2a**	Me	**3a**	74	1.0	**4a**	70	8.0	**5a**	22
1b	Me	Et	NH_2	**2a**	Me	[d]			**4b**	71	6.0	**5b**	23
1a	Et	Me	NH_2	**2b**	Ph	**3b**	68	1.5	**4c**	59	8.0	**5a**	21

[a] Products obtained starting from **1a–c/2a–c** (2:1), THF, NaH (cat.), r.t. (path a, Scheme 1).
[b] Yield of pure isolated products based on starting **2**.
[c] Time of disappearance of the starting **2**.
[d] The reaction gave a complicated mixture.
[e] Products obtained from **1a–c/2a–c** (2:1), THF, NaH (1 equiv), r.t. (path b, Scheme 1).

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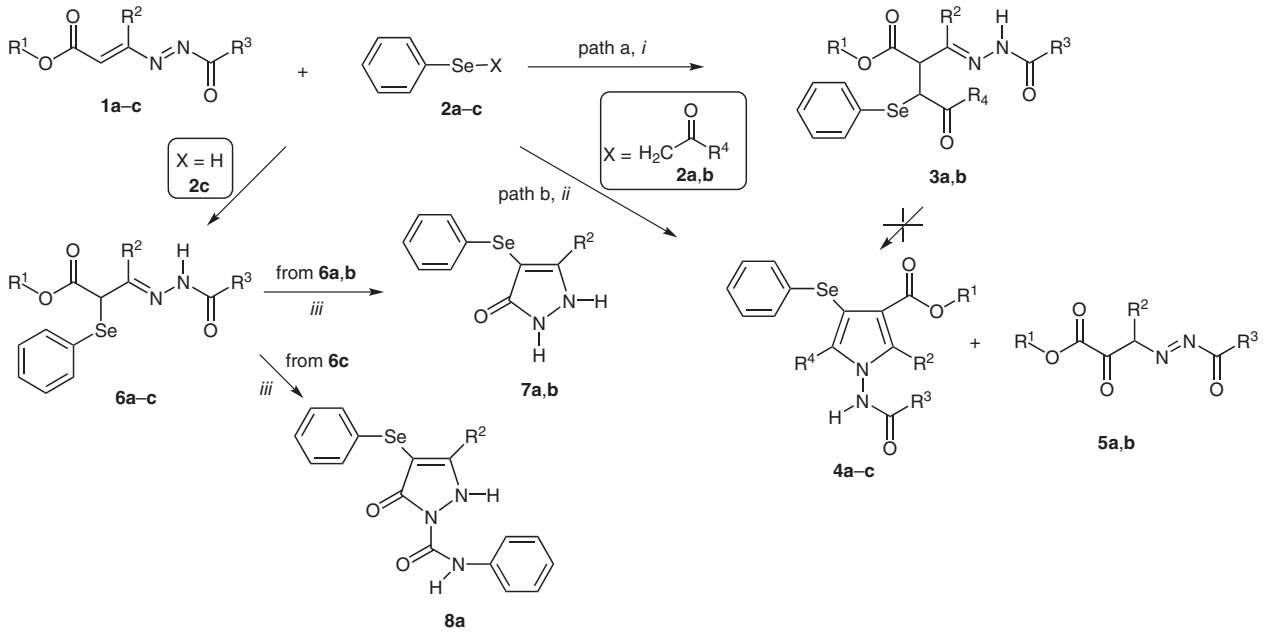


