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Selenoacetalyzation of 4-Formylpyrazoles in the Presence of Trimethylchlorosilane

Lyubov K. Papernaya, Alexandra A. Shatrova, Ekaterina P. Levanova, Alexandr I. Albanov, Lyudmila V. Klyba, Elena V. Rudyakova, and Galina G. Levkovskaya

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky Street, 664033, Irkutsk, Russia

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ABSTRACT: *The reaction of 3,5-dimethyl-4-formylpyrazoles, bearing various substituents at N-1 atom, with propane-1,3-diselenol and 2-hydroxypropane-1,3-diselenol in the presence of TMSCl proceeds without heating to chemoselectively give hitherto unknown 2-(pyrazol-4-yl)-1,3-diselenane hydrochlorides in high yields. The latter are easily transformed to the corresponding free bases—2-(pyrazol-4-yl)-1,3-diselenanes. The ^{15}N chemical shifts of the pyrazole ring in 2-(pyrazol-4-yl)-1,3-diselenanes obtained by 2D HMBC-gp (^{15}N-^{1}H) technique are indicative of the N-2 atom protonation in hydrochlorides.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–10, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21113

INTRODUCTION

Selenoacetals represent universal reagents in organic synthesis and play a pivotal role in the development of organoselenium and theoretical chemistry [1–7]. However, at the present time, a limited number of selenoacetal derivatives, especially cyclic ones, are known [1–3,5–12]. The methods for selenoacetals preparation are laborious and multistage; they often require hardly available and unstable starting selenols. For example, the synthesis of 1,3-diselenanes has not gained an acceptance due to unavailability and extreme instability of propane-1,3-diselenol and its derivatives.

It is also known that propane-1,3-diselenol interacts with aliphatic aldehydes in strongly acidic media [7,11], and only with benzaldehyde and some other aliphatic aldehydes it reacts under milder conditions, that is, in the presence of $ZnCl_2$ [1–3,12].

Alternative methods for the preparation of 1,3-diselenanes involve sparse protocols based on the reaction of substituted 1,2-diselenolanes with dimethyldiazomethane phosphonate in the presence of $BF_3 \bullet (C_2H_5)_2O$ [8, 13]. UV-irradiation of 1,3-bis(alkylseleno)allenes [9] or their reactions with diphenyldiazomethane [10]. Open-chained selenoacetals were known to be synthesized from aldehydes and diphenyldiselenide [14, 15]. It was also reported on 2-phenyl-1,3-diselenan-5-one and its reduced analog 2-phenyl-1,3-diselenan-5-ol, but methods for their preparation were multistage and did not involve the corresponding diselenols [6]. It should be emphasized that the methods reported only cover limited representatives of aromatic selenoacetals, predominantly those bearing the phenyl substituents.

Heteryl-1,3-diselenanes were unknown until our investigations. Earlier, we synthesized 2-(1,3-diselenan-2-yl)thiophenes in 12%–57% yields from

Correspondence to: Lyubov K. Papernaya; e-mail: papern@irioch.irk.ru.

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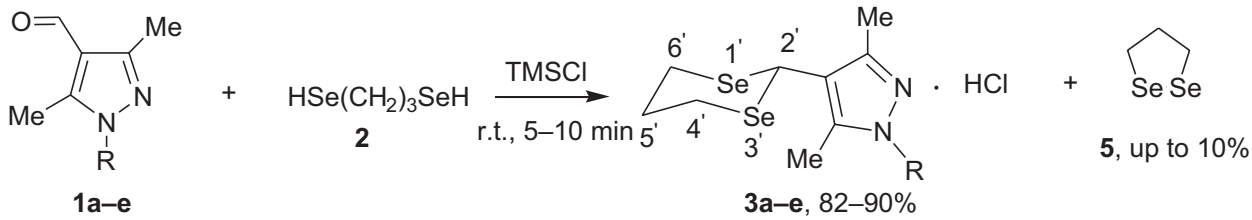


SCHEME 1 Synthesis of 2-(pyrazol-4-yl)-1,3-diselenane hydrochlorides **3a–e**.

propane-1,3-diselenol and thiophene carbaldehydes [16]. It was found that even under mild conditions [–5 to 5°C, trimethylchlorosilane (TMSCl) as a catalyst], selenoacetalyzation was accompanied by the formation of oligomeric products.

RESULTS AND DISCUSSION

In the present work, we have studied for the first time the reaction of formylpyrazoles **1a–e** with propane-1,3-diselenol 2 and 2-hydroxypropane-1,3-diselenol **6**, which became available owing to the preparation methods developed in our earlier study [16]. TMSCl was used as a catalyst.

It should be underlined that the direction of the reaction between pyrazole carbaldehydes and diselenols was not obvious. So, we found that the reaction of pyrazole carbaldehydes with mercaptoethanol in the presence of TMSCl afforded predominantly open-chained bis(2-hydroxyethyl)dithioacetals even under equimolar ratio of the reagents [17], unlike similar reactions of aromatic aldehydes leading to 1,3-oxathiolanes [18].

Here, we have shown that the interaction of propane-1,3-diselenol **2** with aldehydes **1a–e** under equimolar ratio in four- to sixfold excess of TMSCl at room temperature (5–10 min) furnishes novel heterocyclic compounds, 4-(1,3-diselenan-2-yl)-pyrazoles, formed as hydrochlorides **3a–e** in 82%–90% yields (Scheme 1). The reaction was accompanied by the exothermic effect.

Taking into account the results of previously studied reactions of bisfunctional mercaptoethanol with aldehydes **1** [17] and nitrobenzaldehydes [19], we have selected the optimal conditions for the reactions of diselenol **2** with formylpyrazoles **1**. To diminish the possibilities of side transformations of the starting diselenol **2**, the reaction mixtures were not heated and, therefore, all reactions were conducted at room temperature. The application of CH_2Cl_2 as an additional solvent (along with TMSCl) did not practically affect the yield of diselenane **3e**

TABLE 1 Optimization of Se–Se Acetalization Conditions in the Reaction of Aldehyde **1e** and Diselenol **2** in the Presence of TMSCl

Entry	*Molar Ratio* **1e:2:** *TMSCl*	*Solvent (mL)*	*Yield* **3e** *(%)*[a,b]
1.	1:1:6	Neat	87
2.	1:1:4	Neat	86
3.	1:1:1	Neat	69
4.	1:1:4	CH_2Cl_2, 2	88

[a]Yield refers to isolated pure products.
[b]Reaction time is 5 min, room temperature.

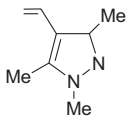
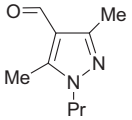
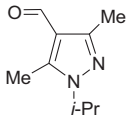
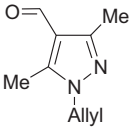
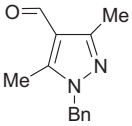
(88%) (Table 1). The decrease of TMSCl content up to equimolar ratio led to the drop in the yield of the target diselenane **3e** (Table 1).

The formation of both open-chained bis(3-selanylpropyl)diselenoacetals and the adducts of diselenol **2** to the allyl moiety of pyrazole carbaldehyde **1d** was not observed in the course of reaction under optimal conditions.

