Tetrahedron 66 (2010) 8772–8777

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

New reaction of 1*H*-pyrazoles with selenium dioxide: one-pot synthesis of bis(1*H*-pyrazol-4-yl)selenides

Maksym Seredyuk [a], Igor O. Fritsky [a,*], Roland Krämer [b], Henryk Kozłowski [c], Matti Haukka [d], Philipp Gütlich [e]

[a] Department of Chemistry, National Taras Shevchenko University, Volodymyrska Str. 64, 01601 Kiev, Ukraine
[b] Anorganisch-Chemisches-Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
[c] Faculty of Chemistry, University of Wrocław, F.Joliot-Curie 14, 50-383 Wrocław, Poland
[d] Department of Chemistry, University of Joensuu, P.O. Box 111, 80101 Joensuu, Finland
[e] Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität Mainz Staudinger Weg 9, 55122 Mainz, Germany

ARTICLE INFO

Article history:
Received 14 May 2010
Received in revised form 6 August 2010
Accepted 31 August 2010
Available online 9 September 2010

Keywords:
Organoselenium compounds
One-pot synthesis
Crystal structure
Nucleophiles
Heterocycles
Reaction mechanisms

ABSTRACT

A novel reaction between 3- and 3,5-substituted pyrazoles with selenium dioxide proceeds with formation of bis(3*R*,5*R*′-1*H*-pyrazol-4-yl)selenides in high yield. On this basis, an efficient one-pot synthetic procedure has been developed. In the case of the unsubstituted pyrazole a selenonium compound has been obtained. The identity and structure of the isolated selenium derivatives have been confirmed by spectral methods and their molecular structures investigated by X-ray analysis.

1. Introduction

Diaryl selenides are central reagents in organoselenium chemistry.[1] They have long proved to be valuable intermediates and useful synthons in organic synthesis as selenium atoms can readily be removed from organic molecules. Also, diaryl and dihetaryl selenides attract considerable attention due to their remarkable biological activity and their potential as efficient antioxidants,[2] antitumor and anti-infective agents,[2b,c] enzyme inhibitors,[2b,c] glutathione peroxidase mimics,[2a,c] and immunomodulators.[2b] Moreover, diaryl selenides themselves are key intermediates in synthesis of a variety of biologically and pharmaceutically important organoselenium compounds such as selenonium salts, selenoxides, selenimines, and selenide dihalides.[1,2b,3] Dihetalryl selenides have rarely been studied and apart from the evident pharmacological interest, these compounds are promising multidentate ligand systems having both 'hard' and 'soft' binding sites for creation of supramolecular frameworks.[4]

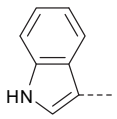
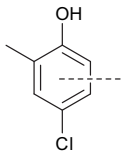
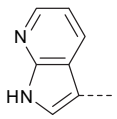
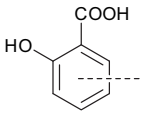
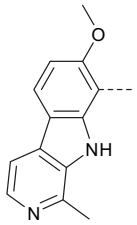
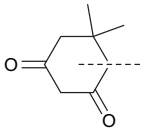
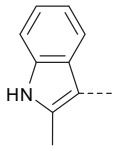
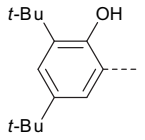
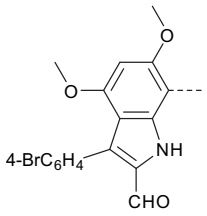
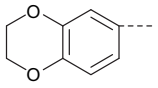
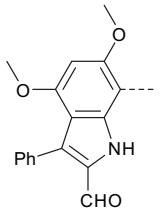
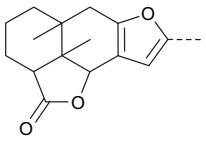
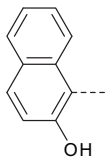
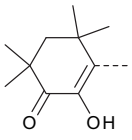
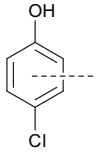
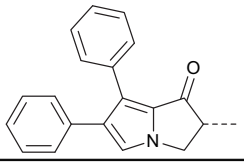
Traditional preparative methods for diaryl selenides include the reactions of metal selenides or selenocyanates with aryl halides, the conversion of aryl halides to the corresponding aryllithium, -magnesium or -tin compounds, and subsequent reaction with diaryl diselenides,[1,2b,5] formation of selenides via diazonium intermediates,[1] the cross-coupling reactions of aryl halides with aryl selenols,[6] or the oxidation of selenols or selenolates.[1,2b] In many cases these methods are laborious and involve multi-step syntheses or have significant limitations or disadvantages. Therefore, in spite of the versatility of available synthetic pathways, there is a high demand for development of convenient and straightforward methods for the synthesis of diaryl selenides.