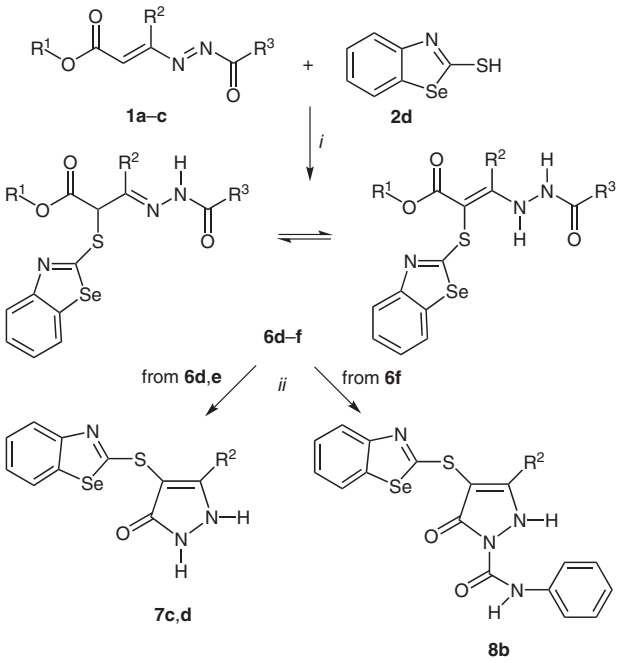
Scheme 1 Synthesis of β-(phenylseleno)hydrazones **3a**,**b**, 4-(phenylseleno)pyrroles **4a**–**c**, 2-oxohydrazones **5a**,**b**, α-(phenylseleno)hydrazones **6a**–**c**, and 4-(phenylseleno)pyrazol-3-ones **7a**,**b**, **8a**. *Reagents and conditions*: (*i*) molar ratio **1a**–**c**/**2a**–**c** = 2:1, THF, NaH (cat.), r.t.; (*ii*) molar ratio **1a**–**c**/**2a**–**c** = 2:1, THF, NaH (1 equiv), r.t.; (*iii*) THF–MeOH (1:1), NaH (1 equiv), r.t.

(Michael-type) by the activated methylene group of **2a**,**b** to the heterodiene system of the conjugated azoalkene **1**. The subsequent intramolecular attack by the C=N nitrogen at the ketonic carbonyl group produces the pyrrole ring closure (**4**) by loss of a water molecule.

With the aim to synthesize new 4-selenium-substituted-pyrazol-3-ones, we have examined the reaction between 1,2-diaza-1,3-butadienes **1a**–**c** and phenylselenol **2c**. The reaction was carried out in tetrahydrofuran at room temperature providing α-(phenylseleno)hydrazones **6a**–**c** in good yields by means of 1,4-addition of the phenylselenol to the heterodiene system of **1** (Scheme 1, Table 2).[16]

Hydrazonic intermediates **6a**–**c** can be easily converted into the corresponding 4-(phenylseleno)-pyrazol-3-ones **7a**,**b** and **8a** by treatment with a stoichiometric amount of sodium hydride in tetrahydrofuran–methanol (1:1) at room temperature (Scheme 1, Table 2).[17] The closure of the pyrazolone ring is due to the base-promoted intramolecular nucleophilic attack of the hydrazonic nitrogen at the ester group, with loss of an alcohol molecule. The formation of 2-N-unsubstituted 4-(phenylseleno)pyrazol-3-ones **7a**,**b** took place by the base-promoted cleavage of the aminocarbonyl group linked to the nitrogen in the position 2 of the pyrazole ring.

Based on these results, we have enlarged our studies to the reaction between 1,2-diaza-1,3-butadienes **1a**–**c** and 2-mercaptobenzselenazole **2d**. The reaction was carried out in tetrahydrofuran at room temperature obtaining α-(1,3-benzoselenazol-2-ylthio)hydrazones **6d**–**f**, by attack of the sulfur atom at the terminal carbon of the azo–ene system (Scheme 2).[15] Yields and reaction times are given in Table 2.



Scheme 2 Synthesis of α-(1,3-benzoselenazol-2-ylthio)hydrazones **6d**–**f** and 4-(1,3-benzoselenazol-2-ylthio)pyrazol-3-ones **7c**,**d**, **8b**. *Reagents and conditions*: *i*, THF, r.t.; *ii*, THF–MeOH (1:1), NaH (1 equiv), r.t.