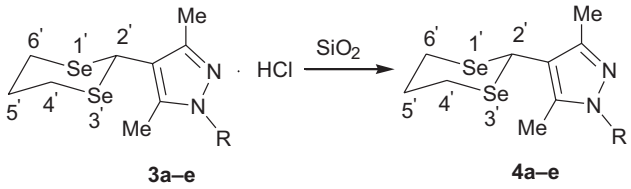
Hitherto unknown hydrochlorides **3d** and **3e** were isolated as individual compounds and characterized by physical and chemical methods; hydrochlorides **3a–c** were used in further transformations without isolation (Table 2).

In the nuclear magnetic resonance (NMR) spectra of hydrochlorides **3d** and **3e**, the resonance signals of the methyl group protons are broadened due to the protonation of N-2 atom and are low-field shifted relative to their positions in the spectrum of bases **4**. Besides, the signals C^3-Me are low-field shifted as compared with protons of the C^5-Me group. Chemical shifts of nitrogen atom of the pyrazole ring, measured by the HMBC-gp (^{15}N-^{1}H) method, are indicative of the N-2 atom protonation in hydrochlorides **3d** and **3e**. So, the resonance signal of compounds **3d** and **3e** is high-field shifted by 80–90 ppm as compared with chemical shifts of free bases **4d** and **4e**.

TABLE 2 Acetalization of Aldehydes **1a–e** with Diselenol **2** in the Presence of TMSCl (Molar Ratio **1**:**2**:TMSCl = 1:1:6)

Entry	*Aldehydes*	*Product* **3a–e**	*Yield (%)* [a,b]	*Product* **4a–e**	*Yield (%)* [a,b]
1.		**3a**	[c]	**4a**	61
2.		**3b**	[c]	**4b**	67
3.		**3c**	[c]	**4c**	56
4.		**3d**	90	**4d**	83
5.		**3e**	87	**4e**	72

[a]Yield refers to isolated pure products.
[b]Reaction time is 5 min; Molar ratio **1**:**2**:TMSCl = 1:1:6.
[c]Not isolated.



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

In the infrared (IR) spectra of hydrochlorides **3a–e**, a broad absorption band, typical for the (NH^+) group, is observed at 2613–2202 cm^{-1}.

Hydrochlorides **3d** and **3e** are readily dehydrochlorided by the column chromatography on silica gel to afford free bases—2-(pyrazol-4-yl)-1,3-diselenanes **4d** and **4e** (Scheme 2).

Similarly, 1,3-diselenanes **4a–c** were isolated by the column chromatography on silica gel of the corresponding reaction mixtures containing mainly unpurified hydrochlorides **3a–c**. Apart from compounds **4a–e**, 1,2-diselenolane **5** (in up to 10% yield) was isolated from the reaction mixtures by column chromatography. Its formation was due to the high instability of the starting diselenol **2**.

Previously, we have shown [20] that even cooled propane-1,3-diselenol undergoes self transformations. Physicochemical properties and NMR spectra of 1,2-diselenolane **5** are close to those reported in the literature [21].

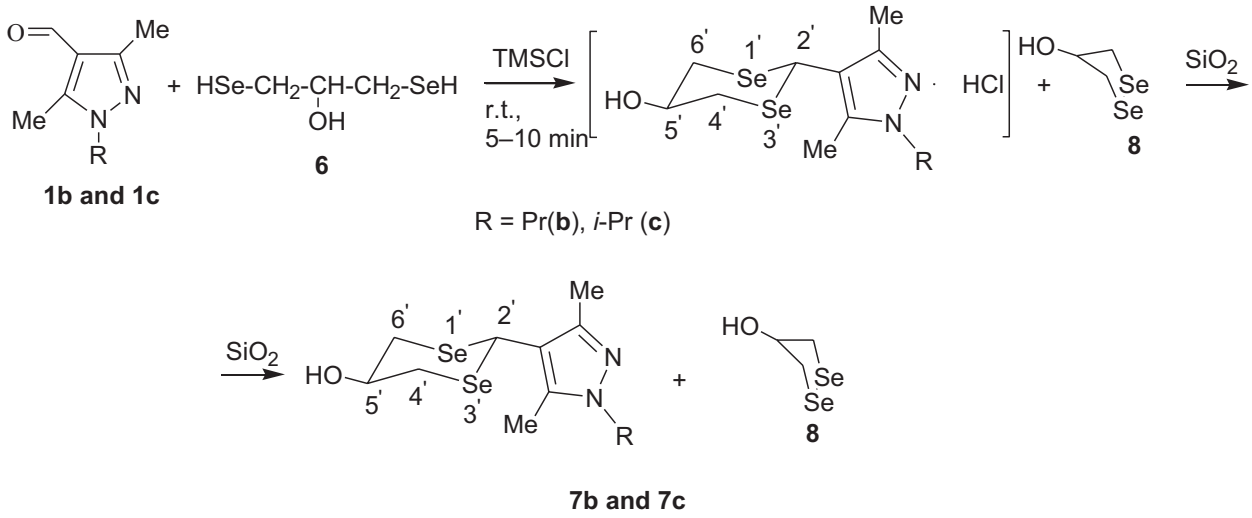
The structure of the diselenanes synthesized **4a–e** was proved by IR and NMR spectroscopy and chromato-mass spectrometry.

In ^1H NMR spectra, 1,3-diselenane fragment of compounds **4a–e** is present as a six-membered cycle having a chair conformation (with equatorial orientation of the pyrazole substituent). In 2D HMBC-gp (^{77}Se-^1H) correlation spectra, cross-peaks of equatorial protons are observed at 4′(6′) – and 5′-carbons with Se atoms. The alteration of optimized values $J_{Se\text{-}H}$ noticeably effects the relative intensity of these cross-peaks: the lowest value of the constant (~10 Hz) leads to the increase of intensity of cross-peaks from equatorial proton in the position 5′ of the ring and, on the contrary, the highest value (~30 Hz) increases the intensity from equatorial protons in the positions 4′(6′)′. This fact as well as spin–spin cross-coupling constants (measured in 1D spectra) indicate that the highest value of the constant (~30 Hz) relates to $^2J^{77}Se\text{-}C_{4'(6')}\text{-}H$, while the lowest value is attributed to $^3J\ ^{77}Se\text{-}C_{5'}\text{-}H$. The absence of the spin–spin interaction of selenium atom with C_2-Hax, as well as disappearance of lower ^3J value (~10 Hz) at substitution of $C\text{-}_{5'}$ equatorial proton by the OH group (compound **7b**) points that the selenium atom interacts only with cycle equatorial protons.

In continuation of this research, we have studied the reaction of pyrazole carbaldehydes **1** with 1,3-diselanyl-2-propanol **6**. The introduction of additional HO-functional group in diselenol significantly extends the possibilities of heterocyclization involving different functional groups and can furnish the corresponding diselenanes or oxaselenolanes.

It has been found that the interaction of aldehydes **1b** and **1c** with diselenol **6** under optimal conditions of diselenanes **3** synthesis is carried out analogously, but with substantially lower selectivity. The formation of a six-membered diselenane cycle is due to the higher stability of this heterocycle (as compared with oxaselenolane) and higher nucleophilicity of the HSe groups.

Hydrochlorides of pyrazolyldiselenanes formed in the reactions were not isolated as individual compounds, but were transformed into 2-(pyrazol-4-yl)-1,3-diselenan-5-ols **7b** and **7c** (Scheme 3).



SCHEME 3 Synthesis of 2-(pyrazol-4-yl)-1,3-diselenan-5-ols **7b** and **7c**.