Direct synthesis of organic selenides from selenium dioxide may be considered as a reasonable alternative approach but is poorly studied. All reported organic selenides prepared from SeO_2 are collected in Table 1. As seen, in several cases this method provides reasonable yields, but mostly selenides are formed only as minor products often requiring laborious separation from precipitated selenium and main products. Among reported direct syntheses of

* Corresponding author. Tel./fax: +38 044 239 33 93; e-mail address: ifritsky@univ.kiev.ua (I.O. Fritsky).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.08.071

Table 1
Reported selenides synthesized accordingly to the equation: $RH+SeO_2 \rightarrow R_2Se$

R	Yield (%)	Ref.	R	Yield (%)	Ref.
	22	7a		—	8b
	44	7b		—	8b
	—	7c		—	8b
	7	7d		25	8c
	31	7e		16	8d
	35	7e		—	8e
	70	8a		45	8f
	—	8b		9	8g

dihetaryl selenides the most investigated is the family of indole derivatives, which form different types of selenides depending on the substituents,[7] while reports on other classes of organic compounds are sporadic.[8] To the best of our knowledge, except our recent studies,[9] pyrazole derivatives were not explored in this type of reaction, however one-step synthesis of pyrazole selenides is attractive in view of their high efficiency toward suppression of carcinoma cells reproduction combined with low toxicity for mammal organisms.[10] Herein, we report the remarkably facile formation of bis(3*R*,5*R*′-1*H*-pyrazol-4-yl)selenides by the reaction of pyrazoles with selenium dioxide.

2. Results and discussion

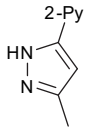
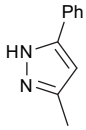
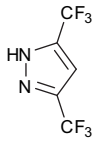
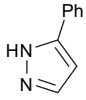
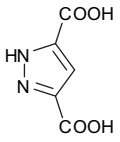
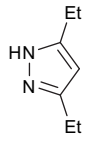
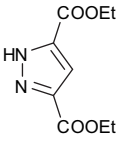
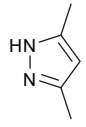
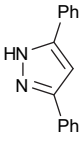
Despite the fact that direct conversion of selenium dioxide to organic selenides was found to be inefficient in most reported cases, reaction with some substituted 1*H*-pyrazole derivatives is an exception to the rule; we have found that it proceeds without selenium sedimentation and results in formation of corresponding selenides in stable high yields.

The initial impetus for an upsurge interest in the reaction was found during an attempt to oxidize the methyl group in 3-methyl-5-(2-pyridyl)-1*H*-pyrazole by SeO_2 in pyridine (taken in 1:1.5 M ratio) to generate a corresponding carboxylic acid. Surprisingly, no acid was formed under these conditions, unlike in the case of 1-methyl-3-(2-pyridyl)-benzene[11] and 4-methyl-6-(2-pyridyl)-pyrimidine,[12] but only the bis(3-methyl-5-(pyridin-2-yl)-1*H*-pyrazol-4-yl)selenide (**1a**) as the sole reaction product was isolated in 64% yield (Table 2). Using the same experimental protocol (1 mol equiv of pyrazole per 1.5 equiv of SeO_2 in refluxing pyridine), the reactivity of a series of pyrazole derivates has been studied (Table 2). The results allowed us to elaborate the general synthetic procedure for bispyrazolyl selenides, in particular for **1b**–**f** (see Table 2 for the chemical formulas), and to elucidate differences in the conversion of different pyrazole derivates. It should be noted, that the chosen ratio between the starting reagents with an excess of SeO_2 was found to be crucial for the formation of the target selenides. Different pyrazole to SeO_2 ratios have been checked in the range from 2:1 to 1:2 and found that the 1:1.5 ratio is optimal. For example, in the case of 1:1 ratio the corresponding selenides were formed in a poor yield.

In all the studied cases the corresponding reaction mixtures and crude products have been subjected to TLC, ESIMS, ^1H, and ^{13}C NMR control. Identity and structure of the isolated selenides were confirmed by a variety of analytical and spectral methods; the molecular structures of **1a**–**d** were investigated by X-ray analysis and are depicted in Fig. 1.