The conversion of hydrazones **6d**–**f** into the corresponding hydrazino-forms was observed directly in the NMR tube, using DMSO-d_6 as solvent, after 168 hours. α-(1,3-Benzoselenazol-2-ylthio)hydrazones **6d**–**f** were converted in excellent yields into 4-(1,3-benzoselenazol-2-ylthio)pyrazol-3-ones **7c**,**d** and **8b**, by treatment with a stoichiometric amount of sodium hydride, in tetrahydro-

Table 2 α-(Phenylseleno)hydrazones **6a–c**, α-(1,3-Benzoselenazol-2-ylthio)hydrazones **6d–f**, 4-(Phenylseleno)pyrazol-3-ones **7a**,**b**, **8a**, and 4-(1,3-Benzoselenazol-2-ylthio)pyrazol-3-ones **7c**,**d**, **8b**

1	R^1	R^2	R^3	2	6	Yield (%)[a]	Time (h)[b]	7	Yield (%)[c]	Time (h)[d]	8	Yield (%)[c]	Time (h)[d]
1a	Et	Me	NH_2	**2c**	**6a**	83	18.0	**7a**	81	0.2			
1b	Me	Et	NH_2	**2c**	**6b**	72	24.0	**7b**	94	0.3			
1c	Me	Me	NHPh	**2c**	**6c**	57	24.0				**8a**	78	0.1
1a	Et	Me	NH_2	**2d**	**6d**	93	0.1	**7c**	99	0.2			
1b	Me	Et	NH_2	**2d**	**6e**	95	0.2	**7d**	95	0.1			
1c	Me	Me	NHPh	**2d**	**6f**	85	0.1				**8b**	97	0.2

[a] Yield of pure isolated products based on 1,2-diaza-1,3-butadienes **1**.
[b] Time of disappearance of the starting compounds **1**.
[c] Yield of pure isolated products based on hydrazones **6**.
[d] Time of disappearance of the starting compounds **6**.

furan–methanol (1:1; Scheme 2, Table 2),[17] according to the same base-promoted mechanism described for the synthesis of **7a**,**b** and **8a**. Also in this case, the base-promoted cleavage of the aminocarbonyl group linked to the nitrogen in the position 2 of the pyrazole ring took place, producing 2-N-unsubstituted 3-oxo-pyrazoles **7a**,**b**.

In conclusion, this work confirms once again the versatility of 1,2-diaza-1,3-butadienes in the construction of highly functionalized heterocyclic systems.[5–7] Furthermore, in consideration of the bioactive importance of organoselenium compounds,[9] the presently described reactions between the above-mentioned 1,2-diaza-1,3-butadienes and some selenium-containing nucleophiles offer a facile access to new Se-substituted pyrroles and pyrazol-3-ones, not easily accessible by other methods.

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(12) (a) **Synthesis of the α-Seleno Ketones 2a,b**
Compound 2a
Phenyl selenyl chloride (5.0 mmol) was added at r.t. to acetone (4 mL), and the solution was stirred for 30 min. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and evaporated under vacuum. The crude product **2a** (89% yield) was used without further purification.
Compound 2b
The phenylselenyl sulfate was generated from $(PhSe)_2$ (1.7 mmol) and $(NH_4)_2S_2O_8$ (2.3 mmol) in MeCN (20 mL) at 80 °C. After 30 min the 1-phenylethanone (1.7 mmol) was added. The mixture was stirred overnight at the same temperature, then was poured into an aq solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by flash chromatography (elution mixture: PE–CH_2Cl_2 = 85:15) to yield **2b** in 40% yield. (b) Spectral data of **2a** and **2b** are identical to those already described in the literature: Houllemare, D.; Ponthieux, S.; Outurquin, F.; Paulmier, C. *Synthesis* **1997**, 101.