Together with the target compound **7** (18%–20% yields), 1,2-diselenolan-4-ol **8** (15%–20% yield) formed via intramolecular cyclization of the starting diselenol **6** (Scheme 3) was identified among the reaction products (NMR). Besides, unreacted initial aldehyde **1** and diselenol **6** remain in the reaction mixtures.

The structure of 1,2-diselenolan-4-ol **8** was unambiguously proved by spectral methods. The NMR and GC–MS data corresponded to those published earlier [22].

The drop of the reaction temperature (up to –15 °C) or sixfold decrease of the molar excess of Me_3SiCl (to 0.5) did not increase the yields of compounds **7b** and **7c**.

The lower selectivity of the reaction as well as lower yields of 2-(pyrazol-4-yl)-5-hydroxy-1,3-diselenanes **7b** and **7c** are likely due to both the competitive reaction of diselenol **6** cyclization to diselenolane **8** and steric and electron effects in 1,3-diselanyl-2-propanol **6** induced by the hydroxyl group.

The presence of the hydroxyl group in diselenol **6** leads to the increase of a part of conformer with adjacent HSe groups and, hence, to the increase of 1,2-diselenolan-4-ol **8** yield (15%–20%) and decrease of pyrazolyl-1,3-diselenan-5-ol **7** amount. Besides, the electron-negative inductive effect of the OH group in 1,3-diselanyl-2-propanol **6** decreases the nucleophilicity of the SeH group and reduces the ability of **6** to interact with the carbonyl group of compounds **1b** and **1c**.

The application of Me_3SiCl in the aldehydes acetalyzation offers some obvious advantages. First, this catalyst ensures the mild conditions of the reaction. Second, there is no need to employ any water-absorbing agents in the reaction, since water evolving during the synthesis reacts with Me_3SiCl to give hexamethyldisiloxane and hydrogen chloride that favors the formation of products **4** and **7**. In their turn, hexamethyldisiloxane and excess Me_3SiCl are easily separated from the products after the reaction completion. Under the mild condition proposed by us (absence of strong bases, room temperature), the reactions of diselenols trimethylsilylation can not be probably realized and silicon–selenium ethers are not formed. The latter were not detected in the reaction mixtures and products.

Taking into account the conditions of the experiment, we believe that Me_3SiCl acts as Lewis acid in this process. The initially formed complex is further transformed to diselenol adduct like in [17].

We do not exclude the formation of α-chloroether $HSeCH_2CHXCH_2SeCHRCl$ (X = H, OH), reported for the reaction of formaldehyde with alkanethiols, the further intramolecular cyclization of which leads to the target diselenoacetals.

The structural study (^1H NMR, see the Experimental) of products **7** has shown that the OH moiety in compounds **7** is in equatorial position toward the diselenane cycle. Such location of the substituents ensures its most remoteness from bulky selenium atoms.

At the same time, it was reported on a 10:90 mixture of equatorially and axially oriented OH group in phenyl-substituted hydroxydiselenan-5-ol [6].

The behavior of pyrazolyl-substituted 1,3-diselenanes **4a–e** under the electron ionization (EI) and chemical ionization (CI) has been investigated. Under EI, all the compounds are studied form the

TABLE 3 Main Characteristic Ions of 4-(1,3-Diselenan-2-yl)-3,5-dimethyl-*N*-substituted-1*H*-pyrazoles **4a–e** in the EI Mass Spectra (70 ev)

	[a] *m/z (I, % from Total Ion Current)*				
Ion/Compound	**4a**	**4b**	**4c**	**4d**	**4e**[c]
$M^{+\bullet}$	324 (9)	352 (8)	352 (6)	350 (9)	400 (5)
$[M - C_3H_6Se]^{+\bullet}$, **A**	202 (42)	230 (31)	230 (24)	228 (22)	278 (22)
$[\mathbf{A} - CHR^1R^2]^+$, **B**, *m/z* 187	(4)	(16)	(6)	(3)	(2)
$[\mathbf{A} - CR^1R^2]^{+\bullet}$, **C**, *m/z* 188[b]	(4)	(16)	(6)	(3)	(2)
$[\mathbf{A} - HSe]^+$, **D**	121 (8)	149 (2)	149 (3)	147 (15)	197 (2)
$[\mathbf{D} - MeCN]^+$, **E**	80 (4)	108 (7)	108 (4)	106 (5)	156 (1)

[a] Se isotope.
[b] ion **C** is imposed on ion **B**.
[c] *m/z* 91 (17) $[C_7H_7]^+$

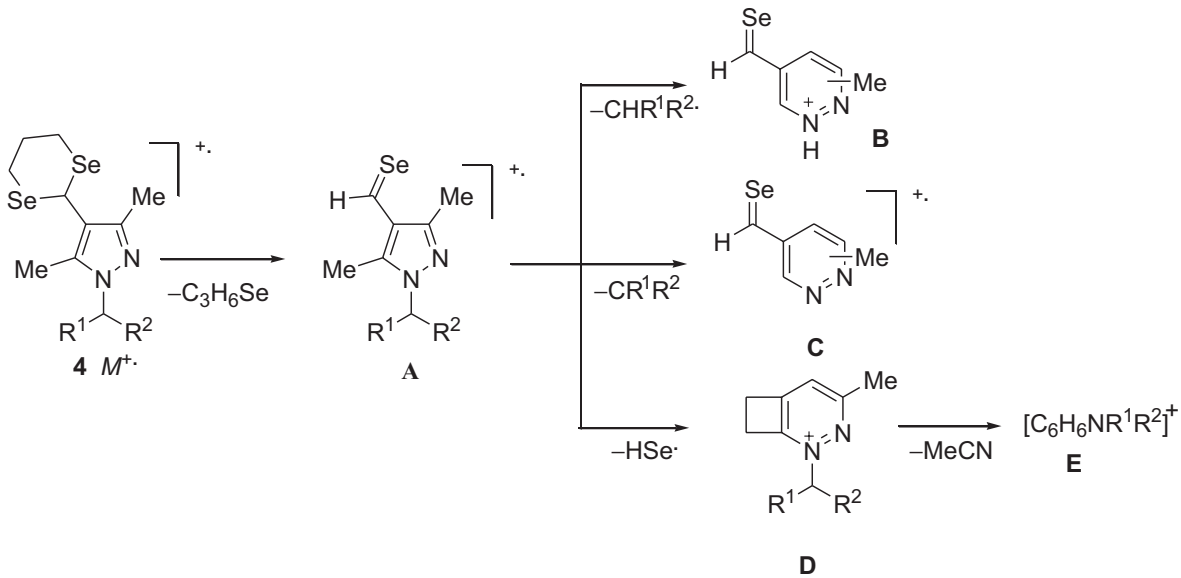
stable molecular ion (W_M) 5%–9% (Table 3). The main direction of the molecular ion fragmentation involves the formation of the odd electron ion $[M - C_3H_6Se]^{+\bullet}$ (ion **A**, Scheme 4, Table 3). However, unlike thienyl-substituted 1,3-diselenanes [16], the further fragmentation of ion **A** is accompanied by either the N–C bond cleavage at N-1 atom of the pyrazole ring to afford ions **B** and **C**, or the elimination of radical $HSe^{\bullet}$ (ion **D**) [23].

Further decomposition of ion **D**, independent of the nature of the substituent at the nitrogen atom, proceeds with the elimination of the MeCN molecule to generate ion **E**. It becomes possible if ion **D** is stabilized due to the expansion of the five-membered cycle to a six-membered one, owing to the methyl group in the position 5 of the pyrazole ring (Scheme 4). In Table 3, the main characteristic ions and their abundances under EI for 1,3-diselenanes **4a–e** are given.