Although we did not conduct any specific studies to elucidate the mechanism of the reaction, on the basis of the obtained structural and ESIMS data we can tentatively propose a reaction pathway from a pyrazole to its selenide depicted in Scheme 1. The first step of the reaction includes a double nucleophilic attack by the C-4 pyrazole carbon on the selenium atom[7b] to afford a selenoxide (**i**), which is also detected in some of the reaction mixtures (Table S1). Further transformation of the oxide includes addition of pyrazole or pyridine with formation of unstable selenonium ions R_2XSe^+ [R, X=3,5-disubstituted-1*H*-pyrazol-4-yl (**ii**′) or X=pyridyl (**ii**″)] (Scheme 1, Table S1), which disappear after drying. Instead, the organic selenide (**iii**) and bispyrazolyl (**iv**′) and pyrazolylpyridine (**iv**″) byproducts are formed as follows from ESIMS spectra of the reaction mixtures. The proposed reaction pathway is confirmed indirectly by the fact that neither selenonium ions nor bispyrazolyl byproduct are formed by treating a bispyrazolyl selenide with pyrazole under the reaction

Table 2
Isolated bis(3*R*,5*R*′-1*H*-pyrazol-4-yl)selenides **1a**–**1f** and tris(1*H*-pyrazol-4-yl)selenonium ethylselenite (**2g**) synthesized accordingly to the equation: $PzH+SeO_2 \rightarrow Pz_2Se$ (Pz_3Se^+), where Pz is pyrazole derivative

Entry	Substrate	Isolated		Yield (%)	Entry	Substrate	Isolated		Yield (%)
		Selenide	Selenonium				Selenide	Selenonium	
1		**1a**	—	64	7		—	**2g**	37
2		**1b**	—	67	8		–[a]	—	—
3		**1c**	—	52	9		–[a]	—	—
4		**1d**	—	62	10		–[a]	—	—
5		**1e**	—	50	11		–[a]	—	—
6		**1f**	—	55					

[a] No organoselenium species were detected in the reaction mixture.

conditions. Furthermore, the ESIMS spectrum of the reaction mixture of bis(3,5-dimethyl-1*H*-pyrazolyl) selenoxide[13] with 3,5-dimethyl-1*H*-pyrazole after boiling in pyridine for 6 h contains peaks of pyrazolylpyridine and **1e** confirming that the selenoxide might be a precursor of **ii** and **iii**, however a more comprehensive study is required to clarify the details of the reaction pathway. We also would like to stress that according to the proposed mechanism the highest yield of the selenide is limited to near 50–67%, with respect to pyrazole.

Earlier two groups reported on aryl selenonium salts synthesized from selenium dioxide in concentrated mineral acids.[8a,b,14] In case of the unsubstituted pyrazole the symmetrical selenonium salt with ethylselenite anion (**2g**) is also a sole product isolated after ethanolic workup, which was investigated by X-ray analysis (Fig. 1), but interestingly no selenonium compounds of 3-methylpyrazole and 3,5-methylpyrazole could be isolated in the solid state. To our opinion differences in the stability of the selenonium compounds in this series might be explained in terms of sterical repulsion between the methyl groups, increasing number of which might cause geometrical distortion of the selenonium ions that make them more inclined toward degradation to selenides.

The course of the reaction is influenced to great extent by electronic nature of the 3,5-substituents. For example, in the case of 3,5-bis(trifluoromethyl)-1*H*-pyrazole no organoselenium species were detected (Table 2), however its structural analog 3,5-dimethyl-1*H*-pyrazole, gave **1e**. Similarly, 1*H*-pyrazole-3,5-dicarboxylic acid, its diethyl ester and 3,5-biphenyl-1*H*-pyrazole are inactive in this reaction (see Table 2). In these four cases ESIMS control of the reaction mixtures revealed the presence of the starting compounds as the only pyrazole-containing species.

The influence of hydrochloric or hydrobromic acid was expected to force the conversion of reagents to higher yield. Nevertheless, the reaction between 3,5-dimethylpyrazole and selenium dioxide in concentrated hydrochloric acid according to the described procedure[8b,c] led to **1f** with a comparable yield (46%). In contrast, an attempt to obtain **1a** from 3-methyl-5-(2-pyridyl)-1*H*-pyrazole in this media was met with no success.