(13) **General Procedure for the Synthesis of β-(Phenylseleno)-hydrazones 3a,b**
To a magnetically stirred solution of 1,2-diaza-1,3-butadiene **1a** as a mixture of *E*/*Z* isomers[18] (1.0 mmol) and 1-(phenylseleno)acetone[12](**2a**) or 1-phenyl-2-(phenylseleno)-ethanone[12] (**2b**, 1.0 mmol) in THF (5 mL) at r.t., a catalytic amount (0.1 mmol) of NaH was added. The reaction mixture was magnetically stirred for 1.0–1.5 h until the disappearance of the starting **1**. β-(Phenylseleno)hydrazones **3a**,**b** were obtained by chromatography on SiO_2 column (elution mixtures: cyclohexane–EtOAc) and by subsequent crystallization from Et_2O-light PE (40–60). The reaction between **1b**,**c** and **2a**,**b** gave complicated mixtures.
Data for Ethyl 2-[*N*-(Aminocarbonyl)ethanehydrazonoyl]-2,5-dideoxy-3-*Se*-phenyl-3-selenopent-4-ulosonate (3a)
Yield 294.5 mg (74%) obtained as yellow solid; mp 148–152 °C. IR (Nujol): ν_{max} = 3420, 3291, 3195, 1765, 1720, 1690 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.08 (t, 3 H, *J* = 6.8 Hz), 1.85 (s, 3 H), 2.32 (s, 3 H), 3.44 (d, 1 H, *J* = 11.6 Hz), 3.97–4.02 (m, 2 H), 4.70 (d, 1 H, *J* = 11.6 Hz), 6.38 (s, 2 H), 7.38–7.47 (m, 5 H), 9.30 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.8 (q), 15.2 (q), 27.7 (q), 49.3 (d), 53.8 (d), 60.8 (t), 125.5 (s), 128.8 (d), 129.1 (d), 136.2 (d), 142.4 (s), 156.9 (s), 169.3 (s), 202.0 (s); during the MS analysis, we have observed only the signals of pyrrole **4a**. Anal. Calcd for $C_{16}H_{21}N_3O_4Se$: C, 48.25; H, 5.31; N, 10.55. Found: C, 48.19; H, 5.39; N, 10.63.

(14) **General Procedure for the Synthesis of 4-(Phenylseleno)-pyrroles 4a–c and 2-Oxohydrazones 5a,b**
To a magnetically stirred solution of 1,2-diaza-1,3-butadienes **1a–c** as a mixture of *E*/*Z* isomers[18] (2.0 mmol) and 1-(phenylseleno)acetone[12] (**2a**, 1.0 mmol) or 1-phenyl-2-(phenylseleno)ethanone[12] (**2b**, 1.0 mmol) in THF (5 mL) at r.t., a stoichiometric amount (1.0 mmol) of NaH was added. The reaction mixture was magnetically stirred for 6.0–8.0 h until the disappearance of the starting **1**. 4-(Phenylseleno)pyrroles **4a–c** and 2-oxohydrazones[14] **5a**,**b** were separated by chromatography on SiO_2 column (elution mixtures: cyclohexane–EtOAc), and they were crystallized from Et_2O-light PE (40–60) or EtOAc–light PE (40–60), respectively.
Ethyl 1-[(Aminocarbonyl)amino]-2,5-dimethyl-4-(phenylseleno)-1*H*-pyrrole-3-carboxylate (4a)
Yield 266.5 mg (70%) obtained as light yellow solid; mp 182–184 °C. IR (Nujol): ν_{max} = 3518, 3374, 3193, 1727, 1704 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.04 (t, 3 H, *J* = 7.2 Hz), 2.10 (s, 3 H), 2.28 (s, 3 H), 4.03 (q, 2 H, *J* = 7.2 Hz), 6.38 (s, 2 H), 7.15–7.19 (m, 2 H), 7.49–7.53 (m, 2 H), 7.73–7.75 (m, 1 H), 9.29 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 10.8 (q), 13.9 (q), 14.2 (q), 58.8 (t), 98.5 (s), 110.3 (s), 118.7 (s), 125.3 (s), 128.2 (d), 128.8 (d), 134.2 (s), 145.9 (d), 156.9 (s), 164.3 (s). MS: *m*/*z* (%) = 383 (23) [M^+ + 3], 381 (100) [M^+ + 1], 379 (57) [M^+ – 1], 378 (21) [M^+ – 2], 377 (22) [M^+ – 3], 375 (2) [M^+ – 5]. Anal. Calcd for $C_{16}H_{19}N_3O_3Se$: C, 50.53; H, 5.04; N, 11.05. Found: C, 50.48; H, 5.21; N, 10.96.