As expected, for compound **4e**, the competitive direction of fragmentation caused by benzyl decomposition is realized [ion *m/z* 91 (17%)].

The 1,3-diselenanes **4** are readily protonated by methane in the gas phase. In the CI mass spectra of these compounds, peak clusters of ions $M^{+\cdot}$ and protonated molecular ions are characterized by maximum abundance (Table 4).

Along with the main direction of fragmentation caused by elimination of the C_3H_6Se molecule, in the spectra CI mode, the peaks of ions $[M - C_2HSe_2]^+$ and $[M - C_3H_5Se_2]^+$ are observed. These peaks can be generated both in the course of ionization and due to the decomposition of $[M + H]^+$ or $M^{+\bullet}$. Besides, the peaks of cluster ions $[M + C_2H_5]^+$ and



$R^1 = R^2 = H$ (**4a**); $R^1 = H$, $R^2 = Et$ (**4b**); $R^1 = R^2 = Me$ (**4c**); $R^1 = H$, $R^2 = vinyl$ (**4d**); $R^1 = H$, $R^2 = Ph$ (**4e**)

SCHEME 4 Pyrazolyl-substituted 1,3-diselenanes **4a–e** under the EI.

TABLE 4 Mass Spectra Positive Mode CI (Methane) of 4-(1,3-Diselenan-2-yl)-3,5-dimethyl-*N*-substituted-1*H*-pyrazoles **4a–e**

	[a] *m/z (I, % from Total Ion Current)*				
Ion/Compound	**4a**	**4b**	**4c**	**4d**	**4e**
[b] $[M + H]^+$	325 (55)	353 (39)	353 (38)	351 (57)	401 (49)
$M^{+\bullet}$	324 (55)	352 (39)	352 (38)	350 (57)	400 (49)
$[M - C_3H_6Se]^{+\bullet}$	203 (10)	230 (9)	230 (7)	228 (7)	278 (8)
$[M - C_2HSe_2]$	139 (7)	167 (13)	167 (13)	165 (6)	215 (9)
$[M - C_3H_3Se_2]$	125 (5)	227 (9)	227 (7)	225 (7)	201 (9)
$[M - C_3H_5Se_2]$	123 (5)	151 (7)	151 (8)	149 (6)	199 (9)
$[M + C_2H_5]^+$	353 (6)	381 (4)	381 (5)	379 (6)	429 (5)
$[M + C_3H_5]^+$	365 (2)	393 (1)	393 (1)	391 (2)	441 (2)
$[(M + C_2H_5) - C_3H_6Se]^+$	231 (1)	259 (1)	259 (1)	258 (1)	307 (1)
$[(M + C_3H_5) - C_3H_6Se]^+$	245 (2)	271 (1)	271 (1)	270 (1)	319 (1)
$[(M + C_2H_5) - C_2H_2Se_2]^+$	167 (2)	195 (4)	195 (4)	193 (2)	243 (1)
$[(M + C_2H_5) - C_3H_4Se_2]^+$	165 (2)	193 (4)	193 (4)	191 (2)	241 (1)

[a] Se isotope.
[b] Ion $[M + H]^+$ is imposed on ion $M^{+\bullet}$.

$[M + C_3H_5]^+$ as well as products of their degradation $[(M + C_2H_5) - C_3H_4Se_2]^+$ and $[(M + C_3H_5) - C_2H_2Se_2]^+$ appear in the spectra (Table 4).

Thus, it has been established that all the studied compounds of **4** under EI form a stable molecular ion, the fragmentation character of which does not depend on the nature and structure of saturated and aromatic heterocycles. The main direction of decomposition during EI and CI is determined by the formation of stable cation-radical $[M - C_3H_6Se]^{+\bullet}$.

CONCLUSIONS

In conclusion, the interaction of a series 4-formylpyrazoles bearing various substituents at 1-N atom with propane-1,3-diselenol **2** and 2-hydroxypropane-1,3-diselenol **6** has been studied for the first time. It has been found that in the presence of TMSCl, the reaction proceeds without heating to chemoselectively afford hitherto unknown bicyclic derivatives, 2-(pyrazol-4-yl)-1,3-diselenane hydrochlorides, which are easily transformed to the corresponding 1,3-diselenanes **4a–e** and **7b** and **7c**.

EXPERIMENTAL

General

^1H, ^{13}C, ^{77}Se, and ^{15}N NMR spectra were run on a Bruker DPX-400 MHz spectrometer (Bruker BioSpin, Rheinstetten, Germany) (^1H, 400.13 MHz; ^{13}C, 100.62 MHz; ^{77}Se, 76.31 MHz, and ^{15}N, 40.56 MHz) for solutions in $CDCl_3$ using TMS (1H, ^{13}C), Me_2Se (^{77}Se), and CH_3NO_2 (^{15}N) as internal standards. IR spectra were recorded on a Bruker Vertex 70 (Eftlinger, Germany) in thin layer (compounds **3a–e**) or in KBr pellets (**4a–e**, **7b**, and **7c**). Mass spectra of EI were recorded on a QP-5050 A instrument (Shimadzu, Kyoto, Japan, quadruple mass analyzer, 34–650 Da). The samples were introduced using the system of direct introduction (DI-50). Temperatures of ions source and samples introduction were selected to ensure qualitative mass spectrum and to exclude thermal destruction of the samples. Mass spectra of CI of positive ions were registered on an Agilent 5975C instrument (Agilent Technologies, Santa Clara, CA). Methane was used as the gas reagent. The samples were introduced via an Agilent 6890N chromatograph (Agilent Technologies) and separated on a chromatographic column HP-5MS (30 m × 0.25 mm × 0.25 μm) at constant rate of the flow; helium was used as a gas carrier.

Aldehydes **1a–e** were prepared by the formylation with the Wilsmeier–Haack reagent [24] of the corresponding 1,3,5-trisubstituted pyrazoles synthesized from 3,5-dimethylpyrazole, halogen alkyls, allyl bromide, and 4-fluoronitrobenzene under the conditions of indoles alkylation [25]. Diselenol **2** was synthesized via the original protocol of reductive cleavage of the Se–Se bond of polytrimethylenediselenide (selenokole) in the system hydrazine hydrate-KOH [16]. 1,3-Diselanyl-2-propanol **6** was prepared according to the method [21]. Other materials were obtained from commercial sources (Sigma-Aldrich Milwaukee, WI). The reaction course and the compounds purity were controlled by thin layer chromatography (TLC) on Silica gel 60 F 254 Merk with $CHCl_3$–MeOH = 95:5 as an eluent.

General Procedure for the Synthesis of 2-(Pyrazol-4-yl)-1,3-Diselenane Hydrochlorides **3a–e**

Propane-1,3-diselenol **2** (0.404 g, 2 mmol) was dropwise added on stirring to a mixture of pyrazole

carbaldehyde **1** (2 mmol) and TMSCl (1.304 g, 12 mmol) at room temperature. The reaction proceeded for 5–10 min and was accompanied by self-heating and separation of the reaction mixture into two layers. The reaction was controlled by TLC. The crude product formed as solid **3a–c** or viscous substance **3d** and **3e** was separated from the liquid part. Unpurified hydrochlorides **3a–c** with an admixture of 1,2-diselenolane were separated on the column to give pure product **4a–c**. For purification, crude product **3d,e** was washed with hexane (three times) and dried in vacuum.