Finally, as well as their mentioned interest for medicine, bis-pyrazolyl selenides can also be used as ligands for supramolecular networks, in which a molecule of the ligand serves as a bidentate bent connector forming polynuclear complexes. The presence of a soft selenium atom in synthesized selenides could allow the coordination to a soft 4*d*- of 5*d*-metal ion and, on the other hand, nitrogen atoms of the pyrazole moieties are good donors for the 3*d*-transition metals.[9]

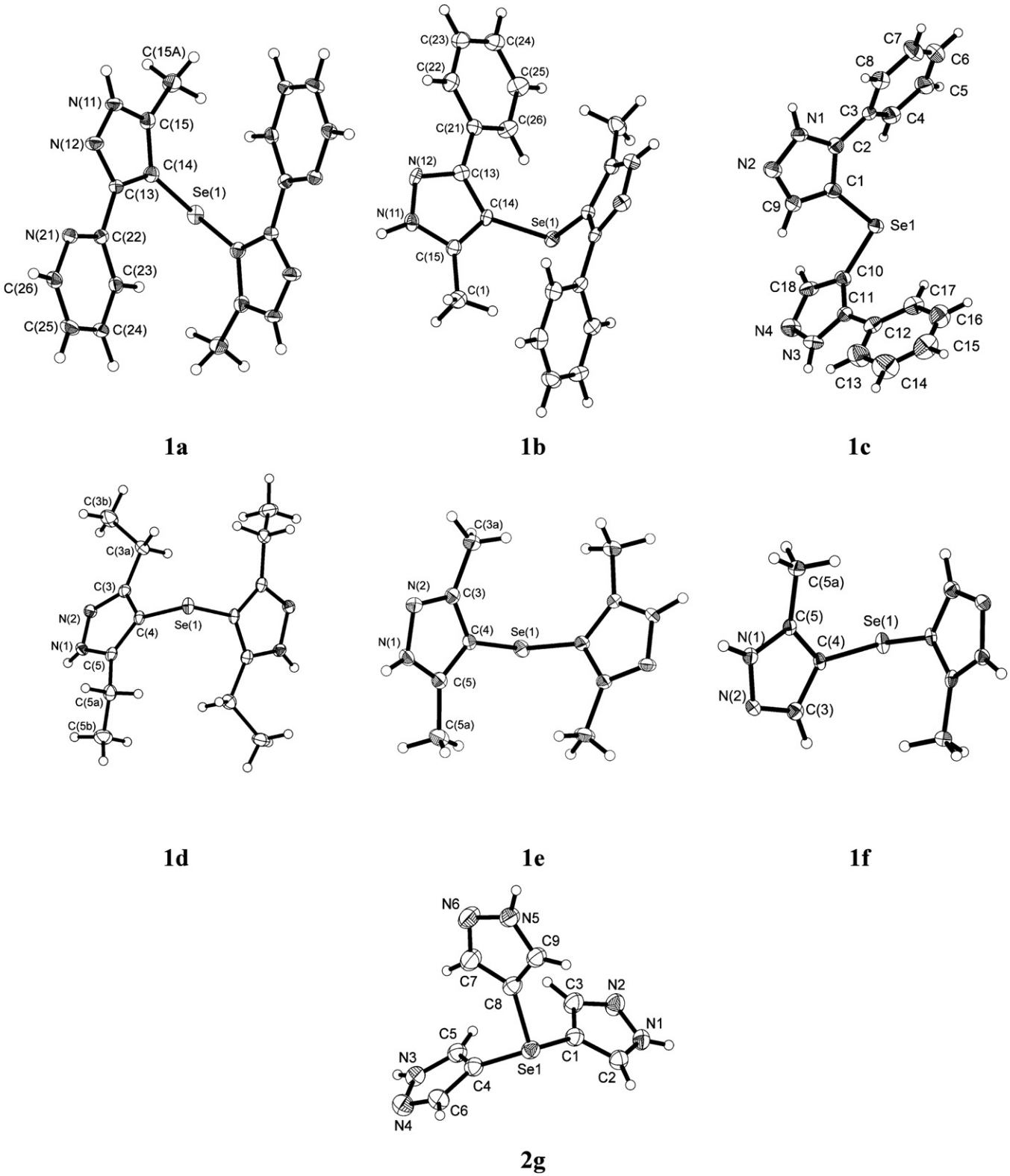
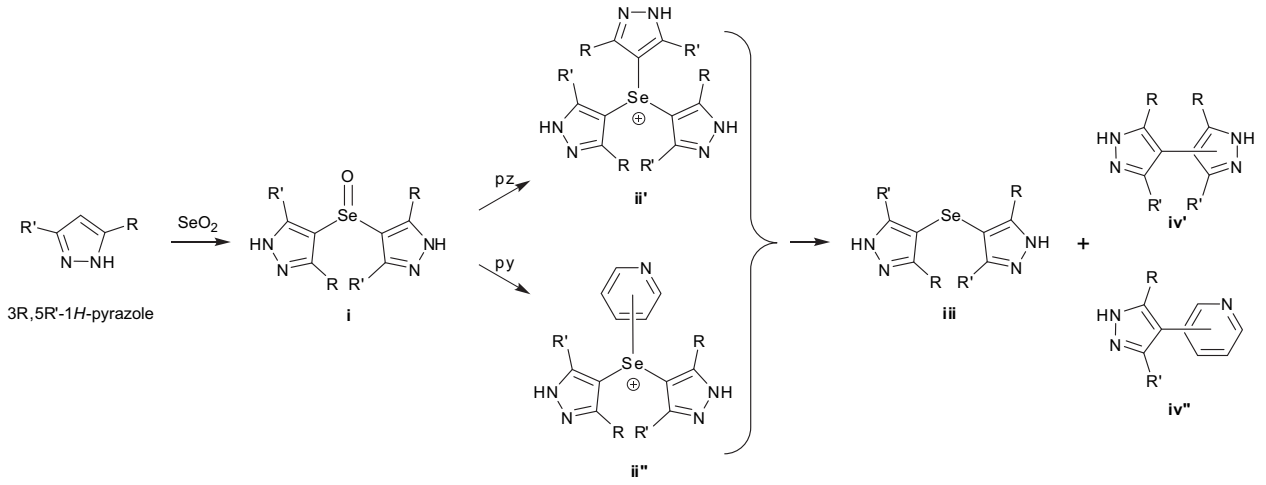