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(16) **General Procedure for the Synthesis of α-(Phenylseleno)-hydrazones 6a–c and α-(1,3-Benzoselenazol-2-ylthio)-hydrazones 6d–f**
A solution of 1,2-diaza-1,3-butadienes **1a–c** as a mixture of *E*/*Z* isomers[18] (1.0 mmol) and phenylselenol(**2c**) or 2-mercaptobenzselenazole (**2d**, 1.0 mmol) in THF (5 mL) was magnetically stirred at r.t., for 0.1–24.0 h until the disappearance of the starting **1**. Hydrazones **6a–c** were obtained by chromatography on SiO_2 column (elution mixtures: cyclohexane–EtOAc) and by subsequent crystallization from Et_2O–light PE (40–60), while hydrazones **6d–f** were crystallized from Et_2O–light PE (40–60), after the evaporation of the reaction solvent. The conversion of α-(1,3-benzoselenazol-2-ylthio)hydrazones **6d–f** into the corresponding hydrazino forms occurred in one week, directly in the NMR tube, using DMSO-d_6 as solvent.
Methyl 3-[(Aminocarbonyl)hydrazono]-2-(phenylseleno)-pentanoate (6b)
Yield 247.5 mg (72%) obtained as white solid; mp 124–126 °C. IR (Nujol): ν_{max} = 3454, 3299, 3191, 1793, 1697 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 0.93 (t, 3 H, *J* = 7.6 Hz), 2.33–2.38 (m, 2 H), 3.60 (s, 3 H), 4.94 (s, 1 H), 6.18 (br s, 2 H), 7.30–7.32 (m, 3 H), 7.54–7.56 (m, 2 H), 9.44 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) : δ = 9.6 (q), 21.0 (t), 50.1 (d), 52.5 (q), 128.1 (s), 128.2 (d), 129.1 (d), 134.1 (d), 145.8 (s), 156.8 (s), 169.8 (s). MS: *m*/*z* (%) = 345 (8)[M^+ + 3], 343 (35) [M^+ + 1], 341 (17) [M^+ – 1], 340 (6) [M^+ – 2], 339 (6) [M^+ – 3], 337 (1) [M^+ – 5], 317 (3), 315 (15), 313 (9), 312 (4), 311 (4), 270 (6), 268 (30), 266 (15), 265 (6), 264 (6), 262 (2), 186 (100). Anal. Calcd for $C_{13}H_{17}N_3O_3Se$: C, 45.62; H, 5.01; N, 12.28. Found: C, 45.48; H, 5.17; N, 12.41.
Ethyl 3-[(Aminocarbonyl)hydrazono]-2-(1,3-benzoselenazol-2-ylthio)butanoate (Hydrazono Form of 6d)
Yield 372.5 mg (93%) obtained as white solid; mp 144–146 °C. IR (Nujol): ν_{max} = 3463, 3313, 3200, 1790, 1692 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.20 (t, 3 H, *J* = 7.2 Hz), 1.98 (s, 3 H), 4.16–4.24 (m, 2 H), 5.51 (s, 1 H), 6.28 (br s, 2 H), 7.29 (t, 1 H, *J* = 8.0 Hz), 7.44 (t, 1 H, *J* = 8.0 Hz), 7.78 (d, 1 H, *J* = 7.2 Hz), 8.04 (d, 1 H, *J* = 6.8 Hz), 9.55 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) : δ = 13.9 (q), 14.5 (q), 57.4 (t), 61.9 (d), 122.5 (d), 124.6 (d), 125.3 (d), 126.4

(d), 138.3 (s), 140.5 (s), 153.6 (s), 156.6 (s), 166.1 (s), 167.5 (s); MS: *m/z* (%) = 400 (1) [M$^+$ + 3], 398 (5) [M$^+$ + 1], 396 (2) [M$^+$ – 1], 397 (1) [M$^+$ – 2], 396 (1) [M$^+$ – 3], 328 (9), 326 (45), 324 (19), 323 (8), 322 (8), 320 (1), 313 (31), 311 (100), 309 (60), 308 (24), 307 (23), 305 (3); Anal. Calcd for $C_{14}H_{16}N_4O_3SSe$: C, 42.11; H, 4.04; N, 14.03. Found: C, 42.31; H, 4.11; N, 14.20.