4-(1,3-Diselenan-2-yl)-3,5-dimethyl-1-prop-2-en-1-yl-1H-pyrazole hydrochloride **3d**. Yellow oil; yield 0.695 g (90%). IR (neat, ν, cm^{-1}): 2958, 2939, 2613–2202 br (NH^+), 1696, 1570, 1468, 1420, 1301, 1246, 1112, 995, 752, 662, 625, 570. ^1H NMR (400.13 MHz, $CDCl_3$): δ, 2.02 (m, $^2J_{5'ax,5'eq} = 14.8$, $^3J_{5'ax,4'ax} = {}^3J_{5'ax,6'ax} = 12.7$, 1H, H-5′$_{ax}$), 2.21 (m, $^2J_{5'eq,5'ax} = 14.8$, 1H, H-5′$_{eq}$), 2.49 (s, 3H, Me-5), 2.59 (s, 3H, Me-3), 2.91 (m, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.7$, 2H, H-4′$_{eq}$, H-6′$_{eq}$), 3.18 (dd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.7$, 2H, H-4′$_{ax}$, H-6′$_{ax}$), 5.09 (d, $^3J = 5.4$, 2H, CH_2N), 5.28 (d, $J_{trans} = 17.1$, 1H, $CH_2 =$), 5.38 (d, $J_{cis} = 10.2$, 1H, $CH_2 =$), 5.42 (s, 1H, H-2′), 5.96 (ddt, $^3J = 5.4$, $^3J = 10.2$, $^3J = 17.1$, 1H, CH =). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 9.8 (Me-5), 10.1 (Me-3), 13.9 ($^1J_{Se\text{-}C} = 73.6$, C-2′), 24.4 (C-5′), 25.4 ($^1J_{Se\text{-}C} = 62.5$, C-4′, C-6′), 50.6 (CH_2N), 118.6 (C-4), 120.7 ($CH_2 =$), 128.9 (CH =), 142.3 (C-5), 143.0 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –188.8 (N-1), –171.4 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 348.9 (dd, $^2J_{Se,\,H\text{-}4'eq} = {}^2J_{Se,H\text{-}6'eq} = 31.5$, $^3J_{Se,H\text{-}5'eq} = 10.3$, Se). Anal calcd for $C_{12}H_{19}ClN_2Se_2$: C, 37.47; H, 4.98; Cl, 9.22; N, 7.28; Se, 41.05. Found: C, 37.21; H, 4.86; Cl, 9.41; N, 7.06; Se, 41.48.

4-(1,3-Diselenan-2-yl)-3,5-dimethyl-1-benz-1-yl-1H-pyrazole hydrochloride **3e**. Yield 0.796 g (87%). IR (film, ν, cm^{-1}): 2954, 2925, 2609–2140 br (NH+), 1701, 1561, 1497. 1454, 1429, 1301, 1245, 1112, 752, 703, 662, 570. ^1H NMR (400.13 MHz, $CDCl_3$): δ, 2.00 (dtt, $^2J_{5'ax,5'eq} = 14.9$, $^3J_{5'ax,4'ax} = {}^3J_{5'ax,6'ax} = 12.4$, $^3J_{5'ax,4'eq} = {}^3J_{5'ax,\,6'eq} = 2.5$, 1H, H-5′$_{ax}$), 2.19 (dtt, $^2J_{5'eq,5'ax} = 14.9$, $^3J_{5'eq,4'ax} = {}^3J_{5'eq,6'ax} = 2.5$, $^3J_{5'eq,4'eq} = {}^3J_{5'eq,6'eq} = 4.9$, 1H, H-5′$_{eq}$), 2.44 (s, 3H, Me-5), 2.61 (s, 3H, Me-3), 2.89 (ddd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.8$, 2H, H-4′$_{eq}$, H-6′$_{eq}$), 3.18 (ddd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.8$, 2H, H-4′$_{ax}$, H-6′$_{ax}$), 5.36 (s, 1H, H-2′), 5.63 (d, 2H, CH_2N), 7.33–7.42 (m, 5H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 10.4 (Me-5), 10.5 (Me-3), 14.2 ($^1J_{Se,C} = 75.5$, C-2′), 24.6 (C-5′), 25.7 ($^1J_{Se,C} = 62.1$, C-4′, C-6′), 52.3 (CH_2N), 119.1 (C-4), 128.2 (C*m*), 129.2 (C*p*), 129.4 (C*o*), 132.6 (C*i*), 142.4 (C-5), 143.4 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –186.0 (1-N), –170.1 (2-N). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 349.1 (dd, $^2J_{Se,H\text{-}4'eq} = {}^2J_{Se,H\text{-}6'eq} = 31.0$, $^3J_{Se,H\text{-}5'eq} = 9.8$, Se). Anal calcd for $C_{16}H_{21}ClN_2Se_2$: C, 44.21; H, 4.87; Cl, 8.16; N, 6.44; Se, 36.33. Found: C, 44.08; H, 4.91; Cl, 8.19; N, 6.38; Se, 36.44.

General Procedure for Preparation of 4-(1,3-Diselenan-2-yl)-3,5-Dimethyl-N-Substituted-1H-Pyrazoles **4a–e**

Hydrochlorides **3a–e** were passed through the column 450 × 15 mm (Silica gel 60, 70–230 mesh), $CHCl_3$–MeOH = 95:5 as an eluent. The product was additionally recrystallized from hexane to give compounds **4a–e** as white crystals.

4-(1,3-Diselenan-2-yl)-1,3,5-trimethyl-1H-pyrazole **4a**. Yield 0.429 g (61%), melting point (mp) 93–95°C. IR (KBr, ν, cm^{-1}): 2920, 2865, 1552, 1473, 1428, 1413, 1386, 1375, 1302, 1250, 1228, 1195, 1118, 881, 849, 757, 727, 655, 630, 624, 582, 568, 548. ^1H NMR (400.13 MHz, $CDCl_3$): δ, 1.98 (dtt, $^2J_{5'ax,5'eq} = 14.9$, $^3J_{5'ax,4'ax} = {}^3J_{5'ax,6'ax} = 12.5$, $^3J_{5'ax,4'eq} = {}^3J_{5'ax,6'eq} = 2.5$, 1H, H-5′$_{ax}$), 2.18 (dtt, $^2J_{5'eq,5'ax} = 14.9$, $^3J_{5'eq,4'ax} = {}^3J_{5'eq,6'ax} = 5.0$, $^3J_{5'eq,4'eq} = {}^3J_{5'eq,6'eq} = 2.3$, 1H, H-5′$_{eq}$), 2.28 (s, 3H, Me-3), 2.33 (s, 3H, Me-5), 2.83 (ddd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.6$, $^3J_{5'ax,4'eq} = {}^3J_{5'ax,6'eq} = 5.0$, $^3J_{4'eq,5'eq} = {}^3J_{6'eq,5'eq} = 2,3$, 2H, H-4′$_{eq}$, H′-6$_{eq}$), 3.09 (ddd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.6$, $^3J_{5'eq,4'ax} = {}^3J_{5'eq,6'ax} = 5.0$, 2H, H-4′$_{ax}$, H-6′$_{ax}$), 3.65 (s, 3H, Me-N), 5.43 (s, 1H, H-2′$_{ax}$). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 10.3 (Me-5), 12.0 (Me-3), 18.5 ($^1J_{Se\text{-}C} = 74.0$, C-2′), 25.04 (C-5′), 25.4 ($^1J_{Se\text{-}C} = 63.3$, C-4′, C-6′), 35.7 (Me-N), 115.22 (C-4), 137.58 (C-5), 145.01 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –185.0 (N-1), –83.3 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 347.5 (dd, $^2J_{Se,H\text{-}4'eq} = {}^2J_{Se,H\text{-}6'eq} = 31.0$, $^3J_{Se,\,H\text{-}5'eq} = 9.8$, Se). MS (EI): *m/z* ($I_{rel}$, %) = 324 (19), 323 (3), 322 (17), 321 (7), 320 (11), 319 (3), 318 (4), 204 (18), 203 (19), 202 (100), 201 (63), 200 (50), 199 (48), 198 (29), 197 (11), 196 (3), 187 (10), 186 (3), 185 (6), 184 (3), 163 (9), 160 (3), 158 (3), 149 (6), 136 (9), 135 (3), 123 (10), 122 9180, 121 (28), 120 (3), 119 (4), 109 (6), 107 (4), 95 (3), 94 (8), 93 (7), 92 (3), 91 (5), 82 (4), 81 (10), 80 (10), 78 (3), 77 (4), 66 (28), 56 (27), 55 (4), 54 (4), 53 (6), 52 (4), 51 (8), 43 (4), 42 (21), 41 (30), 40 (7), 39 (36). Anal calcd for $C_{10}H_{16}N_2Se_2$: C, 37.28; H, 5.01; N, 8.70; Se, 49.02. Found: C, 37.32; H, 5.03; N, 8.73; Se, 48.92.