Fig. 1. Molecular structures and numbering schemes for **1a**–**2g** (50% probability ellipsoids). Solvent molecules and inorganic anions are omitted for clarity.



Scheme 1. A proposed reaction pathway from pyrazole to bis(3*R*,5*R*′-1*H*-pyrazol-4-yl)selenide.

3. Conclusion

Summarizing, we have reported a new reaction of 1*H*-pyrazole and its 3- and 3,5-disubstituted pyrazoles with selenium dioxide and established that in the case of dialkyl- or alkylaryl-derivatives it results in the formation of bis(3*R*,5*R*′-1*H*-pyrazol-4-yl)selenides as the main reaction products in good yields, which enhances the pool of available methods for this class of compounds and should find further application in organic synthesis. The obtained compounds appear to be valuable synthetic intermediates for preparation of various heterocylic and organoselenium compounds of pharmaceutical interest, and polynucleating ligands applicable in crystal engineering and molecular magnetism, and the study of reactivity of bispyrazolyl selenides is currently underway in our laboratories. We also are in the process of expanding the scope of this reaction to other heterocyclic systems.

4. Experimental section

4.1. General

All starting materials were purchased from Aldrich or Fluka and used as received.

ESIMS measurements were done on a Finnagan TSQ 700 mass spectrometer. ^{1}H (400 MHz) and ^{13}C (100.63 MHz) NMR spectra were recorded on a Bruker AC-400 spectrometer at 293 K; δ-values are expressed in parts per million relative to an internal reference. FTIR spectra were recorded on a Perkin–Elmer 983 G spectrophotometer, ν_{max} in cm^{-1} (range 400–4000). CHN analysis was done on a Perkin–Elmer 2400 CHN.

X-ray data collection was done on a Bruker AXS CCD Smart 1000 diffractometer with refinement using SHELXL-97.[15] Crystals of **1a**, **1b**, **1d**, **1f** were obtained in the form of salt with inorganic anions by dissolving of the corresponding selenide in a small amount of the corresponding concentrated aqueous acid and further disposal of the obtained solution in a fridge at 4 °C for several days. Crystals of **1c** and **1e** were grown by slow diffusion of ethereal vapors into a vessel with alcoholic solutions of corresponding selenides over one week. Crystals of **2g** were obtained upon dissolving of dried reaction mixture in ethanol and further cooling of the solution in a fridge at 4 °C overnight.