Ethyl 3-[2-(Aminocarbonyl)hydrazino]-2-(1,3-benzoselenazol-2-ylthio)but-2-enoate (Hydrazino Form of 6d)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.11 (t, 3 H, *J* = 7.2 Hz), 2.30 (s, 3 H), 4.09 (q, 2 H, *J* = 7.2 Hz), 6.28 (s, 2 H), 7.21 (t, 1 H, *J* = 8.0 Hz), 7.39 (t, 1 H, *J* = 8.0 Hz), 7.75 (d, 1 H, *J* = 6.8 Hz), 7.96 (d, 1 H, *J* = 8.0 Hz), 8.60 (s, 1 H), 11.08 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.3 (q), 16.4 (q), 59.9 (t), 82.3 (s), 122.4 (d), 123.7 (d), 125.0 (d), 126.1 (d), 137.8 (s), 156.8 (s), 157.8 (s), 168.7 (s), 172.4 (s), 180.3 (s).

(17) **General Procedure for the Synthesis of 4-(Phenylseleno)-pyrazol-3-ones 7a,b, 8a and 4-(1,3-benzoselenazol-2-ylthio)pyrazol-3-ones 7c,d, 8b**

α-(Phenylseleno)- or α-(1,3-benzoselenazol-2-ylthio)hydrazones (**6a–c** and **6d–f**, 1.0 mmol) were dissolved in a mixture of THF (5 mL)–MeOH (5 mL), and a stoichiometric amount of NaH (1.0 mmol) was added. The reaction mixture was magnetically stirred for 0.1–0.3 h until the disappearance of the starting **6**. Pyrazol-3-ones **7a–d** were obtained from **6a**,**b**,**d**,**e**, respectively, while pyrazol-3-ones **8a**,**b** were obtained from **6c**,**f**, respectively. Products **7a–d** and **8a**,**b** were purified by chromatography on SiO_2 column (elution mixtures: EtOAc–MeOH) and by subsequent crystallization from Et_2O–light PE (40–60).

5-Ethyl-4-(phenylseleno)-1,2-dihydro-3*H*-pyrazol-3-one (7b)

Yield 252.1 mg (94%) obtained as white solid; mp 120–122 °C. IR (Nujol): ν_{max} = 3369, 3116, 1735, 1702, 1636 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.03 (t, 3 H, *J* = 7.6 Hz), 2.35–2.41 (m, 2 H), 7.18–7.32 (m, 4 H), 7.46 (br s, 1 H), 7.57–7.59 (m, 1 H), 8.65 (br s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.1 (q), 20.8 (d), 125.2 (s), 127.7 (d), 128.9 (d), 129.5 (d), 130.8 (s), 158.6 (s), 164.4 (s). MS: *m/z* (%) = 270 (20)[M$^+$ + 3], 268 (100) [M$^+$ + 1], 266 (39) [M$^+$ – 1], 265 (19) [M$^+$ – 2], 264 (21) [M$^+$ – 3], 262 (2) [M$^+$ – 5]. Anal. Calcd for $C_{11}H_{12}N_2OSe$: C, 49.45; H, 4.53; N, 10.48. Found: C, 49.49; H, 4.47; N, 10.41.