4-(1,3-Diselenan-2-yl)-3,5-dimethyl-1-propyl-1H-pyrazole **4b**. Yield 0.469 g (67%), mp 75–77°C. IR (KBr, ν, cm^{-1}): 2952, 2899, 2875, 1549, 1466,

1436, 1421, 1383, 1248, 1113, 847, 757, 725, 652, 626, 606, 572. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ, 0.90 (t, ^3J = 7.3, 3H, *Me*CH_2CH_2), 1.77 (sextet, ^3J = 7.3, 2H, Me*CH*$_2$$CH_2$), 2.00 (dtt, $^2J_{5'ax,5'eq}$ = 15.0, $^3J_{5'ax,4'ax}$ = $^3J_{5'ax,6'ax}$ = 12.7, $^3J_{5'ax,4'eq}$ = $^3J_{5'ax,6'eq}$ = 2.5, 1H, H-5$'_{ax}$), 2.19 (dtt, $^2J_{5'eq,5'ax}$ = 15.0, $^3J_{5'eq,4'ax}$ = $^3J_{5'eq,6'ax}$ = 4.9, $^3J_{5'eq,4'eq}$ = $^3J_{5'eq,6'eq}$ = 2.5, 1H, H-5$'_{eq}$), 2.29 (s, 3H, Me-3), 2.33 (s, 3H, Me-5), 2.85 (ddd, $^2J_{4'ax,4'eq}$ = $^2J_{6'ax,6'eq}$ = 13.6, 2H, H-4$'_{eq}$, H-6$'_{eq}$), 3.10 (ddd, $^2J_{4'ax,4'eq}$ = $^2J_{6'ax,6'eq}$ = 13.6, 2H, H-4$'_{ax}$, H-6$'_{ax}$), 3.87 (t, 2H, CH_2N), 5.44 (s, 1H, H-2$'_{ax}$). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 10.4 (Me-5), 12.3 (Me-3), 11.2 (*Me*CH_2CH_2), 18.9 ($^1J_{Se\text{-}C}$ = 73.6, C-2$'$), 23.6 (CH_3*CH*$_2$$CH_2$), 25.3 (C-5$'$), 25.7 ($^1J_{Se\text{-}C}$ = 62.5, C-4$'$, C-6$'$), 50.5 (CH_2N), 115.1 (C-4), 137.2 (C-5), 145.3 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –174.4 (N-1), –86.2 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 347.7 (dd, $^2J_{Se,\ H\text{-}4'eq}$ = $^2J_{Se,H\text{-}6'eq}$ = 30.6, $^3J_{Se,H\text{-}5'eq}$ = 10.7, Se). MS (EI): *m/z* (I_{rel}, %) = 354 (6), 353 (3), 352 (17), 351 (4), 350 (14), 349 (7), 348 (10), 347 (3), 346 (4), 232 (18), 231 (15), 230 (100), 229 (29), 228 (51), 227 (30), 226 (23), 225 (6), 215 (6), 214 (3), 202 (3), 201 (5), 200 (3), 199 (4), 191 (5), 190 (3), 189 (5), 188 (14), 187 (14), 186 (9), 185 (10), 184 (6), 183 (4), 177 (6), 175 (4), 173 (3), 160 (4), 158 (4), 151 (6), 150 (7), 149 (35), 147 (3), 146 (4), 137 (4), 135 (8), 133 (3), 123 (5), 122 (14), 121 (28), 119 (5), 109 (11), 108 (18), 107 (7), 106 (3), 105 (4), 95 (6), 94 (8), 93 (7), 92 (3), 91 (5), 82 (3), 81 (6), 80 (21), 79 (7), 78 (6), 77 (8), 68 (5), 67 (6), 66 (9), 65 (5), 56 (3), 55 (5), 54 (7), 53 (12), 52 (18), 51 (14), 50 (3), 44 (36), 43 (25), 42 (68),41 (97), 40 (11), 39 (75). Anal calcd for $C_{12}H_{20}N_2Se_2$: C, 41.15; H, 5.76; N, 8.00; Se, 45.09. Found: C, 41.27; H, 5.78; N, 8.03; Se, 44.92.