The presented crystallographic data are deposited under CCDC numbers 299920–299924, 773478, 773479 and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*4.1.1. Bis(3-methyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl)selenide (**1a**·MeOH).* Mixture of 2-(3-methyl-1*H*-pyrazol-3-yl)pyridine[16] (15.92 g, 0.10 mol), selenium dioxide (16.70 g, 0.15 mol) and pyridine (50 mL) was refluxed 6 h, after that pyridine was distilled off under reduced pressure. Syrup-like yellow-to-brown residue was treated with 20 mL of NaOH (6.0 g, 0.15 mol) aqueous solution. The obtained yellowish precipitate was filtered off and washed twice with distilled water and recrystallized from hot methanol. Mp: 212–214 °C. ESIMS (rel int.): *m*/*z* 396.7 [M+H, ^{80}Se]$^{+}$ (100%); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.95 (1H br s, N*H* pz), 8.60 (1H, ddd, *J*=0.9, 1.5, 4.9 Hz, py*H*), 7.97 (1H, d, *J*=7.5 Hz, py*H*), 7.75 (1H, td, *J*=1.5, 7.5 Hz, py*H*), 7.32 (1H, ddd, *J*=0.9, 4.9, 7.5 Hz, py*H*), 1.86 (3H, s, C*H*$_3$); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 152.5, 150.8, 148.7, 138.4, 125.8, 124.5, 123.3, 102.3, 13.3; FTIR (KBr, cm^{-1}): 3300 (m), 3124 (s), 2919 (s), 1592 (s), 1463 (s), 1150 (s), 1061 (s), 998 (s), 787 (s), 623 (s), 515 (s). $C_{19}H_{20}N_6OSe$ requires C, 53.4, H, 4.7, N, 19.7. Found C, 53.5, H, 4.6, N, 19.5.

The same method was used for the preparation of **1b**–**f** starting from the corresponding substituted pyrazoles.

*4.1.2. Bis(3-methyl-5-phenyl-1H-pyrazol-4-yl)selenide (**1b**·MeOH).* Recrystallized from methanol as white crystalline powder. Mp: substance has no definite mp, it begins to soften at 130 °C. ESIMS (rel int.): *m*/*z* 395.1 [M+H, ^{80}Se]$^{+}$ (100%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (2H, dd, J^1=1.4 Hz, J^2=2.7 Hz, 3,5H Ph), 7.27 (3H, m, 2,4,6-H Ph), 1.84 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.7, 143.8, 133.4, 129.5, 128.1, 127.1, 100.4, 12.7; FTIR (KBr, cm^{-1}): 3159 (br), 3058 (br), 2921 (s), 2821 (s), 2000–1650 (m), 1562 (s), 1451 (m), 1272 (s), 1038 (s), 966 (s), 774 (s), 695 (s), 520 (s). $C_{21}H_{22}N_4OSe$ requires: C, 59.3, H, 5.2, N, 13.2. Found C, 58.8, H, 4.9, N, 13.2.

*4.1.3. Bis(3-phenyl-1H-pyrazol-4-yl)selenide (**1c**·0.25C_2H_5OH).* Recrystallized from ethanol as white powder. Mp: 201–203 °C. ESIMS (rel int.): *m*/*z* 367.1 [M+H, ^{80}Se]$^{+}$ (100%); ^{1}H NMR (C_2D_5OD, 400 MHz): δ 7.76 (s, 1H, PzH), 7.67 (m, 2H, 3,5-H Ph), 7.36 (m, 3H, 2,4,6-H Ph); ^{13}C NMR (C_2D_5OD, 100 MHz): δ 151.7, 143.8, 133.4, 129.5, 127.1, 100.4, 12.7. $C_{74}H_{62}N_{16}OSe_4$ requires C, 59.0; H, 4.2; N, 14.9. Found C 58.8, H, 4.3, N, 14.8.

*4.1.4. Bis(3,5-diethyl-1H-pyrazol-4-yl)selenide (**1d**).* Recrystallized from ethanol as white powder. Mp: 217–218 °C. ESIMS (rel int.): *m*/*z* 326.2 [M+H, ^{80}Se]$^{+}$ (100%); ^{1}H NMR (DMSO-d_6, 400 MHz):

δ 2.52 (2H, q, J=7.5 Hz, CH_2) 1.00 (3H, t, J=7.5 Hz, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 152.7, 100.9, 21.2, 15.5; FTIR (KBr, cm^{-1}): 3167(br), 3086(m), 3021(s), 2970(s), 2935(s), 2870(s), 1561(s), 1461 (m), 1277(s), 1036(s), 796(m), 498(s). $C_{14}H_{22}N_4Se$ requires C, 51.6, H, 6.8, N, 17.2. Found C, 51.3, H, 6.7, N, 17.2.