4-(1,3-Benzoselenazol-2-ylthio)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (7c)

Yield 309.1 mg (99%) obtained as white solid; mp 192–194 °C. IR (Nujol): ν_{max} = 3398, 3328, 1739, 1697, 1673, 1655 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.02 (s, 3 H), 7.01 (s, 1 H), 7.15 (t, 1 H, *J* = 7.6 Hz), 7.35 (t, 1 H, *J* = 8.0 Hz), 7.69 (d, 1 H, *J* = 8.0 Hz), 7.86 (d, 1 H, *J* = 8.0 Hz), 8.39 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.4 (q), 80.7 (s), 122.1 (d), 123.2 (d), 124.9 (d), 125.8 (d), 138.0 (s), 153.1 (s), 157.3 (s), 165.8 (s), 184.2 (s). MS: *m/z* (%) = 313 (28) [M$^+$ + 3], 311 (100) [M$^+$ + 1], 309 (52) [M$^+$ – 1], 308(18) [M$^+$ – 2], 307(18) [M$^+$ – 3], 305 (1) [M$^+$ – 5]. Anal. Calcd for $C_{11}H_9N_3OSSe$: C, 42.59; H, 2.92; N, 13.54. Found: C, 42.39; H, 3.01; N, 13.28.

3-Methyl-5-oxo-*N*-phenyl-4-(phenylseleno)-2,5-dihydro-1*H*-pyrazole-1-carboxamide (8a)

Yield 292.1 mg (78%) obtained as white solid; mp 144–147 °C. IR (Nujol): ν_{max} = 3342, 3191, 1721, 1687 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.12 (s, 3 H), 6.98 (t, 1 H, *J* = 7.2 Hz), 7.24–7.28 (m, 5 H), 7.45 (br s, 1 H), 7.51–7.68 (m, 4 H), 11.98 (br s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.0 (q), 110.4 (s), 119.1 (d), 122.1 (d), 127.7 (d), 127.8 (d), 129.0 (d), 129.5 (d), 130.8 (s), 139.1 (s), 147.3 (s), 154.2 (s), 164.8 (s). MS: *m/z* (%) = 375 (20) [M$^+$ + 3], 373 (100) [M$^+$ + 1], 371 (41) [M$^+$ – 1], 370 (19) [M$^+$ – 2], 369 (21) [M$^+$ – 3], 367 (3) [M$^+$ – 5]. Anal. Calcd for $C_{17}H_{15}N_3O_2Se$: C, 54.85; H, 4.06; N, 11.29. Found: C, 54.96; H, 4.17; N, 11.36.

4-(1,3-Benzoselenazol-2-ylthio)-3-methyl-5-oxo-*N*-phenyl-2,5-dihydro-1*H*-pyrazol-1-carboxamide (8b)

Yield 417.1 mg (97%) obtained as white solid; mp 246–248 °C. IR (Nujol): ν_{max} = 3351, 3186, 1706, 1683 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.10 (s, 3 H), 7.05 (t, 1 H, *J* = 7.6 Hz), 7.17 (t, 1 H, *J* = 7.6 Hz), 7.32–7.51 (m, 4 H), 7.54 (d, 2 H, *J* = 8.0 Hz), 7.72 (d, 1 H, *J* = 8.0 Hz), 7.88 (d, 1 H, *J* = 8.0 Hz), 12.21 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.4 (q), 81.2 (s), 119.0 (d), 122.2 (d), 122.7 (d), 123.4 (d), 124.9 (d), 125.8 (d), 129.0 (d), 138.0 (s), 138.7 (s), 149.6 (s), 152.8 (s), 157.2 (s), 165.8 (s), 183.3 (s). MS: *m/z* (%) = 430 (14) [M$^+$ + 3], 428 (45) [M$^+$ + 1], 426 (35) [M$^+$ – 1], 425 (12) [M$^+$ – 2], 424 (13) [M$^+$ – 3], 422 (2) [M$^+$ – 5], 313 (15), 311 (55), 309 (26), 308 (10), 307 (10), 305 (2), 215 (100). Anal. Calcd for $C_{18}H_{14}N_4O_2SSe$: C, 50.35; H, 3.29; N, 13.05. Found: C, 50.39; H, 3.31; N, 13.23.

(18) (a) Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 671. (b) Attanasi, O. A.; Filippone, P.; Mei, A.; Santeusanio, S. *Synthesis* **1984**, 873.