4-(1,3-Diselenan-2-yl)-3,5-dimethyl-1-(1-methylethyl)-1H-pyrazole **4c**. Yield 0.392 g (56%), mp 113–115°C. IR (KBr, ν, cm^{-1}): 2985, 2975, 2927, 1552, 1482, 1422, 1377, 1277, 1243, 1123, 1079, 883, 854, 821, 751, 724, 641, 572, 546 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ, 1.41 (d, ^{3}J = 6.6, 6H, Me_2CH), 1.99 (dtt, $^2J_{5'ax,5'eq}$ = 14.9, $^3J_{5'ax,4'ax}$ = $^3J_{5'ax,6'ax}$ = 12.6, $^3J_{5'ax,4'eq}$ = $^3J_{5'ax,6'eq}$ = 2.5, 1H, H-5$'_{ax}$), 2.19 (dtt, $^2J_{5'eq,5'ax}$ = 14.9, $^3J_{5'eq,4'ax}$ = $^3J_{5'eq,6'ax}$ = 5.0, $^3J_{5'eq,4'eq}$ = $^3J_{5'eq,6'eq}$ = 2.3, 1H, H-5$'_{eq}$), 2.30 (s, 3H, Me-3), 2.34 (s, 3H, Me-5), 2.84 (ddd, $^2J_{4'ax,4'eq}$ = $^2J_{6'ax,6'eq}$ = 13.6, 2H, H-4$'_{eq}$, H-6$'_{eq}$), 3.09 (ddd, $^2J_{4'ax,4'eq}$ = $^2J_{6'ax,6'eq}$ = 13.6, 2H, H-4$'_{ax}$, H-6$'_{ax}$), 4.30 (heptete, 1H, Me_2CH-N), 5.45 (s, 1H, H-2$'_{ax}$). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 10.3 (Me-5), 12.5 (Me-3), 19.0 ($^1J_{Se\text{-}C}$ = 73.6, C-2$'$), 22.4 (Me_2CH), 25.3 (C-5$'$), 25.7 ($^1J_{Se\text{-}C}$ = 62.9, C-4$'$, C-6$'$), 49.4 (Me_2CH-N), 114.8 (C-4), 136.2 (C-5), 145.1 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –163.4 (N-1), –92. 4 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 348.0 (dd, $^2J_{Se,H\text{-}4'eq}$ = $^2J_{Se,H\text{-}6'eq}$ = 30.3, $^3J_{Se,H\text{-}5'eq}$ = 10.3, Se). MS (EI): *m/z* (I_{rel}, %) = 354 (5), 353 (3), 352 (17), 351 (3), 350 (14), 349 (5), 348 (10), 346 (30), 232 (19), 231 (15), 230 (100), 229 (22), 228 (50), 227 (23), 226 (23), 225 (3), 215 (5), 213 (3), 191 (4), 190 (6), 189 (8), 188 (26), 187 (33), 186 (17), 185 (20), 184 (11), 183 (6), 177 (5), 164 (5), 160 (3), 158 (3), 149 (19), 135 (11), 133 (3), 122 (7), 121 (5), 119 (4), 109 (13), 108 (26), 107 (9), 106 (4), 105 (4), 97 (3), 95 (8), 94 (10), 93 (6), 92 (3), 91 (5), 80 (5), 79 (5), 78 (6), 77 (10), 68 (7), 67 (6), 66 (11), 65 (3), 54 (3), 53 (6), 52 (14), 51 (5), 43 (19), 42 (34), 41 (44), 40 (5), 39 (30). Anal calcd for $C_{12}H_{20}N_2Se_2$: C, 41.15; H, 5.76; N, 8.00; Se, 45.09. Found: C, 41.25; H, 5.75; N, 8.02; Se 44.98.

4-(1,3-Diselenan-2-yl)-3,5-dimethyl-1-prop-2-en-1-yl-1H-pyrazole **4d**. Yield 0.576 g (83%), mp 87–89°C. IR (KBr, ν, cm^{-1}): 2902, 2879, 1641, 1549, 1467, 1422, 1379, 1305, 1247, 1195, 1113, 995, 923, 849, 756, 725, 635, 572. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ, 1.99 (dtt, $^2J_{5'ax,5'eq}$ = 14.8, $^3J_{5'ax,4'ax}$ = $^3J_{5'ax,6'ax}$ = 12.7, $^3J_{5'ax,4'\ eq}$ = $^3J_{\ 5'ax,6'eq}$ = 2.6, 1H, H-5$'_{ax}$), 2.18 (dtt, $^2J_{5'eq,\ 5'ax}$ = 14.8, $^3J_{5'eq,4'ax}$ = $^3J_{5'eq,6'ax}$ = 4.8, $^3J_{5'eq,4'eq}$ = $^3J_{5'eq,6'eq,}$ = 2.5, 1H, H-5$'_{eq}$), 2.29 (s, 3H, Me-5), 2.31 (s, 3H, Me-3), 2.83 (ddd, $^2J_{4'ax,4'eq}$ = $^2J_{6'ax,6'eq}$ = 13.6 Hz, 2H, H-4$'_{eq}$, H-6$'_{eq}$), 3.09 (ddd, 2H, H-4$'_{ax}$, H-6$'_{ax}$), 4.56 (dt, ^3J = 5.4, ^4J = 1.5, 2H, CH_2N), 5.44 (s, 1H, H-2$'_{ax}$), 4.96 (ddd, J_{trans} = 16.1, 1H, CH_2 =) and 5.15 (ddd, J_{cis} = 12.0, $^2J \sim {}^4J$ = 1.5, CH_2 =), 5.96 (ddt, 1, CH =). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 10.2 (Me-5), 12.2 (Me-3), 18.5 ($^1J_{Se\text{-}C}$ = 73.5, C-2$'$), 25.1 (C-5$'$), 25.5 ($^1J_{Se\text{-}C}$ = 62.7, C-4$'$, C-6$'$), 51.6 (CH_2N), 115.5 (C-4), 116.9 (CH_2 =), 132.8 (CH =), 137.5 (C-5), 145.6 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –176.3 (N-1), –81.9 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 348.3 (dd, $^2J_{Se,\ H\text{-}4'eq}$ = $^2J_{Se,\ \text{-}H\text{-}6'eq}$ = 30.6, $^3J_{Se,5'\text{-}Heq}$ = 10.2, Se). MS (EI): *m/z* ($I_{rel,}$ %) = 352 (5), 350 (15), 349 (3), 348 (13), 347 (5), 346 (8), 344 (3), 230 (9), 229 (9), 228 (51), 227 (17), 226 (27), 225 (17), 224 (11), 189 (6), 187 (5), 186 (3), 185 (3), 175 (6), 162 (5), 161 (4), 158 (3), 148 (24), 147 (100), 145 (5), 135 (3), 133 (6), 132 (4), 131 (3), 121 (6), 120 (6), 119 (4), 118 (3), 117 (3), 109 (3), 108 (3), 107 (7), 106 (15), 105 (4), 104 (3), 95 (3), 94 (4), 93 (6), 92 (5), 91 (5), 80 (6), 79 (7), 78 (6), 77 (9), 67 (3), 66 (7), 65 (5), 55 (7), 54 (7), 53 (7), 52 (10), 51 (9), 50 (3), 42 (21), 41 (78), 40 (7), 39 (60). Anal calcd for $C_{12}H_{18}N_2Se_2$: C, 41.39; H, 5.21; N, 8.05; Se, 45.35. Found: C, 41.25; H, 5.24; N, 8.07; Se 45.53.

1-Benzyl-4-(1,3-diselenan-2-yl)-3,5-dimethyl-1H-pyrazole **4e**. Yield 0.572 g (72%), mp 83–85°C.

IR (KBr, ν, cm^{-1}): 2932, 2919, 2895, 2876, 1557, 1494, 1454, 1433, 1416, 1362, 1320, 1244, 1189, 1113, 850, 757, 741, 727, 708, 572, 452. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ, 1.96 (dtt, $^2J_{5'ax,5'eq} = 14.9$, $^3J_{5'ax,4'ax} = {}^3J_{5'ax,6'ax} = 12.4$, $^3J_{5'ax,4'eq} = {}^3J_{5'ax,6'eq} = 2.5$, 1H, H-5$'_{ax}$), 2.15 (dtt, $^2J_{5'eq,5'ax} = 14.9$, $^3J5'_{eq,4'ax} = {}^3J_{5'eq,6'ax} = 2.5$, $^3J_{5'eq,4'eq} = {}^3J_{5'eq,6'eq} = 4.9$, 1H, H-5$'_{eq}$), 2.25 (s, 3H, Me-5), 2.33 (s, 3H, Me-3), 2.83 (ddd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.8$, 2H, H-4$'_{eq}$, H-6$'_{eq}$), 3.08 (ddd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.8$, 2H, H-4$'_{ax}$, H-6$'_{ax}$), 5.16 (s, 2H, CH_2N), 5.44 (c, 1H, H-2$'_{ax}$), 7.03 (m, 2H, H*o*), 7.21 (m,1H, H*p*), 7.26 (m, 2H, H*m*). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 10.4 (Me-5), 12.3 (Me-3), 18.5 ($^1J_{Se\text{-}C} = 73.9$, C-2$'$), 25.0 (C-5$'$), 25.5 ($^1J_{Se\text{-}C} = 62.3$, C-4$'$, C-6$'$), 52.7 (CH_2N), 115.8 (C-4), 126.5 (C*m*), 127.4 (C*p*), 128.6 (C*o*), 136.8 (C*i*), 137.6 (C-5), 145.7 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –177.3 (N-1), –82.9 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 348.3 (dd, $^2J_{Se,H\text{-}4'eq} = {}^2J_{Se,H\text{-}6'eq} = 30.6$, $^3J_{Se,\ H\text{-}5'eq} = 10.3$, Se). MS (EI): *m/z* ($I_{rel}$, %):400 (7), 398 (7), 397 (3), 396 (3), 280 (8), 279 (10), 278 (48), 277 (16), 276 (23), 275 (14), 274 (9), 273 (3), 198 (3), 197 (14), 156 (7), 92 (9), 91 (100), 78 (3), 77 (6), 66 (4), 65 (15), 51 (3), 43 (4), 41 (12), 39 (12). Anal calcd for $C_{16}H_{20}N_2Se_2$: C, 48.25; H, 5.06; N, 7.03; Se, 39.65. Found: C, 48.31; H, 5.08; N, 7.05; Se, 39.56.