*4.1.5. Bis(3,5-dimethyl-1H-pyrazol-4-yl)selenide (**1e**·H_2O).* Recrystallized from methanol as yellowish precipitate. Mp: 232–233 °C. ESIMS ESI (rel int.): m/z 271.0 [M+H, $^{80}Se]^+$ (100%); ^1H NMR (DMSO-d_6, 400 MHz): δ 2.17 (s, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 146.6, 101.5, 12.3; FTIR (KBr, cm^{-1}): 3400 (br), 3173 (s), 3086 (s), 2970 (m), 2870 (s), 1562 (s), 1414 (s), 1297 (s), 1095 (s), 1033 (s), 849 (br), 764 (s), 461 (s). $C_{10}H_{16}N_4OSe$ requires: C, 41.8, H, 5.6, N, 19.5. Found C, 41.5, H, 5.8, N, 19.6.

*4.1.6. Bis(3-methyl-1H-pyrazol-4-yl)selenide (**1f**·$2H_2SO_4$).* Recrystallized from ethanol with several drops of sulfuric acid to obtain colorless well formed crystals. Mp: 280–281 °C (decomp.). ESIMS (rel int.): m/z 243.0 [M+H, $^{80}Se]^+$ (100%); ^1H NMR (D_2O, 400 MHz): δ 7.94 (1H, s, PzH), 2.31 (3H, s, CH_3); ^{13}C NMR (D_2O, 100 MHz): δ 147.7, 138.6, 103.5, 9.7. $C_8H_{14}N_4O_8S_2Se$ requires C, 22.0; H, 3.2; N, 12.8, S, 14.7; Found C 21.9, H 3.4, N, 13.1, S 14.5.

*4.1.7. Tris(1H-pyrazol-4-yl)seleninium ethylselenite (**2g**).* Mixture of 1*H*-pyrazole (6.80 g, 0.10 mol), selenium dioxide (16.70 g, 0.15 mol), and pyridine (50 mL) was heated to boiling that after 30 min led to the formation of colorless oil; refluxing was continued for additional 5.5 h. After cooling the pyridine layer was decanted and residual viscous oil was dissolved in ethanol and subjected into a fridge overnight yielded yellowish crystalline hydroscopic precipitate of **2g**. Mp: 250–251 °C (decomp.). ESIMS (rel int.): m/z 280.1 [M, $^{80}Se]^+$ (100%); ^1H NMR (D_2O, 400 MHz): δ 7.99 (6H, s, 3,5-H Pz), 3.56 (2H, q, J=6.4 Hz, $SeOCH_2$), 1.09 (3H, t, J=6.4 Hz, $SeOCH_2CH_3$); ^{13}C NMR (D_2O, 100 MHz): 136.3 (C-3,5 Pz), 103.6 (C–Se), 57.2 (CH_2), 16.5 (CH_3); FTIR (KBr, cm^{-1}): 3113 (m), 3028 (br), 2896 (m), 2846 (m), 2782 (m), 1532 (s), 1381 (s), 1156 (d), 1028 (s), 923 (d), 854 (s), 613 (s), 417 (s). $C_{11}H_{15}N_6O_3Se_2$ requires C, 30.3, H, 3.2, N, 19.3. Found C, 30.1, H, 3.3, N, 19.2.

Acknowledgements

I.O.F. is grateful to the Deutsche Forschungsgemeinschaft (grant GZ: 436 UKR) for financial support.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.08.071. These include ESIMS and crystallographic data for **1a**–**2g**.