1,2-Diselenolane **5** was isolated by column chromatography (Silica gel 60, 70–230 mesh, $CHCl_3$ as eluent) of the reaction mixtures prepared from 4-formylpyrazoles **1a–c** with propane-1,3-diselenol **2** in the presence of TMSCl. The solvent of first fractions was removed under reduced pressure, and then the solid residue was dried in vacuum. Yield 0.030–0.045 g (7–10%). Light yellow crystals, mp 66–67°C (literature data [20]: mp 65–67°C). Spectral characteristics correspond to the previously published ones [20].

Reactions of 3,5-Dimethyl-4-Formylpyrazoles **1b, 1c** *with 1,3-Diselenanyl-2-Propanol* **6**

To a mixture of aldehyde **1b (1c)** (2 mmol) and TMSCl (12 mmol, 1.304 g), 1,3-diselenanyl-2-propanol **6** (2 mmol, 0.436 g) was dropwise added on stirring at room temperature. The reaction proceeded for 5–10 min and was accompanied by self-heating and separation of the reaction mixture into two layers. The liquid part was removed under reduced pressure and compounds **7b** and **7c** were isolated by column chromatography on silica gel (eluent $CHCl_3$–CH_3OH = 99:1) as white crystals.

2-(3,5-Dimethyl-1-propyl-1H-pyrazol-4-yl)-1,3-diselenan-5-ol **7b**. Yield 0.146 g (20%), mp 132–135°C. IR (KBr, ν, cm^{-1}): 3211, 2976, 2956, 2927, 1554, 1497, 1433, 1390, 1382, 1328, 1288, 1192, 1117, 1026, 997, 905, 842, 725, 652. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ, 0.89 (t, $^3J = 7.5$, 3H, *Me*CH_2CH_2), 2.34 (s, 3H, Me-5), 2.31 (s, 3H, Me-3), 1.76 (sextet, $^3J = 7.5$, 2H, Me*CH*$_2$$CH_2$), 2.77 (dd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,\ 6'eq} = 13.0$, $^3J_{4'eq,5'ax} = {}^3J_{6'eq,5'ax} = 3.1$, 2H, H-4$'_{eq}$, H-6$'_{eq}$), 3.10 (dd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 13.0$, $^3J_{5'ax,4'ax} = {}^3J_{5'ax,6'ax} = 10.9$, 2H, H-4$'_{ax}$, H-6$'_{ax}$), 3.87 (t, $^3J = 7.5$, 2H, CH_2N), 4.31 (tt, $^3J_{5'ax,4'ax} = {}^3J_{5'ax,6'ax} = 10.9$, $^3J_{5'ax,4'eq} = {}^3J_{5'ax,6'eq} = 3.1$, 1H, H-5$'_{ax}$), 5.42 (s, 1H, H-2$'_{ax}$). ^{13}C NMR, (100.62 MHz, $CDCl_3$): δ, 10.3 (Me-5), 11.1 (*Me*CH_2CH_2), 12.3 (Me-3), 18.0 ($^1J_{Se\text{-}C} = 72.7$, C-2$'$), 23.5 (Me*CH*$_2$$CH_2$), 30.2 ($^1J_{Se\text{-}C} = 65.2$ Hz C-4$'$, C-6$'$), 50.4 (*C*H_2N), 67.5 (C-5$'$), 112.6 (C-4), 137.1 (C-5), 145.3 (C-3). ^{15}N NMR, (40.56 MHz, $CDCl_3$): δ, –170.5 (N-1), –84.8 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 385.5 (d, $^2J_{Se,4'\text{-}Heq} = {}^2J_{Se,6'\text{-}Heq} = 28.7$, Se). Anal. calcd for $C_{12}H_{20}N_2OSe_2$: C, 39.36; H, 5.50; N, 7.65; Se, 43.12. Found: C, 39.40; H, 5.47; N, 7.59; Se, 43.17.

2-(1-Isopropyl-3,5-dimethyl-1H-pyrazol-4-yl)-1,3-diselenan-5-ol **7c**. Yield 0.135 g (18.4%), mp 87–89°C. IR (KBr, ν, cm^{-1}): 3210, 2974, 2931, 1551, 1499, 1430, 1390, 1328, 1288, 1192, 1116, 1024, 997, 842, 725, 652. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ, 1.38 (d, $^3J = 6.6$, 6H, *Me*$_2$CH), 2.29 (s, 3H, Me-3), 2.32 (s, 3H, Me-5), 2.73 (dd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 12.4$, $^3J_{4'eq,5'ax} = {}^3J_{6'eq,5'ax} = 3.3$, 2H, H-4$'_{eq}$, H-6$'_{eq}$), 3.07 (dd, $^2J_{4'ax,4'eq} = {}^2J_{6'ax,6'eq} = 12.4$, $^3J_{5'ax,4'x} = {}^3J_{5'ax,6'ax} = 10.9$, 2H, H-4$'_{ax}$, H-6$'_{ax}$), 4.28 (heptet, $^3J = 6.6$, 1H, CHN), 4.29 (tt, $^3J_{5'ax,4'ax} = {}^3J_{5'ax,6'ax} = 10.9$, $^3J_{5'ax,4'eq} = {}^3J_{5'ax,\ 6'eq} = 3.3$, 1H, H-5$'_{ax}$), 5.40 (s, 1H, H-2$'_{ax}$). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ, 10.2 (Me-5), 12.4 (Me-3), 18.1 ($^1J_{Se\text{-}C} = 72.7$, C-2$'$), 22.2 (*Me*$_2$CH), 30.2 ($^1J_{Se\text{-}C} = 65.6$, C-4$'$, C-6$'$), 49.3 (Me*C*H), 67.4 (C-5$'$), 112.2 (C-4), 136.0 (C-5), 145.1 (C-3). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ, –160.6 (N-1), –90.8 (N-2). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ, 385.6 (d, $^2J_{Se,H\text{-}4'eq} = {}^2J_{Se,\ H\text{-}6'eq} = 28.7$, Se). Anal calcd for $C_{12}H_{20}N_2OSe_2$: C, 39.36; H, 5.50; N, 7.65; Se, 43.12. Found: C, 39.30; H, 5.52; N, 7.63; Se, 43.18.

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