References and notes

1. (a) Klayman, D. L. *Organic Selenium Compounds, Their Chemistry and Biology*; John Wiley: New York, NY, 1973; (b) Krief, A. *Organoselenium Chemistry*; Springer: Berlin, 1988; (c) Krief, A. In *Comprehensive Organometallic Chemistry II*; Abel, E. V., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, NY, 1995; (d) Wirth, T. *Top. Curr. Chem.* **2000**, *208*.
2. (a) Mugesh, G.; Singh, H. B. *Chem. Soc. Rev.* **2000**, *29*, 347–357; (b) Mugesh, G.; du Mont, W.-W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125–2179; (c) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255–6285.
3. (a) Magdesieva, N. N. *Russ. Chem. Rev.* **1988**, *57*, 161–173; (b) Freudendahl, D. M.; Shahzad, S. A.; Wirth, T. *Eur. J. Org. Chem.* **2009**, 1649–1664.
4. Janiak, C. *Dalton Trans.* **2003**, 2781–2804.
5. Beletskaya, I. P.; Sigeev, A. S.; Peregudov, A. S.; Petrovskii, P. V. *Tetrahedron Lett.* **2003**, *44*, 7039–7041.
6. Gujadhur, R. K.; Venkataraman, D. *Tetrahedron Lett.* **2003**, *44*, 81–84.
7. (a) Bergman, J. *Acta Chem. Scand.* **1968**, *22*, 1883–1887; (b) Minakata, S.; Itoh, S.; Komats, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2992–2997; (c) Khan, M. A.; Raees, H. *Z. Naturforsch., B* **1996**, *51*, 1779–1780; (d) Abele, E.; Popelis, J.; Shestakova, I.; Domracheva, I.; Arsenyan, P.; Lukevics, E. *Chem. Heterocycl. Compd.* **2004**, *40*, 742–746; (e) Jones, A. W.; Wahyuningsih, T. D.; Pchalek, K.; Kumar, N.; Black, D. S. *Tetrahedron* **2005**, *61* 10490–10500.
8. (a) Funk, H.; Weiss, W. *J. Prakt. Chem.* **1954**, *1*, 33–40; (b) Funk, H.; Papenroth, W. *J. Prakt. Chem.* **1960**, *4*, 191–196; (c) Paine, T. K.; Weyhermüller, T.; Bothe, E.; Wieghardt, K.; Chaudhuri, P. *Dalton Trans.* **2003**, 3136–3144; (d) Engman, L.; Hellberg, J.; Ishag, C.; Söderholm, S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2095–2101; (e) Abdykalikova, K.; Nikonov, G.; Zamkova, V. *Khim. Prir. Soedin.* **1989**, *2*, 189–193; (f) Laitalainen, T.; Simonen, T.; Kivekas, R.; Klinga, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 333–340; (g) Dannhardt, G.; Steindl, L. *Arch. Pharmacol.* **1986**, *319*, 749–755.
9. (a) Seredyuk, M.; Haukka, M.; Fritsky, I. O.; Kozłowski, H.; Krämer, R.; Pavlenko, V. A.; Gütlich, P. *Dalton Trans.* **2007**, 3183–3194; (b) Seredyuk, M.; Haukka, M.; Pavlenko, V. A.; Fritsky, I. O. *Acta Crystallogr., Sect. E* **2009**, *65*, m1396; (c) Seredyuk, M.; Moroz, Y. S.; Znovjyak, K. O.; Pavlenko, V. A.; Fritsky, I. O. *Acta Crystallogr., Sect. E* **2010**, *66*, m363; (d) Seredyuk, M.; Znovjyak, K. O.; Moroz, Y. S.; Pavlenko, V. A.; Fritsky, I. O. *Acta Crystallogr., Sect. E* **2010**, *66*, m527.
10. (a) Dorofeenko, Y.G.; Zubarevich, L.A.; Zubarevich, V.L.; Zubarevich, Y.L.; Sanotskii, I.V.; Gryaznov, L.E. Russ. Patent 2185819, 2002; (b) Krylova, M. N.; Kozlova, M. B.; Arkhangel'skaya, A. V.; Dorofeenko, A. I. *Pharm. Chem. J.* **1991**, *25*, 110–113.
11. Sakamoto, T.; Sakasai, T.; Yamanaka, H. *Chem. Pharm. Bull.* **1980**, *28*, 571–577.
12. Strotmeyer, K. P.; Fritsky, I. O.; Ott, R.; Pritzkow, H.; Krämer, R. *Supramol. Chem.* **2003**, *15*, 529–547.
13. Obtained by treating bis(3,5-dimethyl-1*H*-pyrazolyl)selenide (**1e**) with hydrogen peroxide.
14. Epifanov, V. S.; Syskova, V. P.; Konyakhina, L. V.; Nosov, V. N.; Kulikova, L. Y. *Zh. Org. Khim.* **1982**, *28*, 878–881.
15. Sheldrick, G. M. *SHELXS97 and SHELXL97*; University of Göttingen: Germany, 1997.
16. Yu, W.-S.; Cheng, C.-C.; Cheng, Y.-M.; Wu, P.-C.; Song, Y.-H.; Chi, Y.; Chou, P.-T. *J. Am. Chem. Soc.* **2003**, *125*, 10800–10801.